Doctoral Thesis in Chemical Engineering

Rhodium diesel-reforming catalysts
for fuel cell applications

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Αφιερωμένο στην οικογένεια μου
Abstract

Heavy-duty diesel truck engines are routinely idled at standstill to provide cab heating or air conditioning, and in addition to supply electricity to comfort units such as radio and TV. Idling is an inefficient and unfavorable process resulting in increased fuel consumption, increased emissions, shortened engine life, impaired driver rest and health, and elevated noise. Hydrogen-fueled, polymer-electrolyte fuel-cell auxiliary power unit (PEFC-APU) as a silent external power supply, working independently of the main engine, is proposed as viable solution for better fuel economy and abatement of idling emissions. In a diesel PEFC-APU, the hydrogen storage problem is circumvented as hydrogen can be generated onboard from diesel by using a catalytic reformer. In order to make catalytic diesel PEFC-APU systems viable for commercialization research is still needed. Two key areas are the development of reforming catalyst and reformer design, which both are the scope of this thesis. For diesel-reforming catalysts, low loadings of Rh and RhPt alloys have proven to exhibit excellent reforming and hydrogen selectivity properties. For the development of a stable reforming catalyst, more studies have to be conducted in order to find suitable promoters and support materials to optimize and sustain the long-term performance of the Rh catalyst. The next step will be full-scale tests carried out at realistic operating conditions in order to fully comprehend the overall reforming process and to validate promising Rh catalysts. This thesis can be divided into two parts; the first part addresses the development of catalysts in the form of washcoated cordierite monoliths for autothermal reforming (ATR) of diesel. A variety of catalyst compositions were developed containing Rh or RhPt as active metals, CeO$_2$, La$_2$O$_3$, MgO, Y$_2$O$_3$ as promoters and Al$_2$O$_3$, CeO$_2$-ZrO$_2$, SiO$_2$ and TiO$_2$ as support materials. The catalysts were tested in a bench-scale reactor and characterized by using N$_2$-BET, XRD, H$_2$ chemisorption, H$_2$-TPR, O$_2$-TPO, XPS and TEM analyses. The second part addresses the development and testing of full-scale reformers at various realistic operating conditions using promising Rh catalysts.

The thesis shows that a variety of Rh on alumina catalysts was successfully tested for ATR of diesel (Papers I-IV). Also, zone-coating, meaning adding two washcoats on specific parts of the monolith, was found to have beneficial effects on the ATR catalyst performance (Paper II). In addition, RhPt supported on CeO$_2$-ZrO$_2$ was found to be one of the most active and promising catalyst candidates for ATR of diesel. The superior performance may be attributed to higher reducibility of Rh$_x$O$_y$ species and greater dispersion of Rh and Pt on the support (Paper IV). Finally, two full-scale diesel reformers were successfully developed and proven capable of providing high fuel conversion and hydrogen production from commercial diesel over selected Rh catalysts (Papers II-III, V-VI).

**Keywords:** Autothermal reforming, auxiliary power unit, BET, chemisorption, diesel, fuel cell, hydrogen, monolith, reforming catalyst, reformer design, Rh, RhPt alloy, TEM, TPO, TPR, XRD, XPS, zone coating.
Sammanfattning


Nyckelord: Autoterm reformering, BET, bränslecell, diesel, hjälpkraftaggregat, kemisorption, monolit, reformerutformning, reformeringskatalysator, Rh, RhPt, TEM, TPO, TPR, XRD, XPS, vätegas, zonad katalysator.
Publications referred to in this thesis

The work presented in this thesis is based on the following papers, referred to in the text using Roman numerals. The papers are appended at the end of the thesis.

I. X. Karatzas, K. Jansson, J. Dawody, R. Lanza, L.J. Pettersson
   Microemulsion and incipient wetness prepared Rh-based catalyst for diesel reforming

II. X. Karatzas, J. Dawody, A. Grant, E. E. Svensson, L. J. Pettersson
    Zone-coated Rh-based monolithic catalyst for autothermal reforming of diesel

III. X. Karatzas, D. Creaser, A. Grant, J. Dawody, L. J. Pettersson
    Hydrogen generation from n-tetradecane, low-sulfur and Fischer-Tropsch diesel over Rh
    supported on alumina doped with ceria/lanthana.

IV. X. Karatzas, K. Jansson, J. Dawody, Angélica González, L.J. Pettersson
    Autothermal reforming of low-sulfur diesel over bimetallic RhPt supported on Al₂O₃,
    CeO₂-ZrO₂, SiO₂ and TiO₂
    Submitted to Appl. Catal. B.

V. M. Nilsson, X. Karatzas, B. Lindström, L.J. Pettersson
   Assessing the adaptability to varying fuel supply of an autothermal reformer

VI. X. Karatzas, M. Nilsson, J. Dawody, B. Lindström, L. J. Pettersson
    Characterization and optimization of an autothermal diesel and jet fuel reformer
    for 5 kWₑ mobile fuel cell applications
Contributions to the papers

I. I had the main responsibility for writing this paper. I performed all the experimental work included in the paper. TEM analyses were performed by Kjell Jansson.

II. I had the main responsibility for writing this paper. I performed all the experimental work included in the paper. XPS analyses were performed by Ann Grant.

III. I had the main responsibility for writing this paper. I performed all the experimental work included in the paper. XPS analyses were performed by Ann Grant.

IV. I had the main responsibility for writing this paper. The experimental work was a joint effort between myself and Angélica González under my supervision. TEM analyses were performed by Kjell Jansson.

V. I am one of the main authors of this paper. My main responsibilities were parts concerning experimental work such as proposing hypotheses, designing experiments, collecting and recording data, and interpreting obtained results.

VI. I had the main responsibility for writing this paper. I performed all the experimental work included in the paper.
Other publications and conference contributions

Papers on catalysis not included in this thesis

1. D. Creaser, X. Karatzas, B. Lundberg, L.J. Pettersson, J. Dawody
   **Modeling study of 5 kW, autothermal diesel fuel reformer**
   Submitted to Appl. Catal. A.

   **Efficient low temperature lean NO\textsubscript{x} reduction over Ag/Al\textsubscript{2}O\textsubscript{3}
   - Optimization of a possible on-board system**

Conference contributions on catalysis not included in this thesis

   **Reactor design considerations for commercial diesel**
   Poster presented at the 20\textsuperscript{th} North American Catalysis Society Meeting, Houston, TX,

   **Evaluation of diesel reformer and fuel injection system for mobile fuel cell applications**
   Poster presented at the 8\textsuperscript{th} Europacat, Turku/Åbo, Aug 26-31, 2007.

   **Screening study of transportation fuel candidates in a multifuel autothermal reformer using Rh catalysts**
   Oral presentation given at the 14\textsuperscript{th} International Congress on Catalysis, Seoul,

   **Evaluation of a flexible fuel autothermal reformer using Rh catalyst**
   Poster presented at the 5\textsuperscript{th} International Conference on Environmental Catalysis, Belfast,
7. X. Karatzas, B. Lindström, L.J. Pettersson

**Evaluation of a zoned RhPt-Rh catalyst for hydrogen generation from diesel fuel via autothermal reforming**

8. X. Karatzas, B. Lindström, L.J. Pettersson

**Full scale testing of a zoned RhPt-Rh catalyst for autothermal reforming of commercial diesel fuel**

9. X. Karatzas, D. Creaser, L.J. Pettersson

**Hydrogen generation from n-tetradecane and low-sulfur diesel over Rh supported on 0-alumina doped with ceria/lanthana**

10. X. Karatzas, A. González, J. Dawody, L.J. Pettersson

**Hydrogen generation from low-sulfur diesel over Rh-based metallic monolithic catalyst**

11. X. Karatzas, J. Dawody, R. Lanza, L. J. Pettersson

**Microemulsion and incipient wetness prepared Rh-based catalyst for diesel reforming**
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1. Introduction

1.1 Setting the scene

Anthropogenic hazardous emissions are a worldwide concern that need to be dealt with swiftly and reduced drastically in the near term in order to guarantee a sustainable world. An energy sector where the emissions are rapidly increasing is the transport sector. Growing world population, globalization, city urbanization, all these aspects will undoubtedly increase demand for transportation of people and goods. Statistics show that heavy-duty trucks are mainly used for long-haul road transportation of goods [1, 2]. Also, diesel is predominantly used to thrust heavy-duty trucks [1, 2]. The high energy content of the fuel is utilized and converted by a combined mechanical-combustion process taking place in a compression engine forming hazardous HC, CO, and NO\(_x\) emissions as gaseous byproducts [3, 4]. Recent reports show a worldwide rapid increase of annual production, sales and registration of heavy-duty diesel trucks [1-7]. Hence, an increase of diesel truck emissions of hazardous HC, CO, and NO\(_x\), are expected and unavoidable, unless new, efficient and environmentally friendly technological solutions can be adopted and put into use quickly. To date, structured catalysts in the form of washcoated monoliths are installed after the engine into stainless-steel reactor chambers in order to reduce these emissions [3, 4]. These catalytic systems have been proven to be ideal for automobile systems both during the past 30 years and at present. These systems are primarily designed and optimized to function when the diesel truck is in motion (active state), in the driving mode e.g. during highway driving. However, US statistics show that diesel trucks operate regularly in the passive mode (idling mode), up to 40 % of total operating time resulting in a redundant increase of HC, CO, and NO\(_x\) emissions [7-10]. Idling normally takes place at rest stops where the trucks are parked and the compression engines are kept running in order to charge and operate electronic comfort units e.g. A/C, radio, TV and refrigerator. Hydrogen fed, polymer electrolyte fuel-cell auxiliary power unit (PEFC-APU) as external power supply offers a promising alternative to compression engines to reduce idling emissions [11]. Unlike in the compression engine, the employed liquid diesel fuel is catalytically reformed (fragmentized) to produce hydrogen-rich gas that can be fed and used by the fuel cell to generate electricity. The reactor and catalyst development for this application is closely inspired by conventional environmental automotive catalyst design. However, to date, catalytic fuel-cell power generators are still under development requiring much more research in order to make them commercially viable. In particular, the development of diesel-reforming catalysts is very challenging, especially considering the complex and poorly defined composition of the fuel. Limited studies are available using real diesel fuel mixtures. Also, most studies are considering catalysts in the form of a powder. This thesis discusses several papers where the catalyst performance, using engineered substrates in the form of washcoated monoliths, was studied for real-life applications under real reaction conditions.
1.2 Objectives of the work

The main objective of the work presented in this thesis has been to address the challenges of catalytically reforming diesel fuels using Rh-based washcoated cordierite monoliths. The aim is to catalytically fragmentize diesel, by autothermal reforming, into a hydrogen-rich gas mixture that can be fed to a PEFC auxiliary power unit working in the range of 5-10 kW_e. The catalysts have been tested both in a bench-scale and in a full-scale reactor using diesel surrogates and commercial diesel as fuels. Also, fresh and aged catalyst powder samples have been characterized using N_2-BET, XRD, H_2 chemisorption, H_2-TPR, O_2-TPO, XPS and TEM analyses. This thesis highlights and summarizes the main findings from work included in the six appended papers:

- In Paper I, the role of the catalyst preparation technique was investigated. Reverse microemulsion (ME) and incipient wetness (IW) techniques were used for the preparation of Rh-based monolithic catalysts for ATR of diesel in bench-scale operation. However, only the IW prepared catalysts are further discussed in the thesis.

- In Paper II, a screening test was conducted to detect differences in activity between single-layered and zone-coated Rh-based monolithic catalysts for ATR of diesel. The effect of Ce-La promotion was also studied.

- In Paper III, the role of the diesel fuel properties was investigated. In this study, a catalyst with the composition Rh_{3.0}Ce_{10}La_{10}/δ-Al_2O_3 was used to detect differences in reforming activity between the diesel surrogate n-tetradecane, and commercial low-sulfur and Fischer-Tropsch diesel fuels during full-scale operation.

- In Paper IV, the role of the support was investigated for RhPt-based monolithic catalysts for ATR of diesel in bench-scale operation. The support materials tested were Al_2O_3, CeO_2-ZrO_2, SiO_2 and TiO_2.

- In Paper V, the capability of full-scale reactors to catalytically reform a variety of transportation fuels into a hydrogen-rich gas was evaluated. The fuel candidates employed were commercial diesel, gasoline and E85, and renewable methanol, ethanol and dimethyl ether. However, only the diesel fuels are further discussed in the thesis.

- In Paper VI, a new and advanced full-scale reactor was designed and evaluated for autothermal reforming of commercial diesel and jet A-1. Again, only the diesel fuels are further discussed in the thesis.
The content of this thesis is divided into three major parts and a total of 8 chapters. The first part, Chapters 2-5, of this thesis provides information regarding the adaptability of fuel cells in auxiliary power units onboard heavy-duty diesel trucks. Also, an overview of currently available fuel processing, fuel cell and catalyst technology is given. The second part, Chapters 6-7 considers the results and discussions derived from the appended papers. In the third and final part, Chapter 8, some concluding remarks and suggestions for future work are given.

The work presented in this thesis is part of the research program “E4 Mistra” financed by the Foundation for Strategic Environmental Research. The target goal of the program is to reach ultra-low emission levels (0.005 g PM/kWh and 0.1 g NOx/kWh) using a compression ignition engine exhibiting low CO2 emissions in combination with fuel reformers, thermoelectric materials, novel particulate filters and catalytic exhaust-gas after-treatment units. The program had representatives from Swedish academia (KTH - Royal Institute of Technology and Chalmers University of Technology) and industry (Volvo Technology, Höganäs AB and Thermogen).

The work included in this thesis was conducted at the Department of Chemical Engineering and Technology at KTH-Royal Institute of Technology and at Volvo Technology Corporation, Sweden. In addition, a close and active collaboration was established with PowerCell Sweden AB throughout this thesis work. Numerous workshops and meetings took place with key members from PowerCell Sweden AB R&D, with the aim to develop and evaluate an upgraded diesel reformer to be integrated with a fuel-processor prototype based on PEFC-APU technology.
2. Technologies and legislation for abatement of truck idling emissions

2.1 Electrical demands and truck idling

Modern vehicles are equipped with electronic components that are linked together in a complex electrical system handling sophisticated operation such as fuel injection, engine cooling, steering and lighting. The electrical system can be divided into different segments of electricity generators, converters, accumulators and consumers. The conventional electrical system essentially consists of four mechanical parts or categories: an engine, an alternator, a battery and electronic equipment such as A/C and radio. The engine and the alternator are linked together through a rotational steel plug with a serpentine belt ring attachment. When the engine is running, the rotational kinetic energy from the engine is transferred through the rotating belt to the alternator, in which the energy is converted to electricity. The electrical energy from the alternator is then stored and released to charge the battery and to supply power to the surrounding electrical equipment [12]. Table 1 lists power demands for selected electronic components installed onboard automotive vehicles.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Power consumption [W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motronic, electrical fuel pump</td>
<td>250</td>
</tr>
<tr>
<td>Radio</td>
<td>20</td>
</tr>
<tr>
<td>Electric radiator blower</td>
<td>120</td>
</tr>
<tr>
<td>Interior heating, fan</td>
<td>120</td>
</tr>
<tr>
<td>Heating, rear window</td>
<td>200</td>
</tr>
<tr>
<td>Low-beam headlamps</td>
<td>110</td>
</tr>
<tr>
<td>Indicator lamp, instrument panel</td>
<td>22</td>
</tr>
<tr>
<td>Front fog lamps</td>
<td>110</td>
</tr>
<tr>
<td>Stop lamps</td>
<td>42</td>
</tr>
</tbody>
</table>

As seen in Table 1, the electrical demand can vary depending on which item is employed. It should be emphasized that the electrical load requirements of each item, encountered during vehicle operation, are not constant. For instance, the electrical power demand is season based; e.g. air conditioners are more frequently used in the summer, while seat heating is used in the winter. Also, different magnitudes of load are needed depending on duty cycle. Long-term loads are employed e.g. for lighting, while short-term loads are used e.g. for signaling of stop and turn lights. Also, the power consumption during continuous operation of the electronic devices is uneven. Typically higher power loads are used at start, during the first couple of minutes, when activating devices, e.g. seat and rear window heaters [12]. Electrical demands can vary depending of the type of vehicle. In general, higher power loads are employed in heavier vehicles, such as long-haul heavy-duty diesel trucks, as a larger number of electronic comfort accessories (refrigerators, microwaves, TV) are found onboard the cabin.
of the truck. Currently new items, e.g. Wifi, GPS, computers, are being installed onboard the truck. Furthermore, in the future, onboard diagnostics, such as NO\textsubscript{x} technology will be present and installed with additional indicator icons on the instrument panel and sensors positioned in the diesel truck exhaust system. This increasing number of electronic items and diagnostics will undoubtedly increase the overall electrical power consumption of the truck. Estimates have shown that in extreme cases, electrical loads of up to 5-10 kW\textsubscript{e} will be required [7-11]. This new requirement will change the configuration of the electrical system; new robust alternators and larger batteries with higher voltage output will be needed. This is negative as the upgraded units will require larger volumes and greater weight support inside the front chassis of the trucks [12].

Another problem occurs when the electronic comfort accessories are used. Most studies involving truck driver behavior have shown that most of these items are used in the idling mode [7-11]. Idling mode refers to a continuous operation of the vehicle main engine while the vehicle is at standstill. Idling can take place during urban driving when frequent stop-and-go situations are common. However, the total average time period of this type of idling is relatively short. Instead, long periods of idling are most problematic when the truck is parked. In these scenarios, heavy-duty diesel trucks are routinely idled at truck stops to provide cab heating or air conditioning, as well as to provide electricity to truck accessories such as stereos, interior lights, TV, computers and refrigerators. These scenarios are typical in the US, where there are approximately 450 000 long-haul heavy-duty diesel trucks operating daily, traveling more than 800 km from their home bases and whose truck drivers spend more than 300 days per year sleeping in the cabin [7-11]. In these cases, idling is a necessity in order for the truck driver to take a rest and sleep in the cabin in a comfortable manner. Statistics show that diesel trucks operate in the idling mode on an average 6 h per day and 20-40 % of total operating time [9, 10]. This is detrimental as idling can cause numerous problems. Firstly, during idling, the engine speed is at its minimum as less work is carried out by the compression engine. This can be problematic for a conventional electrical system since the alternator operating efficiency increases as a function of the rotational speed of the engine. Hence, during idling mode, the overall efficiency of the diesel-to-electricity conversion through the alternator is poor due to low engine speed. Studies have shown that only 2-10 % of the energy content of the fuel is converted to electricity [7, 9, 11]. Another problem with the idling mode is the increased fuel consumption. Estimates have shown that ~4-6 % of the fuel is consumed during idling [7, 12]. In general, roughly 0.1 dm\textsuperscript{3} fuel is needed to generate 100 W of electricity [12]. Other problems related to idling are the increased noise levels and mechanical wear of the engine. However, the biggest problem is the increased idling emissions which are causing negative environmental impact and impaired health risks. Predictions have shown that the US adult population is at 50 % greater risk of getting cancer as a result of idling emissions, in particular due to elevated HC, NO\textsubscript{x} and PM exposure [13]. Statistics show that a total of 190 000 tons NO\textsubscript{x} are emitted yearly from US heavy-duty diesel trucks, and steadily increasing, due to idling [10].
As a result of increasing loads of idling emissions, stringent anti-idling regulations are being enacted in the US, particularly in the state of California. In California, since January 2008, heavy trucks whose total weight exceeds 5 metric tons are only allowed to idle for a maximum of 5 min [14]. Together with stringent anti-idling regulations, incentives and tax reductions are also set forward by the Californian Air Resources Board and the US Congress promoting installations of anti-idling technologies in older diesel trucks [11, 14]. In Europe a smaller number of long-haul heavy-duty diesel trucks, ~100 000 in total, are found on roads daily compared to the US [4, 7]. Furthermore, different truck driver behaviors are reported, where long term idling does not normally take place at rest-stops [7]. Therefore, at the moment, no European anti-idling regulations exist concerning diesel trucks. However, there are reports that a growing number of comfort devices are being requested and installed onboard modern European long-haul diesel trucks, which may automatically result in extended periods of long-term idling [7]. Hence, one may assume it is a matter of time before similar idling emissions standards are passed by the EU. Historically, the California emissions regulations, which are considered the most stringent to follow, are setting the standard worldwide and frequently being adopted in Europe [3].

2.2 Auxiliary power units

A possible solution to reduce idling emissions lies in using an auxiliary power unit which can generate the amount of electricity needed independently of the truck engine. To date, some applications are commercially available, while others are still under development. In Table 2, US targets for APU systems are listed [15]. As seen in the table, the target specifications are expressed in terms of efficiency, weight, volume, cost, durability and start-up.

Table 2. US 2015 targets for stationary and mobile APU systems [15].

<table>
<thead>
<tr>
<th></th>
<th>Stationary</th>
<th>Mobilea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall electrical efficiency [%]</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>Power density [W/dm³]</td>
<td>100</td>
<td>35</td>
</tr>
<tr>
<td>Specific power [W/kg]</td>
<td>100</td>
<td>40</td>
</tr>
<tr>
<td>Specific cost [$/kWe]</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>Lifetime [h]</td>
<td>35 000</td>
<td>15 000</td>
</tr>
<tr>
<td>Start-up time [min]</td>
<td>15-30</td>
<td>10</td>
</tr>
</tbody>
</table>

a Based on diesel fuel-cell auxiliary power units (1-10 kWₑ) running on standard ultra-low sulfur diesel. It should be noted that the type of fuel cell is not explicitly addressed in the specifications given by the US DOE.

Idle reduction technologies, in the form of auxiliary power units, can be divided into two categories: stationary and mobile. Stationary typically involves an external power outlet device that is plugged on the truck, while mobile applications are integrated into the diesel trucks. A commercially available and popular stationary application employed in the US is truck stop electrification (TSE) [4, 7-11]. Major advantages with TSE utilities are low investment costs and a simple and robust technology.
However, only a few sites are currently available in the US, a total of 131 locations are spread out in 34 states on routes with heavy traffic [4, 7, 11]. Another drawback is that even if all trucks stops were electrified, predictions have shown they would only cover half of the total number of the existing heavy-duty trucks [4, 7, 11]. Also, another negative aspect with TSE is that each location requires significant space due to the length and large volume of the trucks. As a result, only a small number of trucks can be electrified at each TSE location at a time [4, 7].

Table 3 lists and compares mobile auxiliary power units that are proposed for the abatement of diesel truck idling emissions. Mobile idle reduction technologies that are commercially available are diesel internal combustion engine (ICE) APU and battery electric APU. Diesel ICE-APU are highly efficient and capable of providing the necessary electricity during heating as well as cooling of the cabin. Furthermore, they can be plugged with TSE. However, these units have poor durability; they also operate at a high noise level and emit large concentrations of NOx and PM [4]. Hence, despite the high efficiency, these units may cause sleep disorder, potential health hazard, and in addition, are not likely to pass future idling emission regulations. At the moment, diesel ICE-APU sales are low; only 3% of all new trucks sold in the US include this unit [8]. Battery electric APUs can exist in two varieties depending on power source material: as lead acid or as Li-ion. Lead acid batteries are commercially available while Li-ion batteries are still under development. A seen in Table 3, benefits of using a battery as APU are low cost (lead acid), low weight and volume (Li-ion charged). However, most of these batteries fail to provide the necessary average power outlet of 5 kWₑ at a 10 h minimum operation time. The latter fact is based on the minimum amount of resting hours compulsory for long-haul truck drivers [7]. The total market share of battery electric APUs in the US is believed to be low and the exact sale numbers are unknown at the moment.

<table>
<thead>
<tr>
<th></th>
<th>Diesel ICE 5 kWₑ</th>
<th>Battery, lead acid 40 kWh</th>
<th>Battery, Li-ion 40 kWh</th>
<th>Diesel SOFC 5 kWₑ</th>
<th>Diesel PEFC 5 kWₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost [€]</td>
<td>7000-9000</td>
<td>6000</td>
<td>20 000</td>
<td>&gt;50 000</td>
<td>&gt; 10 000</td>
</tr>
<tr>
<td>Efficiency, max [%]</td>
<td>30</td>
<td>17-21</td>
<td>17-21</td>
<td>35-45</td>
<td>30-40</td>
</tr>
<tr>
<td>Volume [dm³]</td>
<td>150-400</td>
<td>500</td>
<td>220-250</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Weight [kg]</td>
<td>180-230</td>
<td>1000</td>
<td>285-300</td>
<td>100-150</td>
<td>150</td>
</tr>
<tr>
<td>Durability [h]</td>
<td>&gt; 4000</td>
<td>&gt; 3000</td>
<td>5000-10000</td>
<td>10 000</td>
<td>2500</td>
</tr>
<tr>
<td>Start up time [min]</td>
<td>&lt; 2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>60</td>
<td>6-30</td>
</tr>
</tbody>
</table>

Other mobile idle reduction technologies that are still under development are fuel-cell based APU systems. To date, there are two competing technologies: diesel Solid Oxide Fuel Cell (SOFC) and diesel Polymer Electrolyte Fuel Cell (PEFC). In both cases a fuel processor is needed where a fuel reformer converts the diesel to H₂ and CO that are used as energy feedstocks in the fuel cells.
Fuel cell utilities have great benefits offering fuel savings, silence during operation and lower emissions. Studies have shown that fuel consumption can be reduced by 67 to 82 % [4, 10, 13]. For instance, a study by Lutsey et al. [10] have shown that only 0.6 dm$^3$/h is needed for a FC-APU utility, compared to 3.5 dm$^3$/h under normal circumstances using the truck engine, in order to generate 5 kW$_e$ during idling mode. Also, total life-cycle emission predictions have shown that NO$_x$ pollutants from FC-APU will be 99 % lower compared to idle operation of diesel engines [13]. As seen in Table 3, both fuel cell types have similar properties and advantages. They both provide high efficiency, small weight and volume. However, SOFC and PEFC have one great disadvantage, the total cost. The cost is often related to the type of material and number of operating units that are needed for APU operation.

There are some great differences between SOFC and PEFC and different technical barriers that need to be overcome. As seen in Table 3, diesel SOFC has an overall higher efficiency and durability compared to PEFC. Also, SOFC can run both on H$_2$ and CO. However, the operating temperature of SOFC lies in the vicinity of 800-1000 °C [18, 19]. This high temperature requires heat-resistant and often expensive cell materials [18]. Another problem with SOFC is the long start-up time. The start-up time of 60 min is a major disadvantage as US DOE targets only allows a maximum of 10 min of initiation (Table 2). This is due to the truck drivers’ need to quickly utilize the comfort units in the cabin during resting. Another major problem with SOFC is the long-term stability of the cell material. Frequent start-ups and shutdowns are known to cause thermal decomposition and fast deactivation of the cell material [18, 19]. Other known problems related to the cell material are poor cell sealing, mechanical shock effects, oxidation of anode electrolyte and complex integration of ceramic parts [18]. Unlike SOFC, PEFC runs only on H$_2$ and at lower operating temperatures, 70-200 °C, enabling faster response and start-up, ~6-30 min (Table 3). Also, due to the low operating temperature, the durability of the material in relation to start-ups and shutdowns of the APU is not an issue [11, 16, 20]. Hence, less expensive cell materials can be used; moreover the fabrication of the cell is less complicated which lowers the total production cost [7]. However, there are some major drawbacks with the diesel PEFC-APU mostly related to the low impurity tolerance of the cell, in particular towards CO. Studies have shown that very low CO quantities, less than 10 ppm, are mandatory in order for the PEFC to function properly [16, 20, 21]. As a result, CO clean-up units such as water-gas shift (WGS) and preferential oxidation (PrOx) are needed in order to lower the CO concentration to acceptable levels. These units are often placed between the fuel reformer and the fuel cell in the FC-APU scheme (see Figs. 1-2). The addition of CO clean-up units makes the diesel PEFC-APU set-up more complex, compared to diesel SOFC-APU.
At the moment, TSE is the most popular APU utility in the US [4, 8]. Analysts predict that FC-APU poses the biggest threat towards TSE [8]. A fast and successful introduction of FC-APU in the US market is considered crucial in order to prevent TSE from becoming well-established and standardized [8, 11]. Among the available FC-APU technologies PEFC is predicted to reach the market fastest. The quicker response, the shorter start-up time, along with the higher stability of cell material and lower cost of the PEFC unit, compared to SOFC, are believed to be winning features making it a more attractive solution for a FC-APU utility onboard heavy-duty diesel trucks [7, 11]. It should be emphasized that PEFC-APU systems are also proposed to be implemented in other markets e.g. onboard forklifts, camper vans, boats, scooters and aviation applications [7, 11, 16]. However, these niche markets are considered too small. At the moment, diesel PEFC-APU onboard heavy-duty trucks offer more lucrative sales and are closer to reach the point of commercial breakthrough [7, 8]. Examples of diesel PEFC developers are: Ballard Power Systems, Volkswagen/Idatech and PowerCell Sweden AB [11, 22].
To date, further research is still needed in order to make a diesel PEFC-APU system a practical and feasible option for commercialization. As mentioned previously, the process scheme for a diesel PEFC-APU is complex and consists of three major segments; a fuel reformer, CO-clean up units and the fuel cell. In order to make PEFC commercially available significant cost savings and higher efficiencies are required in each segment. Cost reductions can be obtained by further development of the active materials in each segment, which are catalysts and electrodes. A higher efficiency of the fuel processor can be achieved by smarter reactor designs, better integration of each segment and better understanding of the overall process. One key segment where smarter, less expensive catalyst and reactor designs as well as process assessment are still needed is the fuel reformer. The fuel reformer can be described as the “heart” of the FC-APU. Poor reformer performance can result in a negative “domino effect” causing degeneration and deactivation of the other components in the subsequent segments. Typically, the bad performance is often coupled to the catalyst composition and reactor design of the fuel reformer. Hence, extensive research is needed in these two areas which are the scope of this thesis. An example of a block scheme for a diesel PEFC-APU can be seen in Fig. 2. Depending on the fuel quality a prereforming step can be installed to purify the fuel as well as vaporize it prior to entering the catalytic reformer. Also, an afterburner, an air supply, a water tank and heat exchangers are also needed to heat up as well as cool the system. Chapters 3-4 treat diesel fuel properties and diesel fuel processor involving fuel reforming technologies; CO clean up and PEFC will also be discussed briefly. The research progress and results concerning the reforming catalyst and the reactor design of the diesel reformer and are discussed in Chapters 5-7.

Fig. 2. Diesel PEFC-APU block scheme including flow diagram. The APU system includes high and low temperature water-gas shift (WGS) units denoted as HTS and LTS. Also a preferential oxidation (PrOx) unit is depicted.
3. Fuel processing

3.1 Onboard fuel processing for hydrogen production

As mentioned previously in section 2.2, a fuel processor is needed in order to operate an FC-APU. Fuel processing can be defined as the conversion of a raw material into an energy-rich gas mixture. The energy conversion can occur either homogeneously or heterogeneously. Homogeneous reactions are typically thermal processes, while heterogeneous reactions are mostly catalytic where the catalyst is often in the solid state. Often heterogeneous catalysis is employed for fuel processing as it normally results in less expensive, faster and more reliable energy conversion. To date, catalytic fuel processing is an established industrial process often used in stationary applications [23, 24]. A typical example is found in the petroleum industry where natural gas is processed to produce hydrogen. In this case, hydrogen is used to hydrotreat HC fuels (e.g. gasoline and jet fuel) removing undesired and stable compounds containing sulfur and nitrogen from the molecular structures of the long HC chains in the fuel mixtures [23, 24]. Hydrogen can also be used for synthetic fuel production, for example Fischer-Tropsch (FT) diesel. Hence, hydrogen has several interesting and useful properties. In a PEFC-APU system the high energy content of hydrogen, ~240 kJ/mol [19, 24, 25], is wanted in order to convert it and generate electricity using the fuel cell. The physical and chemical properties of hydrogen can be seen in Table 4.

Table 4. Hydrogen properties [19, 24, 25].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>H2</td>
</tr>
<tr>
<td>Molecular weight [g/mol]</td>
<td>2.016</td>
</tr>
<tr>
<td>Freezing point @ 1 bar [°C]</td>
<td>-259</td>
</tr>
<tr>
<td>Boiling point @ 1 bar [°C]</td>
<td>-253</td>
</tr>
<tr>
<td>Gas. density [kg/m³]</td>
<td>0.09</td>
</tr>
<tr>
<td>Liq. density [kg/m³]</td>
<td>77</td>
</tr>
<tr>
<td>Gas viscosity @ -252.77 °C [mPa·s]</td>
<td>0.00085</td>
</tr>
<tr>
<td>Heat of vaporization [kJ/mol]</td>
<td>0.92</td>
</tr>
<tr>
<td>Lower heating value [kJ/mol]</td>
<td>240</td>
</tr>
<tr>
<td>Autoignition temperature in air [°C]</td>
<td>571</td>
</tr>
<tr>
<td>Flammability limits in air [vol%]</td>
<td>4-77</td>
</tr>
</tbody>
</table>

Although hydrogen has high energy content, the gas energy density is low ~0.011 MJ/dm³, meaning large volumes are needed in order to store pure gaseous hydrogen [19, 24, 25]. This is often termed the “hydrogen storage problem”. In a diesel PEFC-APU, the hydrogen storage problem is circumvented as gaseous hydrogen is generated onboard from liquid diesel, with an energy density of ~38.6 MJ/dm³, by a catalytic reformer [19, 24, 25]. Hence, the term “onboard fuel processing”. However, it is a major challenge to transform and size down an industry-sized stationary fuel processor into a smaller mobile FC-APU system that can be fitted onboard a diesel truck. As mentioned previously in section 2.2, the
overall efficiency, volume and weight are significant features to consider for a mobile FC-APU system. There are additional properties to consider, specific for onboard fuel processing and PEFC-APU systems. These additional properties can be seen in Table 5.

Table 5. US 2011 targets for stationary applications for power output of 5-250 kW. Equivalent technical targets for mobile onboard fuel processors and PEFC-APU are not included in the US DOE specifications [15].

<table>
<thead>
<tr>
<th>Property</th>
<th>Fuel processor</th>
<th>PEFC-APU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall electrical efficiency [%]</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Specific cost [$/kW]</td>
<td>220</td>
<td>750</td>
</tr>
<tr>
<td>Start-up time [min]</td>
<td>-</td>
<td>&lt;30</td>
</tr>
<tr>
<td>Transient response time (from 10 to 90 % power) [s]</td>
<td>60</td>
<td>3</td>
</tr>
<tr>
<td>Lifetime [h]</td>
<td>40 000</td>
<td>40 000</td>
</tr>
<tr>
<td>Ambient temperature limits [°C]</td>
<td>-35 to +40</td>
<td>-35 to +40</td>
</tr>
<tr>
<td>Cold start time (rated power, from -20 °C to ambient) [min]</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Noise [dB(A)]</td>
<td>&lt;55</td>
<td>&lt;55</td>
</tr>
<tr>
<td>CO content (steady state) [ppm]</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>CO content (transient) [ppm]</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>H2S content (dry) [ppbv]</td>
<td>&lt;4</td>
<td>-</td>
</tr>
<tr>
<td>Total emissions (combined NOx, CO, SOx, PM and HC) [g/kWh]</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Number of cold start cycles</td>
<td>-</td>
<td>2000</td>
</tr>
</tbody>
</table>

As seen in the table, the target specifications also include the transient response time, ambient temperature limitations, cold start time, noise levels, CO and H2S levels, total emission levels and number of cold start cycles. These features are essential in order to ensure fast, safe and reliable operation with minimal negative impact towards humans and the environment. Other issues that are critical are safety management of the processed hydrogen fuel itself. Looking back at Table 4, hydrogen is a light, low viscosity, highly reactive, highly flammable and volatile gas that can easily be ignited in air. Hence, hydrogen must be handled with care; precautions must be taken to prevent high concentration build-ups in narrow spaces. However, this latter problem is often neglected as hydrogen can easily disperse in air due to its high buoyancy. Nevertheless, smart and safe engineering should be taken into account, especially in order to make PEFC-APU systems a secure, practical and feasible solution in heavy-duty diesel trucks.

3.2 Fueling fuel processors

Hydrogen is a highly reactive gas that in nature is always found bonded to other elements or molecules, either in organic or inorganic compounds. Hence, a suitable hydrogen carrier source must be located, retrieved and processed in order to release hydrogen and make use of its high energy. There are several other ways of producing hydrogen besides fuel processing. Electrolysis, gasification, photosynthesis and microbial digestion are mentioned as alternatives using e.g. water, biomass or waste material as feedstock [26]. However, adapting these processes in a mobile APU is considered a
vast challenge and also somewhat unrealistic at the moment. Most of these processes lack high overall efficiency, high hydrogen production rate, low manufacture cost and low energy demand during processing [26]. Also, the hydrogen generation technologies that are most likely to succeed in being implemented, e.g. in the transport sector, are those that are most easily adopted in an existing fuel infrastructure [7, 11]. In the case of onboard fuel processing, the raw material is a liquid transportation fuel such as diesel and gasoline. Hence, standardized infrastructure solutions, e.g. fuel distribution and refueling stations, already exist for these conventional transportation fuels. One may argue the use of fossil-fueled onboard fuel processors can be considered a long-term and sustainable solution, especially since recent reports claim that the oil peak occurred already in 2002, and a decline of annual rate of raw oil production is expected [27]. However, recent reports also show a worldwide rapid increase of annual production, sales and registration of heavy-duty diesel trucks [1-7]. Hence, an increase of diesel truck emissions is expected and unavoidable, unless new efficient and environmentally friendly technological solutions can be adopted and put into use quickly. Therefore, diesel PEFC-APU is considered an excellent mid-term solution until new, renewable, cleaner and sustainable transportation fuels can be successfully integrated in our infrastructure. A fuel that is considered as a viable diesel substitute is dimethyl ether (DME). DME is a colorless, non-hazardous, biodegradable gaseous compound (at atmospheric pressure and room temperature), with a higher cetane number (~55) than diesel [11]. The molecular structure consists of two methyl groups linked together by an ether bound (CH$_3$-O-CH$_3$). Hence it does not contain any C-C bond or sulfur, and consequently neither soot formation nor sulfur compounds are formed in the exhaust gases and emitted. In Sweden, several recent studies have demonstrated that DME has been successfully produced in pilot plants by black-liquor gasification and then tested as transportation fuel in Volvo trucks [11]. However, at the moment, diesel is the most utilized transportation fuel worldwide for propulsion of heavy-duty truck vehicles [7, 11]. For instance, in Sweden, 98 % of all heavy-duty trucks found on road run on diesel [2]. Therefore, a PEFC-APU system intended for heavy-duty truck employment should be based on diesel as feedstock. Hybrid systems, meaning one fuel for operating the truck engine and another fuel for the FC-APU, could also be an alternative. However studies, based on truck driver attitudes, have shown low interest in hybrid systems due to increased costs, complexity and maintenance [7, 28]. Hence, a single-fuel system, including both the engine and the PEFC-APU-system, using diesel, is the favored solution at the moment. The diesel fuel properties are briefly discussed in the following section.

3.3 Diesel fuel
On August 10, 1896, the German engineer, Rudolf Diesel successfully demonstrated the use of his patented diesel engine in a public display [4, 29]. The superiority of the mechanical efficiency of the diesel engine compared to the steam-powered engine laid the foundation, and a new era of
diesel-driven transportation vehicles was begun [4, 29]. To date, more than 100 years later, reports have shown that diesel engine usage is gaining new grounds as higher annual sales are reported both in Europe and in the US [1, 2, 5, 7]. Advantages with diesel engines are: superior fuel economy, durability, low HC and CO emissions, high torque, high reliability, low fuel cost and low maintenance cost [4, 12, 29]. These major advantages are the main reasons as to why diesel engines are extensively installed and used in heavy-duty trucks. However, there are some disadvantages as well, such as: high noise level, weight, high NOx and PM emissions, high engine cost and low exhaust temperature [4, 12, 29]. The diesel engine, aka compression ignition (CI) engine, is basically an internal combustion engine where diesel and air are injected and compressed together in a sealed stainless steel chamber/cylinder. The compression, which is carried out by a piston, causes self-ignition of the fuel and the resulting chemical energy is converted into mechanical energy, which is used to thrust the vehicle. Diesel is an excellent fuel for this process due to its high energy content, compressibility and ignitability. The ignition quality of the fuel is measured by the cetane number. The average cetane number of diesel ~50 [4, 12, 29].

Diesel is a complex and rich mixture of thousands of hydrocarbons, most of which have carbon numbers from 10 to 22 and boiling points ranging from 185 to 290 °C [4, 12, 29]. The fuel is practically solely derived by fractional distillation of petroleum crude oil. The composition of the crude oil can vary depending on the origin. In general, there are three major classes of hydrocarbons in the petroleum crude oil composition: paraffinic, naphthenic and aromatic. The crude oil is distilled and processed in refineries where it also undergoes hydrocracking, isomerization, alkylation and hydrotreating in order to produce purified and refined transportation fuels such as jet fuel, gasoline and diesel. The refined diesel fuels contain a high number of n-paraffins which are known for having high cetane number. The diesel fuel also contains cycloparaffins, aromatics and minor concentrations of sulfur as well. The latter is detrimental as it can cause corrosion, mechanical wear, sulfur emissions and also deactivation of the exhaust gas catalyst [4, 12, 23]. The sulfur content of commercial diesel varies depending on where manufactured and used. In Sweden, a maximum sulfur content of 10 ppm is allowed while in the US the corresponding content is 15 ppm [4, 14, 30]. Diesel can also be obtained synthetically by gas-to-liquid (GTL), biomass-to-liquid (BTL) or transesterification processes. Characteristic for synthetic diesel, aka Fischer-Tropsch diesel, is that it contains a higher number of n-paraffins, very little aromatics and virtually no sulfur. Besides these natural ingredients, a large number of additives are also added in commercial diesel in order to improve the engine performance, fuel handling, fuel stability and contaminant control properties. The additives can be added to the fuel at three different stages: in the refineries, in the fuel distribution system (pipelines), or by retailers and end-users in the aftermarket [4, 29]. Examples of additives are corrosion inhibitors, de-icers, detergents, cetane enhancers, lubricity improvers, flow improvers, wax anti-settling additives, cloud-point depressants, antifoam additives, dispersants and demulsifiers [4, 29].
3.4 Diesel reforming

There are great differences between diesel employment for compression engines and diesel usage in fuel reforming. In the case of the compression engine, the fuel is injected through a nozzle at high pressures, ~2 000 bar [12], blended with air and compressed to ignite in order to make use of the chemical energy for vehicle propulsion. The main work in the compression engine is done mechanically using a piston. In diesel reforming, no mechanical work is carried out. Instead, the main work is done through heterogenous reactions which involve reactions between gaseous diesel and a solid catalyst with the aim to produce a hydrogen-rich gas. Hence, in a diesel PEFC-APU system the liquid fuel has to be heated and vaporized first in order to facilitate the heterogeneous reactions. Also, the fuel has to be injected at significantly lower pressures, ~7-10 bar [31]. Too high pressures may result in large build-ups of unconverted liquid fuel on the catalyst surface which can cause mechanical damages to the catalyst, disturbance in the flow pattern and reactor plugging [24, 32-34]. Hence, finding fuel injectors suitable for diesel reforming with excellent fuel dispersion capabilities that operate at low pressures and volumetric flows can be tricky. In addition, the mixture preparation is a crucial step in reforming. In diesel reforming, different reforming technologies can be employed in which diesel is blended with either air, pure oxygen or steam as main reactant (see section 3.4.2). The gas mixture has to be well-blended to avoid local variations, e.g. air/fuel ratios, in order to prevent hot-spots that can cause undesired side reactions such as carbon formation (see section 3.4.3) and damage the catalyst [24, 26, 34]. Also, the compactness of the reforming system is important in order to simplify heat management and to obtain high thermal efficiency. For instance, heat generated from oxidation reactions throughout reforming is often used by the catalyst to facilitate and promote hydrogen generation reactions. Hence, in order to prevent redundant heat losses, a variety of novel reaction designs can be used in a diesel reformer which differ significantly from conventional combustion steel-chamber design present in a compression engine. The reactor designs used for the full-scale diesel reforming in this thesis can be found in Chapter 7.

3.4.1 Fuel-pretreatment and pre-reforming

Apart from differences in fuel injection, mixing, product aim and reactor design, another fuel-reforming consideration is the diesel fuel itself. For instance, although the fuel additives in diesel are known to have beneficial effect on the compression engine performance, in fuel reforming they have the opposite effect. The organometallics, e.g. Fe, Sr clusters, present in the additives can easily adsorb onto the reforming catalyst surface blocking active sites and thus resulting in catalyst deactivation. The additive fraction in the fuel is usually low and thus often disregarded in fuel reforming. Instead the sulfur and rich aromatic compounds in diesel are more challenging. In particular, sulfur can be problematic as it, in the form of gaseous SO\textsubscript{2} and H\textsubscript{2}S, easily can become attached on the reforming catalyst surface and onto the electrodes of the fuel cells (see Chapter 4) causing deactivation.
Fuel pretreatment, e.g. desulfurization, using zinc oxide as adsorbents traps, see Eq. 1, can be carried out in the gas phase at ~350 °C to remove sulfur prior to reforming [24, 26, 34].

Sulfur removal

\[
H_2S + ZnO \rightarrow ZnS + H_2O
\]

\[\Delta H = -75 \text{ kJ/mol}\] (1)

In addition to desulfurization, a pre-reforming step can also be integrated in the APU scheme, placed prior to the diesel reformer (see Fig. 2). The aim of pre-reforming is to convert heavy fuels, such as jet fuel, diesel and gasoline, into lighter HC compounds in order to facilitate the reforming process carried out by the sequential main catalytic reformer. Other benefits of using a pre-reformer are that factors such as coke formation, which is known to cause catalyst deactivation, can be minimized. Typical coke precursors are stable aromatic compounds such as benzene that are present in the fuel and olefins, e.g. ethylene, which are formed as byproducts during reforming. The latter phenomenon is described in more detail in section 3.4.3. Pre-reforming reactions are usually carried out at lower reaction temperatures. For instance, for diesel, pre-reforming reaction temperatures in the range of 300 to 450 °C have been reported [24]. Examples of pre-reforming technologies are cool flame technology, pyrolysis and catalytic cracking [24]. In the work summarized in this thesis neither fuel pre-treatment nor pre-reforming took place prior to diesel reforming. Three kinds of diesel fuels were tested for fuel reforming. The fuel candidates were the diesel surrogate n-tetradecane, commercial Swedish diesel (MK1) and synthetic Fischer-Tropsch diesel. The physical and chemical properties of the fuels are listed in Table 6. The effect of the fuel properties of the employed diesel fuels on fuel reforming was studied at full-scale in Paper III, which is discussed in more detail in Chapter 7.

Table 6. Comparison of properties for the diesel fuels used in this thesis [4, 30, 35, 36].

<table>
<thead>
<tr>
<th>Property</th>
<th>n-tetradecane</th>
<th>Diesel MK1</th>
<th>FT-diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average chemical formula</td>
<td>C_{14}H_{30}</td>
<td>~C_{14}H_{26}</td>
<td>~C_{14}H_{26}</td>
</tr>
<tr>
<td>Molecular weight [g/mol]</td>
<td>198.4</td>
<td>~194</td>
<td>~194</td>
</tr>
<tr>
<td>Boiling point @ 1 bar [°C]</td>
<td>253</td>
<td>180-290(^a)</td>
<td>350(^c)</td>
</tr>
<tr>
<td>Vapor pressure @38 °C [bar]</td>
<td>negl. (20°C)</td>
<td>negl.</td>
<td>negl.</td>
</tr>
<tr>
<td>Liq. density @15 °C [kg/m(^3)]</td>
<td>760</td>
<td>800-820</td>
<td>800</td>
</tr>
<tr>
<td>Liq. viscosity @40 °C [mPa-s]</td>
<td>1.7</td>
<td>2-4(^{25°C})</td>
<td>~2.9</td>
</tr>
<tr>
<td>Heat of vaporization [MJ/kg]</td>
<td>0.25</td>
<td>0.27</td>
<td>n.a.</td>
</tr>
<tr>
<td>Lower heating value [MJ/kg]</td>
<td>44</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>Autoignition temperature [°C]</td>
<td>220</td>
<td>206(^b)</td>
<td>n.a.</td>
</tr>
<tr>
<td>Flammability limits in air [vol%]</td>
<td>0.5-6.5</td>
<td>1-5</td>
<td>n.a.</td>
</tr>
<tr>
<td>Sulfur content max [wt ppm]</td>
<td>0</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Aromatic content max [vol%]</td>
<td>0</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Cetane number min [n-cetane]</td>
<td>93</td>
<td>50</td>
<td>80</td>
</tr>
</tbody>
</table>

\(^a\) T95.  
\(^b\) n-Cetane  
\(^c\) T95, initial boiling point not given
3.4.2 Reforming technologies

To date, there are three primary reforming technologies used to generate hydrogen from hydrocarbon fuels: partial oxidation (PO), steam reforming (SR) and autothermal reforming (ATR), as shown in Eqs. (2-4) \[23, 24, 26\].

Partial oxidation is a dynamic, exothermic process that uses oxygen or air as reactant to convert diesel into a hydrogen-rich gas (Eq. 2). A major advantage with PO is that high operating temperatures can be employed making it more sulfur tolerant and resulting in low methane formation. However, the high temperatures can also be problematic as they result in a decrease in hydrogen production. They also result in high carbon formation and hot spots which often cause catalyst deactivation. Another drawback with PO is that it requires continuous cooling of the reactor during operation \[23, 24, 26\].

Steam reforming is a slower, endothermic process that requires heat, frequently provided by an external heating source, in order to maintain continuous operation. It also requires an external water supply in order to generate and supply steam for the fuel reforming process. On the other hand, it does not require any oxygen and thus coke formation and hot spots are not an issue. Furthermore, as seen in Eq. 3 it has the highest hydrogen production out of the three reforming processes \[23, 24, 26\].

ATR is a combination of the two processes, PO and SR, as seen in Eq. 4. During ATR, heat is generated by the exothermic PO initially and used by the subsequent endothermic SR to increase the hydrogen production resulting in a thermoneutral process. The thermoneutral process is beneficial as it does not require any external cooling or heating of the reactor during operation. Also, ATR can be carried out at moderate reaction temperatures and at atmospheric pressure resulting in low methane and soot formation \[23, 24, 26\]. Furthermore, studies have shown that ATR is an ideal reforming process for a diesel PEFC-APU system as it is a dynamic and energy-efficient process capable of handling the frequent start-ups and shutdowns occurring both during transient and steady-state operation of the diesel trucks \[11, 37, 38\].

**Partial oxidation (PO)**

\[
C_zH_y + \frac{x}{2}(O_2 + 3.76N_2) \rightarrow xCO + \frac{y}{2}H_2 + \frac{x}{2}3.76N_2
\]  \(\Delta H^0 < 0 \text{ kJ/mol}\)  

**Steam reforming (SR)**

\[
C_zH_y + xH_2O \rightarrow xCO + (x + \frac{1}{2}y)H_2
\]  \(\Delta H^0 > 0 \text{ kJ/mol}\)
**Autothermal reforming (ATR)**

\[ C_x H_{y} + \frac{x}{4} \left( O_2 + 3.76N_2 \right) + \frac{x}{2} H_2O \rightarrow xCO + \left( \frac{x}{2} + \frac{y}{2} \right) H_2 + \frac{x}{4} 3.76N_2 \]

\[ \Delta H^0 \approx 0 \text{ kJ/mol} \]

In this thesis, ATR was used as reforming technology. In the following section more details are given concerning the ATR characteristics such as operating parameters and reforming chemistry.

### 3.4.3 ATR characteristics, operating parameters and reforming chemistry

ATR of diesel is a complex process in which the rich variety of fuel compounds can give rise to a series of main reactions and side reactions taking place in the gas phase and on the active sites of the catalyst surface. In general, the common belief concerning the main reactions is that PO initiates ATR, followed by SR. The latter fact is frequently proven in several ATR studies involving temperature measurements [11, 24, 32, 39-42]. For instance, temperature reading along the length of the reactor has shown that the ATR temperature profile consists of an initial maximum followed by a decrease as shown in Fig. 3. The first part is ascribed to the “oxidation zone” where predominantly exothermic reactions occur due to PO, while the second part is ascribed to the “reforming zone” where mainly endothermic reactions take place due to SR. In general, the oxidation zone covers approximately 1/3 of the reactor volume, while the reforming zone takes up the remainder of the reactor volume. These trends will be discussed in more detail in Chapter 6 where a zoned catalyst was tested for ATR of diesel. Also results in this thesis show the characteristic ATR temperature profile.

![Diagram of ATR temperature profile](image)

**Fig. 3. ATR temperature profile.**
In ATR, the most important operating parameters are the steam-to-carbon (H$_2$O/C) and oxygen-to-carbon (O$_2$/C) ratios in the feedstock composition [11, 24, 26]. The feedstock ratios are derived by dividing the reactants moles (H$_2$O and O$_2$) with the carbon moles present in the employed fuel. Optimal ratios for ATR of diesel can be determined for instance by means of thermodynamic equilibrium calculations at thermoneutral conditions (ΔH~0). However, in reality, excess air, meaning higher O$_2$/C ratios, are often implemented in order to trigger and sustain the ATR reactions as well as to compensate heat losses [11, 24, 26]. Also, the ratios are often empirically derived as the optimal values of the H$_2$O/C and O$_2$/C ratios can differ significantly depending on the quality of the diesel fuel, reforming catalyst and reactor design employed [11, 24, 26].

Fig. 4. ATR of diesel simulations. The effect of various O$_2$/C and H$_2$O/C ratios (x-axis) on H$_2$ and CO production (y-axis), at constant a) H$_2$O/C=2.0 and b) O$_2$/C=0.4 using model compounds, C$_{14}$H$_{26}$ and C$_{16}$H$_{34}$, respectively, at T=700-800°C. The depicted results are taken from references [11, 34].

Comparing thermodynamic equilibrium calculations with the actual experimental results can be complicated. As mentioned previously, the complex and rich fuel content, as well as the large variety of diesel fuels, can give rise to a series of main and side reactions, thus, making it exceedingly difficult to predict the actual outcome of the product gas composition. In general, a model compound is regularly used to calculate the experimental diesel conversion as well as to simulate the product gas distributions. Examples of thermodynamic equilibrium calculations for diesel using model compounds, C$_{14}$H$_{26}$ and C$_{16}$H$_{34}$, respectively, can be seen in Fig. 4a-b. In general, as seen in the figures, increasing the O$_2$/C decreases the hydrogen production as the ATR reforming process is pushed closer towards the operating range for partial oxidation. Increasing the H$_2$O/C promotes the SR reactions by slightly enhancing the level of hydrogen concentration and lowering the carbon monoxide formation in the product gas. Also, for ATR of diesel, typical reaction temperatures are in the vicinity of 700-900°C [11, 24]. In this thesis, the effect of the operating parameters H$_2$O/C and O$_2$/C were studied in Paper III, see Chapter 7.
In fuel reforming, achieving complete conversion of the diesel is crucial; not only due to the issue of fuel penalty, but also due to the risk that unconverted diesel can easily deactivate the subsequent segments in the PEFC-APU scheme. For instance, a high fuel slip from the reformer can deactivate the fuel cell; the long hydrocarbon chains in diesel can easily become attached onto the electrodes and Nafion membranes, hindering the transport of the hydrogen ions from the anode to the cathode side (see Chapter 4) [16, 20, 21, 24]. Hence, diesel conversion is an important parameter to consider when evaluating the reactor as well as the catalyst performances. However, calculating the diesel conversion in commercial diesel fuels can be challenging due to the rich and complex content. Nevertheless, it is critical to use real commercial diesel fuels for fuel reforming. This in order to gain a wider and deeper perspective as to how the real fuel mixture affects the conversion, the distribution of the product gas, and deactivation mechanisms such as coke deposition and sulfur adsorption. In this thesis, the fuel conversion was calculated by means of model compound assumptions e.g. C_{14}H_{26} (see also Table 6) by using both FTIR and GC analyses. The methodology is described in detail in Papers III and V. In short, for the FTIR, the diesel conversion was calculated by using a diesel response Y-predictor incorporated in a method file provided by MKS Instruments [43]. For the GC analysis, the conversion was estimated by means of atomic carbon balances.

Regardless of the reforming technology employed the major products in the product gas, termed “reformate”, include H₂, CO, CO₂ and CH₄ [24, 26]. For ATR, steam and nitrogen (if air is used as reactant) can also be present in the reformate. In general, a good indicator that the conversion of diesel is excellent is that only methane and no other higher order alkanes is present in the reformate [11, 24]. Furthermore, studies have shown that methane has a negligible effect on the PEFC performance [44]. However there are other HC products besides alkanes that can be generated during diesel reforming. Ethylene, C₂H₄, with double C=C bonds, can also be present in the reformate as a major by-product. In diesel reforming, generating a low level of ethylene concentration in the reformate is considered crucial as ethylene is a well-known coke precursor. Several studies have shown that a higher level of ethylene concentration in the reformate, with increased time on stream, is often a clear indication of increased carbon deposition taking place on the active sites of the catalyst surface [45-48]. Besides blocking active sites, coke can also cause mechanical breakage of the particles leading to severe pressure drops and reactor plugging. The latter reaction phenomenon often results in lower reforming rates as well as catalyst deactivation. Besides splitting of C=C bonds (Eq. 6), coke can also be generated by the reaction of carbon monoxide with hydrogen, Eq. 7, and by the Boudouard reaction, Eq. 8 [11, 24, 26].

There are three ways to prevent coke formation: high reaction temperatures by increasing the O₂/C ratio, high H₂O/C ratios and elevated pressures [11, 24, 34, 45-48]. In the refining industry, the most common way to remove coke species is by surplus oxygen in the feed stream for a short period of time...
in order to promote removal of coke species from the catalyst surface through oxidation reactions. However, it should also be noted that the extra addition of oxygen can also be counterproductive causing damages to the catalyst as the surface temperature will be significantly elevated during the oxidation process, leading to possible losses of active metal particles from the catalyst [24, 45, 46]. Furthermore, an increase in O₂/C can lead to total oxidation (aka complete combustion) resulting in surplus CO₂ formation and hydrogen losses as seen in Eq. 9 [11, 24]. Hence, for ATR, the O₂/C ratio is carefully selected to make sure that the reaction is carried out at rich phase, meaning a surplus of fuel in comparison to air (λ<1) to hinder potential total oxidation reactions.

\[
C_xH_y \rightarrow xC + C_{m-x}H_{y-2x} + xH_2 \\
\Delta H = \text{Hydrocarbon dependent}
\]

\[
2CO \leftrightarrow C + CO_2 \\
\Delta H = 172 \text{ kJ/mol}
\]

\[
CO + H_2 \leftrightarrow C + H_2O \\
\Delta H = -131 \text{ kJ/mol}
\]

\[
C_xH_y + x(O_2 + 3.76N_2) \rightarrow xCO_2 + \frac{y}{2}H_2O + x3.76N_2
\]

Hence to summarize, besides fuel conversion, two other important parameters to consider when evaluating the reforming catalyst performance is the ethylene formation and the amount of CO and CO₂ in the reformate. For instance, CO₂ can also affect the PEFC performance in a negative way, however the overall negative effect is considerably less compared to CO contamination (Chapter 4). In addition to ethylene formation, other known side reactions that can take place during diesel reforming are water-gas shift (WGS) and methanation, see Eqs. 10-14.

In this thesis FTIR, GC and NDIR analyses were used to calculate the experimental diesel conversion and to measure the concentrations of the product gases in the reformate. The catalyst performance was determined in terms of diesel conversion, S_{CO2} selectivity (expressed as CO₂/(CO₂+CO)), and total hydrogen and ethylene concentrations in the reformate. Catalyst and reformer design development will be discussed in more detail in Chapters 5-7.
3.5 CO clean-up technologies

As mentioned previously in sections 2.2 and 3.4.3, the product gas from the fuel reformer contains high concentrations of CO (often >5 % depending on the fuel processed [26]), that need to be significantly reduced by CO clean-up units in order to prevent the fuel cell, PEFC, from deactivating by CO poisoning. The CO clean-up units are also used to increase and maximize the hydrogen concentration in the reformate prior to feeding the fuel cell. There are three CO clean-up technologies primarily used to reduce CO and improve the H₂ yield: water-gas shift (WGS), preferential oxidation (PrOx) and methanation, Eqs. 10-14 [11, 24, 26, 49].

Water-gas shift (WGS)

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \]
\[ \Delta H = -41.1 \text{kJ/mol} \]  

(10)

Preferential oxidation (PrOX)

\[ CO + \frac{1}{2}O_2 \rightarrow CO_2 \]
\[ \Delta H = 283 \text{kJ/mol} \]  

(11)

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]
\[ \Delta H = 242 \text{kJ/mol} \]  

(12)

Methanation

\[ 3H_2 + CO \leftrightarrow H_2O + CH_4 \]
\[ \Delta H = -254 \text{kJ/mol} \]  

(13)

\[ 4H_2 + CO_2 \rightarrow 2H_2O + CH_4 \]
\[ \Delta H = -165 \text{kJ/mol} \]  

(14)

The water-gas shift is a mildly exothermic reaction that usually takes place in two reaction stages (due to thermodynamic limitations) using two consecutive adiabatic beds. The first stage, termed the high temperature shift (HTS), is carried out at reaction temperatures of 400-500 °C typically using iron/chromium oxides as catalysts. In the second stage, termed the low temperature shift (LTS), the gas is cooled and fed to the second adiabatic bed at 200 °C using copper/zinc oxides as representative catalysts. The CO content after WGS treatment is usually around 1% while the relative H₂ concentration can be increased by ~20% [11, 24, 26].
Preferential oxidation can also be used to further reduce the CO concentrations to levels below 10 ppm. The reaction is carried out under excess of air (λ~1.5-2.0) at 150-250 °C over typically noble metal catalysts such as Rh, Pt and Ru [11, 24, 26, 49]. Undesired and unavoidable hydrogen losses also take place during the CO removal using PrOx. In general, 0.5 to 1 mol of hydrogen is consumed for each mol of CO converted, see Eqs. 11-12. Furthermore, reverse WGS reactions can also take place leading to further adverse hydrogen losses.

A methanation unit can also be included as a final CO removal step in the onboard fuel processor scheme to further reduce CO to sufficiently low ppm levels. The benefits of using methanation are that it does not require any air or oxygen as feedstock reactant making the overall CO clean-up scheme less complex. Also, CO₂ can be reduced using methanation. However, as with the case of PrOx, the use of methanation is not often implemented as CO removal since the main reaction involves using hydrogen as reactant, hence resulting in additional hydrogen losses. As seen in Eq. 13, 3 moles of hydrogen are consumed for each mole of CO converted. The reaction is typically carried out at 150-250 °C over Ni and Ru catalysts [24, 26, 49].
4. Fuel cell technology

4.1. PEFC components and operating scheme

As mentioned previously in section 3.1, the high energy chemical content of hydrogen (~240 kJ/mol) is converted by the fuel cell, PEFC, to electricity. The main reactions are electrochemical oxidations and reductions, and the resulting main product is steam. The overall efficiency of this process is high ~60 % [19, 20]. Also, high current densities, up to 1.0 W/cm², can be achieved [50].

The PEFC is basically made of two electrode catalysts with an electrolyte placed in between. The electrolyte is typically a membrane that allows proton transfer to take place. Therefore, PEFC can also be referred to as proton exchange membrane fuel cell (PEMFC). The constitution of the electrodes and membrane is normally referred to as a membrane electrode assembly (MEA). As seen in Fig. 5, the main components of the MEA are: anode and cathode catalysts, gas diffusion layers (GDL), and a proton exchange membrane [19]. The general scheme of the PEFC operation is also shown in Fig. 5. Furthermore, the oxidation, reduction and overall reactions are given in Eqs. 15-17.

**Anode reaction**

\[ H_2 \rightarrow 2H^+ + e^- \]  \hspace{1cm} (15)
The reactants, air and hydrogen-rich gas (purified reformate), enter the MEA system through bipolar plates (see Figs. 5-6). On the anode side, hydrogen diffuses through the thickness of the GDL in order to access the electrode catalyst surface layer where it reacts and dissociates to form electrons and protons. The electrons are transported to an external circuit in order to generate electricity while the protons (in the form of hydronium ions, H$_3$O$^+$) transfer over the membrane (termed vehicular diffusion) to access the cathode side where they react with oxygen to form steam \[16, 19\]. In general, approximately 3500 Ndm$^3$H$_2$/h (based on pure hydrogen) is needed to generate 5 kW$_e$ by PEFC \[11\]. Furthermore, in a PEFC-APU system, approximately 80% of the hydrogen feed is utilized by the fuel cell to generate electricity \[11, 24\]. The rest of the hydrogen is often used to heat the APU system, e.g. by employing an afterburner as seen in Fig. 2.

The gas diffusion layer materials are typically carbon fiber-based porous media $\sim$100-300 μm in thickness \[16, 19\]. The GDL is composed of multiple carbon fibers that are linked together, by weaving, to form a cloth, or bonded by resins to form a thin paper. The main objectives of the GDL are to provide: a stable electronic connection between the bipolar plates and the electrodes, a sure passage for efficient reactant transport and heat and water removal, mechanical support for the MEA, and finally, prohibit corrosion and erosion effects caused by the gas media \[16, 19, 21, 24\]. The membrane, $\sim$10-175 μm in thickness, is typically made of sulfonated polymer materials. A popular membrane is Nafion®, developed by Dupont, which consists of perfluorosulfonic acid in which the sulfonic acid functional groups provide charged sites (-SO$_3^-$) for the proton transfer to take place \[16, 19, 21, 24\]. The core of Nafion® is made of polytetrafluoroethylene (PTFE) which provides the physical strength of the membrane. Other important features of the membrane are to exhibit high ionic conductivity, be chemically and thermally stable and finally provide mechanical robustness during the electrochemical reactions \[16, 21\]. The electrode catalysts for anode and cathode are typically platinum and platinum alloys supported on carbon $\sim$10 μm in thickness. Examples of typical alloying elements are Ru, Ni, Fe, V, Mn and Cr. In order to facilitate the reactant mass transport and electrochemical reactions efficiently the catalysts should exhibit excellent ionomer properties, good Pt dispersion on the support and sufficient void spaces \[16, 19, 21\].
Fig. 6 shows the single cell, the fuel cell stacking principle and a commercial PEFC unit. A single cell is not adequate enough to produce the electricity needed for PEFC-APU utility. Ideally a single cell should produce $\sim$1.23 V however in reality the voltage production level lies in the vicinity of 0.5-0.8 V [11]. Therefore, the cells are connected in series or in parallel, termed “stacking”, in order to generate high voltage. However, stacking makes the overall reactant/product supply and removal, and heat management challenging. For instance, high loads of heat are generated during the electrochemical reactions that need to be removed and cooled using the bipolar plates [16, 19, 51]. In general, half of the hydrogen fed to the fuel cell is converted to electricity while the other half results in heat losses [19]. Insufficient cooling or reactant feeding can result in starvation causing chronic cell material damage and thus steady degeneration of the PEFC long-term performance. Also, stacking leads to increased thermal and electrical resistance of the fuel cell [16, 19, 51].

During the last decade major breakthroughs have been accomplished in reducing the cost and expanding the lifetime of the PEFC. The current status regarding the cost and lifetime of a PEFC is $\sim$61 kW and 2500 h, respectively [16]. However, despite recent positive progress, these values are not adequate as they both are below the US DOE 2015 target requirements by 50 % [15, 16]. The fabrication cost of the membrane and the Pt loading of the electrode catalyst are the major cost factors that need to be reduced. Regarding the Pt loading, the US DOE requirement is $\sim$0.2 mg/cm$^2$ [15]. Recently, a commercial company managed to develop a functional electrode catalyst, using a PtCoMn formulation, with $\sim$0.15 mg/cm$^2$ Pt loading, which is below US DOE limits [16]
4.2. PEFC contaminants and effects

Ideally the fuel cell should be fed with pure hydrogen in order to ensure sustainable and long-term operation. However, due to the hydrogen storage problem (see section 3.1), hydrogen-rich reformate gas is used as feedstock instead. This results in several contaminant problems making the fuel cell the “weakest link” in the diesel PEFC-APU scheme. As mentioned in section 4.1, Pt and Pt alloys are predominantly used as electrode catalysts for the fuel cell operation. Although Pt exhibits excellent electrochemical properties it is highly sensitive towards CO, a typical reformate byproduct [11, 16, 20, 21, 24]. In particular on the anode side, carbon monoxide adsorbs strongly on the Pt surface making the active sites inaccessible for hydrogen dissociation reactions. This mechanism results in cell voltage drops and eventually fuel cell deactivation. Adding Ru as Pt alloy is a known countermeasure towards CO poisoning [16, 20, 21, 24]. Higher humidity and higher operating temperature and pressures can also be employed. However, raising the temperature and pressure to prevent CO poisoning can be difficult as the optimal operating temperature and pressure of the PEFC are quite low, ~80 °C and 1 atm [16, 19, 20, 24]. This operation condition is mainly used to maintain the wettability of the Nafion® membrane. Both the reactant gases and the membrane are wetted with steam in order to facilitate the proton transfer and preventing dry-out of the fuel cell. The latter can result in starvation of the fuel cell. The deactivation mechanisms of CO poisoning are given in Eqs. 18-20 [20].

\[
\begin{align*}
\text{CO poisoning} \\
\text{CO} + Pt & \rightarrow Pt - CO_{ads} \quad (19) \\
2CO + 2Pt - H_{ads} & \rightarrow 2Pt - CO_{ads} + H_2 \quad (20)
\end{align*}
\]

The reformate contains other impurities such as H₂S and CO₂ that can also damage the fuel cell. In particular low ppm levels of H₂S can severely damage the fuel cell. For CO₂, the poisoning effect is much less detrimental as the PEFC can withstand high loads of CO₂, up to 250 000 ppm, see Table 7. The deactivation mechanism of H₂S and CO₂ are similar to CO poisoning, see Eqs. 21-23 [20]. For CO₂, reverse WGS takes place at first where CO is generated and later adsorbed on Pt.

\[
\begin{align*}
\text{H₂S poisoning} \\
H_2S + Pt & \rightarrow Pt - S_{ads} + H_2 \quad (21) \\
H_2S + Pt & \rightarrow Pt - H_2S_{ads} \quad (22)
\end{align*}
\]

\[
\begin{align*}
\text{CO₂ poisoning} \\
CO_2 + 2Pt - H_{ads} & \rightarrow Pt - CO_{ads} + H_2O + Pt \quad (23)
\end{align*}
\]
A small amount of air in the anode gas feed stream, termed “air bleeding”, can be used to remove the adsorbed reformate impurities from the Pt sites by oxidation reactions. Furthermore, recycling of anode gas can also be implemented to prevent large build-ups of reformate impurities on the gas diffusion layer and on the anode catalyst [11, 52].

There are other sources and other types of contaminants that can damage the fuel cell. These are listed in Table 7 in which the impurities, load limits, typical damage areas on PEFC and deactivation mechanism are also included. Contaminants present in the air feeding on the cathode side can cause similar damages on the fuel cell as reformate impurities [16, 20]. Also, chronic material losses, in the form of cations from the bipolar plates can lead to corrosion effects and membrane degradation [53].

Table 7. A selection of contaminants reported for PEFC performance losses. The table includes the origin of contaminants, level of impurity loads, damage areas on PEFC, and deactivation effects and losses. CL=electrode catalysts, GDL=gas diffusion layers. The data given in the table is taken from references [16, 20, 21, 53].

<table>
<thead>
<tr>
<th>Source of impurities</th>
<th>Type of contaminant</th>
<th>Load limits [ppm]</th>
<th>Damage area</th>
<th>Deactivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>NOx</td>
<td>0.1</td>
<td>Membrane</td>
<td>Ohmic,</td>
</tr>
<tr>
<td></td>
<td>SOx</td>
<td>0.5</td>
<td>Membrane,</td>
<td>Ohmic, Kinetic</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>30</td>
<td>Membrane</td>
<td>Ohmic</td>
</tr>
<tr>
<td>Reformate</td>
<td>CO</td>
<td>5</td>
<td>CL,</td>
<td>Kinetic</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>250 000</td>
<td>CL,</td>
<td>Kinetic</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>1</td>
<td>CL, Membrane</td>
<td>Kinetic</td>
</tr>
<tr>
<td>Bipolar metal plate</td>
<td>Fe³⁺, Ni³⁺, Cu²⁺</td>
<td>100</td>
<td>Membrane, GDL</td>
<td>Ohmic, Mass transfer</td>
</tr>
<tr>
<td>Membrane</td>
<td>Na⁺, Ca²⁺</td>
<td>n.a.</td>
<td>Membrane</td>
<td>Mass transfer</td>
</tr>
<tr>
<td>Sealing gasket</td>
<td>Si</td>
<td>n.a.</td>
<td>CL, Membrane</td>
<td>Ohmic</td>
</tr>
<tr>
<td>Coolants</td>
<td>Si, Al, K</td>
<td>100</td>
<td>CL, Membrane</td>
<td>Ohmic</td>
</tr>
<tr>
<td>Compressors</td>
<td>Oils</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

As seen in Table 7, there are basically three major types of contamination effects: (1) kinetic losses, which are poisoning effects caused by contaminant coverage on the surface layers of the anode and cathode; (2) ohmic losses, take place when the proton conductivity of the membrane is reduced; and (3) mass transport losses, often caused by modifications in the structure and hydrophilic/hydrophobic properties of the MEA’s components [16, 20, 21, 54].

4.3. HT-PEFC

Recent PEFC research focuses on developing new membrane materials that can be operated at higher temperatures, in the vicinity of 100-200 °C [20, 54]. These fuel cells, termed high-temperature polymer electrolyte fuel cell (HT-PEFC), have several benefits. Firstly, and most importantly, higher loads of CO can be fed and tolerated. As a result, the number of CO clean-up units can be significantly reduced, e.g. excluding LT-WGS and PrOx, offering substantial cost savings and volume
reduction in the mobile diesel PEFC-APU set-up (see Figs. 1-2). For instance at $T\sim 200\, ^\circ\text{C}$, CO loads up to 30,000 ppm can be tolerated by HT-PEFC without causing any detrimental cell voltage drops [20, 54]. Secondly, the water and heat management can be simplified. For instance, the cooling of the fuel cell and the heat removal are facilitated due to higher temperature gradients. Thirdly and finally, the kinetics involving the cathode reactions can be significantly enhanced [20, 54].

A HT-PEFC utility has some major disadvantages as well. For instance, dehydration can be problematic at higher operating temperatures. It can be difficult to maintain the wettability of the membrane and the feed gases at relatively high humidity. Also, higher operating temperatures can cause Pt sintering effects on the surface of the electrode catalyst as well as intensified corrosion effects [54].

At the moment, HT-PEFC is still in the early development stages [54]. Examples of membrane materials tested for HT-PEFC are: modified Nafion® involving integration of hygroscopic oxides and solid inorganic proton-conductor groups on the membrane structure; sulfonated polyaromatic polymers and composite membranes, and acid-base polymer membranes [54]. The most popular membrane material tested for HT-PEFC is $\text{H}_3\text{PO}_4$-doped polybenzimidazole [54, 55].
5. Reforming catalyst design

5.1 Development of Rh-based diesel-reforming catalysts

Heterogeneous catalytic materials implemented for diesel reforming can be divided into various groups and subgroups based on their respective operating parameters, reaction temperatures and the type of diesel fuel employed. In this thesis, Rh and RhPt were used as the main active metals in the catalytic materials employed for diesel reforming. Furthermore, most of the Rh and RhPt catalysts tested for ATR of diesel were cordierite monoliths coated with alumina supports (Papers I-III). Ceria-zirconia, silica and titania-supported catalysts were also tested in one study (Paper IV). Most of these catalysts were prepared by using the incipient wetness technique.

In the following sections a short description regarding the catalyst design, composition and preparation will be included prior to a summary of the bench-scale and characterization results taken from Papers I-IV, described in Chapter 6. The zoned catalyst design and activity results are discussed specifically in section 6.3, Chapter 6. The full-scale results are discussed in Chapter 7.

5.2 Carrier

The catalyst design can be divided into three parts: carrier, support and active material. The carrier, also referred to as the substrate, is often manufactured in a specific way with a unique geometrical form and appearance. The latter property is often regarded as a significant parameter in catalyst design. In particular, the shape and structure of the carrier determine and facilitate the transport of the gaseous reactants and products between the bulk phase and the catalyst surface. Examples of different carriers are pellets, mesh and monolith. For reforming processes, monoliths shaped like a honeycomb structure (see Fig. 7) are frequently employed for hydrogen generation [11, 23, 24]. Monoliths exhibit many promising and important features such as: high geometric surface area, low pressure drop, no external mass transfer or internal diffusion limitations, uniform distribution of gas flows, simple to scale up, excellent thermal shock resistance and mechanical strength [3, 23, 24, 56]. Monoliths can be made of a variety of materials such as ceramics, foam and metal. Ceramic monoliths are made through extrusion and the material can be composed of e.g. cordierite (2MgO·2Al₂O₃·5SiO₂), mullite (3Al₂O₃·2SiO₂) and alumina titania (Al₂O₃·TiO₂) [3, 23, 24, 56]. Metallic monoliths are made of a series of corrugated or flat plates/bends that are linked together into a circular form with specific channel patterns. Typical metal materials are stainless steel and FeCrAlloy (73% Fe, 15-20% Cr, 5% Al and traces of rare earth metals) [3, 23, 24, 56]. In Fig. 7, two uncoated monoliths are displayed, one ceramic and one metallic.
Fig. 7. Uncoated monolithic carriers. Left: Honeycomb-structured cordierite monolith (2MgO·2Al₂O₃·5SiO₂) with straight square-shaped channels. Right: Metallic monolith (FeCrAlloy) with sinusoidal channels composed of series of assembled corrugated/flat metal foils and an external mantle.

For automotive applications, catalytic combustion and reforming processes cordierite monoliths are frequently used. This is due to the low cost, low thermal expansion with thin walls, high operating temperatures (~1200 °C) and simple coating with the catalytic material [3, 23, 24, 56].

In this thesis, cordierite monoliths were used and coated with active material. The ease of coating the catalytic material plays a major role when designing and evaluating diesel-reforming catalysts. In general, it requires extensive research to optimize the adhesion between the catalytic material and metallic monoliths. For instance, for metallic monoliths composed of FeCrAlloy, a thermal pretreatment of the carrier is mandatory in order to generate small layers of alumina whiskers that can form strong bonds with the active material [56]. Typically, the level of adhesion of the coated metallic monolith is often evaluated by thermal shock and vibration tests [56]. Thermal shocks usually involve inserting the coated sample in an oven, e.g. at 900 °C for 30 min, followed by quenching the sample in cold water. This procedure is repeated 3-4 times, and the mass loss of the coat is then measured by weighing the monolith after each session. The vibration testing cycle is similar; the coated sample is instead put in an ultrasonic acetone bath for 30 min followed by drying and weighing. Hence, by working with cordierites, adhesion tests and factors such as potential catalytic material losses with increased time on stream can be essentially excluded when evaluating the overall catalytic performance of the diesel-reforming catalyst.

5.3 Support

Honeycomb cordierite monoliths have a fairly smooth surface which makes it difficult to anchor and coat the catalytic material onto the carrier [3, 57]. Also, cordierite monoliths are known to have low surface area (~1.0 m²/g) and porosity. The latter properties can be problematic as in most cases they result in agglomeration of active metal particles that are added or impregnated within the small
pore volumes of the carrier. Consequently, the dispersion of active metals is low and thus a larger amount will be needed, resulting in an expensive catalyst. In general, a good dispersion of the active metal particles is crucial as it often results in higher overall activity and lower catalyst cost. Hence, in order to improve the adhesion, surface area and porosity of the carrier a support is used (see Fig. 8). The support not only improves the dispersion of the metals; it can also enhance the activity, stability and durability of the catalyst [3, 57, 58]. In this thesis four supports were tested: alumina, ceria-zirconia, silica and titania (see sections 5.3.1-5.3.4). In general, there are two ways to coat the catalytic material onto the carrier. The support can be coated directly on the carrier, often referred to as “washcoat”, followed by the impregnation of the noble metals. The other alternative is that the support is first mixed and impregnated with the noble metals followed by coating on the carrier [3, 57, 58]. In this thesis, the latter procedure was implemented. In general, this approach is recommended as it presents a better alternative ensuring that the noble metals are uniformly dispersed throughout the support material.

![Fig. 8. Washcoat deposit of the support and active material on the monolithic wall inside the channels [59].](image)

### 5.3.1 Alumina
Alumina, $\text{Al}_2\text{O}_3$, is a common support material for exhaust gas-cleaning and reforming catalysts due to its low cost, high surface area and thermal stability [3, 57, 58, 60-62]. Alumina can exist in a large variety of crystallographic phases. One of the most common phases used for catalytic applications is $\gamma$-alumina, due to its high surface area. If $\gamma$-$\text{Al}_2\text{O}_3$ is subjected to high temperature (around 1000-1100 ºC), the stable phase $\alpha$-$\text{Al}_2\text{O}_3$ will start to form, which will drastically decrease the surface area of the material [57]. This transformation can proceed through the formation of the metastable transition phases $\delta$- and $\theta$-$\text{Al}_2\text{O}_3$, starting from a temperature of about 850 ºC [57]. For reforming, high surface area crystalline structure of gamma ($\sim 150$ m$^2$/g) and delta ($\sim 100$ m$^2$/g)
alumina are frequently employed as catalyst supports [11, 63-65]. Alfa alumina has a typical surface area of ~10-20 m²/g.

5.3.2 Ceria-zirconia
Ceria-zirconia, CeO₂-ZrO₂, has been used extensively as support for TWC and methane-reforming catalysts [3, 4, 23, 59]. Ceria is a stable single metal oxide with high surface area (~270 m²/g), high melting point (~2600 ºC) and excellent oxygen storage capacity. The latter is based on ceria’s ability to switch between Ce⁴⁺ under oxidizing conditions and Ce³⁺ under reducing conditions. Also, ceria can promote the dispersion and reduction of noble metals, and enhance water-gas shift reactions [66, 67]. Zirconia is added to ceria in order to improve the thermal stability, reducibility and sulfur tolerance ability of ceria [59].

5.3.3 Silica
Silica, SiO₂, can also be used for TWC and reforming applications [3, 4, 57]. An advantage with using silica as carrier is that it exhibits exceedingly high tolerance towards sulfur poisoning. Furthermore, it can provide high surface areas in the vicinity of 300-400 m²/g [3, 4, 57]. However, on the downside, silica holds a certain degree of surface acidity due to minor water content which is bonded within the pores of the material. The latter ability makes silica inappropriate for applications in alkaline environment [57]. Also, the thermal stability of silica is lower than for alumina [4, 57].

5.3.4 Titania
Titania, TiO₂, is an inert material, which just as silica has excellent properties inhibiting potential sulfur deposits on the catalyst surface during reforming [4, 57]. Titania can exist in three crystal phases [57]: as brookite, anatase and rutile. The crystallographic forms of these species differ significantly as brookite is present in rhombohedral form, anatase is tetragonal and rutile is close-packed tetragonal [57]. Typically anatase is mostly utilized for high-temperature catalytic applications as it has a higher surface area (50-120 m²/g) and thermal stability than the other phases [4, 57].

5.4 Promoters
The addition of promoters can improve the activity, selectivity, stability and durability of the catalyst [3, 24, 57, 58]. In this thesis, the effect of the promoters was studied in two ways: firstly, to detect differences in activity in terms of diesel conversion and hydrogen generation, and secondly, to detect disparities in stability by observing the degree of coke deposition. In this thesis, ceria and lanthana were used as promoters for delta-alumina supported Rh catalyst (Papers II-IV). As mentioned previously, ceria has excellent oxygen storage ability which can reduce the extent of carbon deposition on the catalyst surface. Ceria can also promote the dispersion
and reduction of noble metals, and enhance the water-gas shift reactions [66, 67]. La is known to improve the thermal stability and inhibit adverse phase transitions of alumina towards low surface \( \alpha \)-\( \text{Al}_2\text{O}_3 \) by forming stable structures with delta alumina [68-70]. MgO-\( \text{Y}_2\text{O}_3 \) was tested as promoter for ceria-zirconia (Paper IV). Studies have shown that MgO can improve the activity of Rh [71-74], while \( \text{Y}_2\text{O}_3 \) can enhance the thermal stability of \( \text{ZrO}_2 \) [4, 59]. \( \text{CeO}_2-\text{ZrO}_2 \) was used as promoter for silica to improve the hydrogen generation capability and thermal stability of the support material (Paper IV). Finally, MgO was used as promoter for the titania-supported Rh catalyst (Paper IV).

5.5 Rh and RhPt alloys as active metals for ATR of diesel

There are many criteria to consider when designing catalysts for diesel reforming. First of all, the selection of suitable active metals is critical. The metals must be stable at high temperatures. For ATR of diesel, the reaction temperature is \(~700\text{-}900\) °C [11]. Secondly, the metals must also prevent coke formation, endure poison such as sulfur and fuel lubricants, typically present in diesel [11]. Thirdly and finally, the metals should also provide high fuel conversion, high \( \text{H}_2 \) production and \( \text{CO}_2 \) selectivity in order for the PEFC-APU to function accurately and optimally [11, 24].

Inexpensive base metals such as Ni, Co and Fe have been tested and shown high activity and selectivity for ATR; however the durability and stability of these catalyst materials are poor due to catalyst deactivation, e.g. volatilization of active metal particles, sintering effects and coke deposition on active sites [75, 76]. Noble metals, although more expensive, show high diesel-reforming activity as well as great tolerance towards typical poisons such as sulfur [11, 24]. Some noble metals are more promising candidates than others. For instance Ru, a relatively inexpensive noble metal, shows high initial activity for diesel reforming, however, the material exhibits low tolerance towards carbon deposition [11]. Furthermore, results also show that a high degree of volatilization of active Ru particles takes place with increased time on stream [11]. Palladium has also been used successfully for diesel reforming. For instance, Pd-Pt alloy shows excellent long-term stability and can easily withstand severe sulfur and coke poisoning effects at high reaction temperatures, however, this is at the price of lower fuel conversion and hydrogen generation [77]. Platinum is also used, often alloyed with other base or noble metals as Pt particles alone are known to severely sinter at temperatures exceeding 450 °C [24] as well as deactivate by coke deposits and volatilization [78]. To date, most of the reforming catalysts tested for ATR of diesel include Rh and Rh alloys, e.g. RhPt, as main active components in the catalyst composition [11, 24, 78-81]. Several studies have shown that Rh and RhPt alloys are superior in reforming activity, selectivity and stability compared to other noble metal and base metal catalyst formulations [11, 24, 78-81]. However, Rh is an extremely expensive metal: US$ 2380/ounce (~58 €/g) [82]. Therefore, the major challenge with Rh diesel-reforming catalyst design is to lower the total cost of the catalyst. This can be done by keeping the weight loadings of the
Rh and RhPt-alloys at a minimum but at the same not losing any significant catalyst activity. In addition, the total cost can be further reduced by finding suitable promoters and supports that can enhance the reforming activity as well as prolong the lifetime of the catalyst. Hence, the scope of this thesis is to try to evaluate various formulations of Rh catalysts for ATR of diesel with the aim to maintain the noble metal loading as low as possible as well as finding suitable promoters and supports.

5.6 Catalyst preparation

There are a number of different techniques for preparing reforming catalysts. The choice of preparation technique is critical as it often affects the performance of the catalytic material. The most common way to add the active metals onto the support is by dry impregnation, also referred to as the incipient wetness (IW) technique [3, 56-58].

5.6.1 Incipient wetness

During IW, the support is impregnated by an aqueous solution of the metal precursor, often nitrates, in order to fill up the pores of the support. The impregnation is completed when the surface of the support starts to become wet (hence the term “dry impregnation”). The impregnated material is then dried and calcined in order for the crystalline metal particles to be formed and stabilized within the pores of the support. This method is easy and straightforward to implement. On the other hand, the dispersion can be low since the particle positioning of the impregnated metals is stochastic which may lead to redundant particle agglomeration as well as large particle size distributions.

In this thesis, IW was predominantly used to prepare the catalyst material. The nitrate precursors were diluted with Milli Q water and impregnated sequentially onto the support, starting with the promoters. The impregnated supports (in powder form) were then dried at 110 °C for a minimum of 30 min and calcined in air at 800 °C for 3 h.

5.6.2 Washcoating

Washcoating is the most common technique for applying the catalyst material onto the monolith [3, 56-58]. The easiest way to do this is by using the dipcoating procedure [3, 56-58]. The impregnated supports are blended with solvent to form a slurry. The monolith is then dipped into the slurry, hence the term “dipcoating”, coated and dried repeatedly in order to form a uniform washcoat with of some given thickness. The choice of solvent is important as it can affect the viscosity of the slurry as well as the effectiveness of washcoating. Typical solvents are ethanol and water as they are easy to remove by drying during as well as after washcoating is completed.

Prior to wascoating, the powders in the slurry are often milled in order to reach the required particle size. The particle size distribution of the washcoat is a critical parameter as it affects the mechanical
strength of the washcoat, as well at the level of adhesion onto the carrier [3, 4, 58]. In general, particles that are too large in size result in poor washcoating. A rule of thumb is that the size of the particle ought to be of the same dimension as the macropores of the supporting ceramic monolith [24, 56]. The particle size distribution also affects the rheological properties, in particular the viscosity. For instance, the viscosity of alumina slurries is known to change with milling and stirring time [83].

**Catalyst preparation route**

**IW method + washcoating**

In the work reported in this thesis, ~20 wt% of catalytic powder was suspended in ethanol to form slurry. The slurries were then ballmilled for ~24 h to ensure a uniform slurry suspension. After completion of the ballmilling process, prior to commencing the washcoating procedure, the slurries were put in a magnetic mixer and stirred continuously in order to preserve the viscosity of the slurry and to prevent sedimentation of the particles. During the dipcoating, the monolith (400 cpsi) was carefully immersed into the slurry and withdrawn. Excess slurry was then removed by blowing air through the honeycomb channels. The samples were dried at 110 °C for a minimum of 30 min to evaporate and remove the ethanol solvent. The dip-coating procedure was repeated until catalyst loadings of 20 wt% of the total weight (monolith and active material) were reached. This corresponds to a washcoat loading of ~100 g/dm³. The coated monoliths were then calcined in air at 800 °C for 3 h to stabilize the washcoat and remove potential impurities. The catalyst preparation route can also be seen in Fig. 9.

**Fig. 9.** Preparation route of the Rh-based monolithic catalysts using the incipient wetness (IW) technique and ethanol-slurry dipcoating procedure.
5.7 Evaluating the performance and tailoring the composition of a Rh catalyst

When designing the Rh catalyst an important issue is to understand the interactions between the Rh and Rh-alloys as well as the interactions of the active metals with the promoters and the support. One way to do this is to develop a large number of catalysts in which the important variables such as noble metal loading, alloy ratios, number of promoters, promoter loadings, choice of support, differ significantly. The latter is also known as “catalyst screening test”. Changing the catalyst properties stepwise facilitates the overall understanding when interpreting the activity results in order to define the role of the active metals, promoters and supports. In this thesis the Rh loading was varied while the Pt loading was kept constant at 1 wt%. Approximately 0.5, 1.0 and 3 wt% of nominal Rh loadings were impregnated onto the support. In another experimental series the weight ratio between Rh and Pt was kept constant at 1/1 (w/w) while the promoters’ weight loading ranged from 4 to 10 wt%.

Another way to understand the interactions of the catalyst components is to examine and compare the physicochemical properties between the fresh and the aged state of the catalysts. Fresh state of the catalyst refers to the catalyst properties examined prior to reforming experiments. Aged state denotes catalysts that have been exposed to reactant gas feed for a given number of hours and removed afterwards from the reformer for examination. Comparing fresh and aged catalyst is useful in order to detect any major changes in bulk and surface properties that may be caused by deactivation mechanisms such as sintering, volatilization, coke deposition and sulfur adsorption. In this thesis, fresh powder samples were analyzed by N\textsubscript{2}-BET, XRD, H\textsubscript{2} chemisorption, H\textsubscript{2}-TPR, and TEM analyses. The fresh powder samples were taken from the catalyst preparation prior to deposition onto the monoliths. Aged powder samples were analyzed by O\textsubscript{2}-TPO and TEM analysis. The aged powder samples were collected by cutting the aged monoliths in half and scraping off the interior washcoat by using a scalpel.

Summing all the results obtained from the catalyst screening tests as well as the characterization of the catalysts facilitates the overall understanding of the catalytic performance in relation to the physicochemical properties. Hence, the washcoat can be carefully tailored and optimized stepwise, with the aim to improve the overall performance of the catalyst. In this thesis, the main findings and final discussion regarding the favored catalyst composition for diesel reforming will be included in the conclusion part given in Chapter 8.
6. Bench-scale operations and characterization of Rh catalysts (Papers I-IV)

6.1 Summarizing Paper I

In Paper I, 3 incipient wetness (IW) prepared alumina-supported catalysts were evaluated for ATR of diesel at bench-scale. The samples tested contained the nominal weight loading of 0.5 wt% Rh, 1.0 wt% Rh, and 1 wt% Rh + 1 wt% Pt on γ-alumina, respectively. The washcoats were deposited on 400 cps monoliths with dimensions d=20.5 mm, l=30.5 mm and calcined at 800 °C for 3 h.

6.1.1 Characterization of fresh γ-alumina supported samples

The washcoat properties of the fresh IW samples can be seen in Table 8. The γ-Al₂O₃ powder used in the synthesized IW catalysts had an initial surface area of 150 m²/g.

Table 8. Washcoat properties of fresh incipient wetness (IW) γ-alumina supported Rh and RhPt catalysts. The surface area and porosity was measured by N₂-BET, the dispersion and crystallite size of Rh were determined by H₂ chemisorption, while the crystallite size of Pt was determined by XRD at 2θ=86° using the Scherrer equation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area [m²/g]</th>
<th>Pore volume [cm³/g]</th>
<th>Pore diameter [Å]</th>
<th>H/Rh [%]</th>
<th>d_p(Rh) [nm]</th>
<th>d_p(Pt) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh₀.₅-IW</td>
<td>131</td>
<td>0.93</td>
<td>285</td>
<td>58</td>
<td>1.9</td>
<td>n.a.</td>
</tr>
<tr>
<td>Rh₁.₀-IW</td>
<td>134</td>
<td>0.95</td>
<td>282</td>
<td>56</td>
<td>2.0</td>
<td>n.a.</td>
</tr>
<tr>
<td>Rh₁.₀Pt₁.₀-IW</td>
<td>132</td>
<td>0.92</td>
<td>278</td>
<td>n.a.</td>
<td>n.a.</td>
<td>30</td>
</tr>
</tbody>
</table>

As seen in Table 8, all IW samples had a high surface area, 132-134 m²/g, after the impregnation and calcination stages were completed. Also, the Rh dispersion in the monometallic samples was good, in the vicinity of ~57. Interestingly, according to the XRD analysis, the Pt crystallite size in the bimetallic sample was large, ~30 nm. Also, the XRD analysis revealed that the Pt content was in the metallic state as seen in Fig. 10.

![XRD pattern of Rh₁.₀Pt₁.₀-IW](image)

**Fig. 10.** XRD patterns of Rh₁.₀Pt₁.₀-IW. Reflections of (□) metallic Pt.
Furthermore, Rh phases were not detected by XRD indicating that the rhodium particles are small and well-dispersed on the support. The latter observation confirms the results from the H₂ chemisorption analysis where the Rh crystallite size for the IW samples was in the range of 1.7 to 2.0 nm, as seen in Table 8. Regarding the presence of metallic Pt, it is possible that the high calcination temperature, 800 °C, employed during the catalyst preparation stage, may have caused formation and agglomeration of the metallic Pt particles. Other groups have presented similar results [78]. In general, platinum oxides, e.g. PtO and PtO₂, are unstable and can easily decompose to form metallic Pt at temperatures above 500 and 550 °C, respectively [84-88]. Also, Pt particles are known to sinter at temperatures exceeding 450 °C [24].

The presence of metallic Pt was also confirmed by H₂-TPR and TEM analyses. Peaks ascribed to PtO were not present in the TPR profiles for Rh₁.₀-IW and Rh₁.₀Pt₁.₀-IW, respectively, as seen in Fig. 11. In general, three distinct peaks were identified; one small at 100 °C which can be ascribed to reduction of bulk rhodium oxides, one major at 450 °C which is due to hydrogen spillover effect on the support and finally another peak at 800 °C which can be ascribed to reduction of rhodium aluminates [89]. The Rh peaks detected by TPR are small indicating that the majority of the rhodium species were non-reducible and strongly bonded to the support. The strong rhodium-alumina interactions may have been caused by the high calcination temperature employed in this study, 800 °C. At this calcination temperature, rhodium particles become highly mobile and may enter defects and voids in the alumina support making them inaccessible for hydrogen reduction. Other groups have presented similar TPR results [90, 91]. Another trend that can be noted in the TPR profiles is that the addition of Pt onto the alumina support lowered the reducibility of the different rhodium species. A possible explanation to this reduction trend is that Pt forms RhPt alloys with Rh leading to a decrease of accessible rhodium oxides and rhodium aluminates on the support. This particular alloy trend was detected and confirmed...
by the TEM analysis. TEM analysis performed on R$_{1.0}$Pt$_{1.0}$-IW confirmed the presence of Rh$_{x}$O$_{y}$, RhPt and Pt. The average diameter of the smallest single Rh and Pt particles was approximately 10 nm and 22 nm, respectively. Elemental analyses of the Rh$_{1.0}$Pt$_{1.0}$-IW sample reveal that some of the catalyst particles contain either Rh or Pt, but most of them have a composition indicating an alloy between them, Rh$_{x}$Pt$_{1-x}$. Also, most of the Rh particles were present as oxides, Rh$_{x}$O$_{y}$. Furthermore, some of the Rh$_{x}$O$_{y}$ particles were found bonded directly with Rh$_{x}$Pt$_{1-x}$ alloys. A possible crystal formation of a Rh$_{x}$O$_{y}$-Rh$_{x}$Pt$_{1-x}$ bond can be seen in Fig. 12.

6.1.2 Activity of $\gamma$-alumina supported samples

In this thesis, all bench-scale experiments were carried out in a vertically mounted stainless steel tubular reactor with ID=23.7 mm, see Fig. 13. The reaction conditions were $T_{\text{feed}}$=650 °C, $\text{H}_2\text{O/C} \sim 2.5$, $\text{O}_2/\text{C} \sim 0.49$, TOS=3 h, GHSV=13 000 h$^{-1}$ and $P=1$ atm. A standard diesel fuel (S$\sim$6ppm, C/H$\sim$6.43 (w/w)) whose physical and chemical properties are in close correlation to Swedish Environmental Class 1 diesel (MK 1) (Table 6), was used as feedstock. The product gases were analyzed using a Gasmet Cr-200 Fourier Transform Infrared Spectrometer (FTIR) and a Maihak modular system S710 equipped with a non-dispersive infrared sensor (NDIR) and TCD as seen in Fig. 13.
The activity results in Table 9 show that the IW catalysts are highly active for ATR of diesel. As seen in the table, the diesel conversion and hydrogen generation were both high and in the vicinity of 94.5-96.1 % and 22-26 vol %, respectively. Interestingly, the lowest diesel conversion was noted for the bimetallic sample, ~94.5%. Also, a high ethylene concentration, ~4400 ppm, was detected.

Table 9. Activity results of the incipient wetness (IW) alumina supported Rh catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$X_{\text{diesel}}$</th>
<th>$S_{\text{CO2}}$</th>
<th>$H_2$</th>
<th>$C_2H_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh$_{0.5}$-IW</td>
<td>96.1</td>
<td>51</td>
<td>26</td>
<td>3100</td>
</tr>
<tr>
<td>Rh$_{1.0}$-IW</td>
<td>95.8</td>
<td>54</td>
<td>22</td>
<td>2800</td>
</tr>
<tr>
<td>Rh$<em>{1.0}$Pt$</em>{1.0}$-IW</td>
<td>94.5</td>
<td>57</td>
<td>24</td>
<td>4400</td>
</tr>
</tbody>
</table>

6.1.3 Characterization of aged catalysts

In diesel reforming, ethylene is a well-known coke precursor which can often lead to deactivation of the reforming catalysts due to coke deposition on the active metal sites [11, 24, 34, 45-48]. In general, the higher the ethylene concentration in the product gas streams the greater the risk of getting severe carbon deposits on the employed catalyst [48]. The extent of coke deposition can be determined by performing an $O_2$-TPO analysis. The $O_2$-TPO analysis of the aged IW samples can be seen in Fig. 14. In general, two trends can be observed: the increase of Rh loading on alumina lowered the coke deposition while the addition of Pt had the opposite effect.
Fig. 14. TPO profiles of aged IW catalysts, and fresh cordierite.

In general, four peaks were identified. The initial small oxidation peak detected at ~100 ºC can be ascribed to possible carbon formation on the surface active metals, the second peak in the interval ~300-400 ºC may be due to coke deposits on bulk metallic centers, while the third peak in the interval ~500-600 ºC may be due to coke species on the support [92, 93]. Regarding the final peak at ~1000 ºC, it may be ascribed to oxidation of unconverted graphite that is still present in the samples [94, 95].

Finally, TEM analysis on the aged sample Rh1.0Pt1.0-IW did not show any clear evidence of deactivation mechanisms such as sintering. On the contrary, most of the RhOx crystals were found to have shrunk in size. A possible explanation to the shrinking phenomenon is that RhOx species switch oxidation state from e.g. Rh3+ to metallic Rh0. This suggests that a reducing environment, due to SR reactions, is predominant during ATR of diesel, causing the formation of metallic Rh0. A similar observation was noted in the XPS analysis of aged samples, which are discussed in section 6.3.1.

6.1.4 Possible correlations between characterization and activity results.
To summarize, this paper provides information about the bulk and surface states of the active metals, the interaction between Rh and Pt and also the interaction with the alumina support. It can be seen that Rh is well dispersed and strongly bonded with the support. As for Pt, it is present solely in the metallic state. Also, it sinters considerably during calcination and alloys with Rh. In addition, Pt is more prone to form bonds with coke during reforming. The Pt sintering effect, the predominant RhPt formation and the higher degree coke formation are believed to affect the catalyst performance negatively. In general, the lower activity noted for the bimetallic sample, in terms of diesel conversion, may be ascribed to lower accessibility of rhodium oxides and the higher extent of coke deposition on the catalyst. The possible link between the accessibility of rhodium oxides and diesel conversion will be discussed in more detail in the following sections, summarizing Papers II-IV.
6.2 Summarizing Papers II-III

In Papers II-III, a wide selection of IW-prepared alumina-supported catalysts was evaluated for ATR of diesel at bench-scale. Unlike in Paper I, δ-alumina was used as support. Also, ceria and lanthana were added as promoters.

6.2.1 Characterization of fresh δ-alumina supported and Ce-La-promoted samples

The washcoat properties of the fresh IW samples can be seen in Table 10. The δ-Al₂O₃ powder used in the synthesized IW catalysts had an initial surface area of 105 m²/g. The delta-alumina support was made by calcining γ-Al₂O₃ at 1000°C for 1 h. Peaks ascribed to delta-alumina can be seen in the XRD profile for sample Rh₃.₀Ce₁₀La₁₀/δ-Al₂O₃, see Fig. 15.

Table 10. Washcoat properties of fresh incipient wetness (IW) δ-alumina supported and Ce-La promoted Rh and RhPt catalysts. The surface area and porosity were measured by N₂-BET, the dispersion and crystallite size of Rh were determined by H₂ chemisorption, while the crystallite size of Pt was determined by XRD at 2θ=86° using the Scherrer equation.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition</th>
<th>Surface area [m²/g]</th>
<th>Pore volume [cm³/g]</th>
<th>Pore diameter [Å]</th>
<th>H/Rh [%]</th>
<th>dp(Rh) [nm]</th>
<th>dp(Pt) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>δ-Al₂O₃</td>
<td>105</td>
<td>0.92</td>
<td>349</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R₁.₀P₁.₀</td>
<td>Rh₁.₀P₁.₀/δ-Al₂O₃</td>
<td>94</td>
<td>0.59</td>
<td>250</td>
<td>n.a</td>
<td>n.a</td>
<td>30</td>
</tr>
<tr>
<td>R₁.₀</td>
<td>Rh₁.₀/δ-Al₂O₃</td>
<td>95</td>
<td>0.62</td>
<td>261</td>
<td>48</td>
<td>2.3</td>
<td>-</td>
</tr>
<tr>
<td>R₃.₀</td>
<td>Rh₃.₀/δ-Al₂O₃</td>
<td>94</td>
<td>0.60</td>
<td>258</td>
<td>40</td>
<td>2.8</td>
<td>-</td>
</tr>
<tr>
<td>R₁.₀P₁.₀A</td>
<td>Rh₁.₀P₁.₀Ce₁₀La₅.₀/δ-Al₂O₃</td>
<td>88</td>
<td>0.60</td>
<td>270</td>
<td>n.a</td>
<td>n.a</td>
<td>n.d</td>
</tr>
<tr>
<td>R₃.₀B</td>
<td>Rh₃.₀Ce₁₀La₁₀/δ-Al₂O₃</td>
<td>80</td>
<td>0.43</td>
<td>185</td>
<td>42</td>
<td>2.6</td>
<td>-</td>
</tr>
</tbody>
</table>

As seen in Table 10, the surface area and the Rh dispersion on the δ-alumina supported catalysts were lower compared to γ-alumina supported catalysts (see Table 8). This trend can be expected due to weaker active metal and support interactions between Rh and δ-alumina [57, 61]. Furthermore, as seen in Table 10, the increase of active metals and promoters loadings on alumina decreased the surface area and porosity. Also, large metallic Pt peaks with a size of ~30 nm were present on the bimetallic sample, Rh₁.₀P₁.₀/δ-Al₂O₃. Interestingly, Pt was not detected on the promoted sample indicating that Pt is better dispersed with the addition of Ce and La. In general, regarding the XRD analysis for all Ce-La-promoted samples, only diffraction peaks from ceria and the support material were observed. The latter can be seen in Fig. 16, as peaks ascribed to fluorite-structured CeO₂ [96, 97] are present at 2θ=28.5, 48.5 and 56.5°. The XPS analyses of the fresh IW samples R₁.₀P₁.₀A and R₃.₀B, respectively, which are discussed in more in detail in section 6.3.1, showed the presence of finely dispersed surface Rh species in the form of RhiOₓ, metallic Pt, CeO₂ and La (in the dispersed phase).
Fig. 15. XRD patterns of Rh\textsubscript{3.0}Ce\textsubscript{10}La\textsubscript{10}/δ-Al\textsubscript{2}O\textsubscript{3}. Reflections of (c) fluorite-structured CeO\textsubscript{2} on δ-Al\textsubscript{2}O\textsubscript{3}.

The reducibility of the active metals and promoters on alumina can be seen in Fig. 16. As seen in the figure, the TPR profile of Rh\textsubscript{3.0}Ce\textsubscript{10}La\textsubscript{10}/δ-Al\textsubscript{2}O\textsubscript{3} revealed three positive peaks. One major peak is located at 150 ºC, while the other two are smaller and found at 450 and 900 ºC, respectively. The reduction peak present at 150 ºC can be ascribed to reduction of bulk rhodium oxide species Rh\textsubscript{2}O\textsubscript{3} [89], the peak at 450 ºC is caused by hydrogen spillover effect in the alumina support [89], while the peak at 900 ºC can be attributed to cerium oxides [98, 99]. Rhodium aluminates, platinum and lanthanum oxides were not detected by TPR. The effect of the promoters can also be seen in Fig. 16. As seen in the figure, the addition of Ce and La improves the hydrogen uptake of the bulk rhodium oxides at 150 ºC. Also, the addition of La improves the reducibility of ceria at 900 ºC. Other groups have reported similar observations regarding Ce-La interactions [100, 101].

Fig. 16. TPR profiles of 10 wt% Ce, 10 wt% Ce + 10 wt% La, R\textsubscript{3.0} and R\textsubscript{3.0}B. The hydrogen consumption is displayed as function of temperature. See Table 10 for catalyst formulation.
6.2.2 Activity results. The effect of Rh loading and Ce-La promoters

The effect of the Rh loading and Ce-La promoters on the catalyst performance can be seen in Table 11. The increase of Rh loading from 1 to 3 wt% improved the overall performance of the catalyst by increasing the diesel conversion and hydrogen generation as well as lowering the level of ethylene. The addition of Pt to the unpromoted alumina had the opposite effect. The addition of Ce and La had a significant positive effect on the performance of the catalysts. The biggest improvement in activity was noted for the sample Rh1.0Pt1.0Ce10La5.0/δ-Al2O3. Indeed, the ethylene concentration was significantly reduced, more than tenfold, from 4000 ppm to 300 ppm. Also, the H2 concentration was the highest, around 39 vol%.

Table 11. Activity results of the incipient wetness (IW) alumina supported and Ce-La promoted Rh catalyst.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition</th>
<th>XDiesel [%]</th>
<th>SCO2 [%]</th>
<th>H2 [vol %]</th>
<th>C2H4 [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1.0P1.0</td>
<td>Rh1.0Pt1.0/δ-Al2O3</td>
<td>94.5</td>
<td>56.5</td>
<td>23.6</td>
<td>4000</td>
</tr>
<tr>
<td>R1.0</td>
<td>Rh1.0/δ-Al2O3</td>
<td>95.8</td>
<td>53.8</td>
<td>25.4</td>
<td>2900</td>
</tr>
<tr>
<td>R3.0</td>
<td>Rh3.0/δ-Al2O3</td>
<td>97.7</td>
<td>50.9</td>
<td>32.9</td>
<td>2700</td>
</tr>
<tr>
<td>R1.0P1.0A</td>
<td>Rh1.0Pt1.0Ce10La5.0/δ-Al2O3</td>
<td>99.1</td>
<td>47.4</td>
<td>39.2</td>
<td>300</td>
</tr>
<tr>
<td>R3.0B</td>
<td>Rh3.0Ce10La10/δ-Al2O3</td>
<td>99.9</td>
<td>52.9</td>
<td>35.6</td>
<td>300</td>
</tr>
</tbody>
</table>

6.2.3 Possible correlations between characterization and activity results

To summarize, Papers II-III provide further information regarding the role of RhOx species and Ce-La promotion on delta alumina-supported diesel-reforming catalysts. In general, the characterization results showed the presence of finely dispersed bulk and surface Rh species in the form of RhOx, metallic Pt, CeO2 and La (in the dispersed phase). The H2-TPR analysis showed that rhodium oxide reducibility, at T~100-200°C, increased in the following order: R1.0P1.0 < R1.0 < R3.0 < R1.0P1.0A < R3.0B. The exact same trend was noted in the diesel conversion: 94.5 < 95.8 < 97.7 < 99.1 < 99.9. Hence, the reducibility of RhOx species can be correlated with the activity in terms of diesel conversion. This trend will also be discussed and seen in Paper IV.

Regarding the role of Pt, again, the same trend in activity was noted for the unpromoted delta alumina sample Rh1.0Pt1.0/δ-Al2O3 as discussed in Paper I (section 6.1.2) seen in Table 9 and 11, respectively; the addition of Pt lowers the reducibility of Rh which lowers the fuel conversion, as well as results in high ethylene production. Interestingly, the addition of Ce-La significantly improved the catalyst activity. The extent of Pt interaction with Ce and La is not fully understood. The XRD analysis showed that the Pt dispersion was improved with the addition of Ce-La. Hence, the higher degree of Pt dispersion could very well be a possible reason for the higher activity.
6.3 Zone-coating of monoliths (Paper II)

In order to optimize the reforming catalyst performance one must first recognize and understand the overall reactions that take place within the monolith channels. In general, it is well recognized that ATR is a combination of initial PO and subsequent SR. Recent publications have provided new insights regarding where and when these major reactions occur inside the monolith channels of the reforming catalyst. In particular, intra catalyst measurements using Spaci-MS technology have shown that partial or total oxidation and high temperatures occur close to the entrance of the catalyst. In the remaining major part of the catalyst, steam reforming is the dominating reaction [11, 24, 32, 39-42]. These intra reaction sequences can be seen in Fig. 17, which are results from a Spaci-MS study carried out by Michael et al. [42]. In Fig. 17 a-d, the reactant and product gas distributions, and gas phase and surface catalyst temperature measurements for PO/ATR of CH₄ using a Rh catalyst are shown.

![Fig. 17a-d. Intra gas and temperature profiles for PO/ATR of CH₄ using a Rh-coated monolithic catalyst [42]. Published with the permission of Elsevier.](image)

As seen in Fig. 17a, all oxygen is consumed initially at x=2 mm due to PO reactions, while in Fig. 17b the H₂ concentration reaches its maximum in the final half of the catalyst due to SR reactions. Also, in Fig. 17d, T peaks are noted at the front of the monolith at x=0-3 mm, due oxidation reactions in which the surface temperature of the catalyst exceeds the gas phase temperature by approximately 100 °C. Finally, the extra addition of 10-40 % H₂O in the feedstock promotes H₂ generation as well as lowers the temperature up front.
Hence, based on this information a zoned catalyst can be an interesting solution for ATR of diesel. In this paper, the concept of the zoned catalyst is taken to mean coating a cordierite monolith with two different layers of washcoat of some given length in the axial direction. The first layer is intended to promote the PO reactions while the second layer enhances the SR reactions. Thus, heat generated from PO can be used directly in situ for SR. To date, the zoning concept is often used for the manufacture of three-way catalysts (TWC) for exhaust gas after-treatment [3, 102]. For a TWC catalyst, typically a higher loading of platinum group metals (PGM) is put in the front part of the catalyst to aid light-off and to oxidize CO and HC, while the rear part, used for NOx conversion, can consist of either lower PGM loading or of low amounts of Rh [3, 102, 103]. Also, a recent patent has emerged where zone-coated monolith catalyst is registered and used for PO of methane [104].

6.3.1 Zone-coated monoliths for ATR of diesel: preparation, activity and characterization

In paper II, a zoned catalyst was tested for ATR of diesel. The front washcoat was composed of Rh$_{1.0}$Pt$_{1.0}$Ce$_{10}$La$_{5.0}$/$\delta$-Al$_2$O$_3$ while the second washcoat was made of Rh$_{3.0}$Ce$_{10}$La$_{10}$/$\delta$-Al$_2$O$_3$. The preparation of the zoned coated catalyst can be seen in Fig. 18. Each end of the monolith was dip-coated to a given axial length with designated slurries. The boundary line of the zoned catalyst, located at l=10 mm, consisted of a small uncoated area approximately 2 mm wide as seen in Fig. 19.

Fig. 18. Preparation of zoned catalyst.

Fig. 19. Image of the zoned catalyst.
As seen in Table 12, the bench-scale activity results of the zoned coated catalyst were improved in terms of diesel conversion, hydrogen production and low ethylene formation. The zoned catalyst was also tested full-scale, which is described in more detail in Chapter 7.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition</th>
<th>Coating type</th>
<th>X_{Diesel}</th>
<th>S_{CO2}</th>
<th>H_{2}</th>
<th>C_{2}H_{6}</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1.0P1.0A</td>
<td>Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta-Al_{2}O_{3}</td>
<td>Uniform</td>
<td>99.1</td>
<td>47.4</td>
<td>39.2</td>
<td>300</td>
</tr>
<tr>
<td>R3.0B</td>
<td>Rh_{3.0}Ce_{10}La_{10}/\delta-Al_{2}O_{3}</td>
<td>Uniform</td>
<td>99.9</td>
<td>52.9</td>
<td>35.6</td>
<td>300</td>
</tr>
<tr>
<td>Z</td>
<td>Layer 1: Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta-Al_{2}O_{3}</td>
<td>Zoned</td>
<td>99.9</td>
<td>45.4</td>
<td>40.4</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Layer 2: Rh_{3.0}Ce_{10}La_{10}/\delta-Al_{2}O_{3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Finally, an XPS analysis was performed on the zoned catalyst to comprehend and to verify the in-situ reactions taking place within the channels of the coated monolith. As seen in Table 13, the XPS measurements provided valuable information on the surface composition and oxidation state both of the fresh powder samples of each washcoat (R_{1.0}P_{1.0}A and R_{3.0}B) and the corresponding aged samples of the washcoats taken from the zoned catalyst. For the fresh samples, rhodium was found to be present in its oxidized state with a binding energy in the range of 308.4-308.8 eV [105]. For platinum, the Pt(4d) peaks occur at about 314.0 eV which is metallic [105]. For ceria, the binding energy of the Ce 3d_{5/2} line is found at 881.2-881.8 eV, indicating CeO_{2} [105-107]. The XPS survey spectrum shows that La(3d) peaks are found at 834.2-834.6 eV with a La/Al ratio in the range of 0.091-0.099 indicating that La is in the dispersed phase [108, 109].

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Rh_{3d_{5/2}}</th>
<th>Pt_{4d_{3/2}}</th>
<th>Ce_{3d_{5/2}}</th>
<th>La_{3d_{5/2}}</th>
<th>Rh/Al</th>
<th>Pt/Al</th>
<th>Ce/Al</th>
<th>La/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh R_{1.0}P_{1.0}A</td>
<td>308.4</td>
<td>314.0</td>
<td>881.2</td>
<td>834.6</td>
<td>0.036</td>
<td>0.016</td>
<td>0.010</td>
<td>0.099</td>
</tr>
<tr>
<td>Fresh R_{3.0}B</td>
<td>308.8</td>
<td>-</td>
<td>881.8</td>
<td>834.2</td>
<td>0.031</td>
<td>-</td>
<td>0.008</td>
<td>0.091</td>
</tr>
<tr>
<td>Aged Z, x=1 mm</td>
<td>306.6</td>
<td>n.d.</td>
<td>881.6</td>
<td>834.8</td>
<td>0.007</td>
<td>0.000</td>
<td>0.016</td>
<td>0.045</td>
</tr>
<tr>
<td>Aged Z, x=9 mm</td>
<td>306.4</td>
<td>314.0</td>
<td>881.4</td>
<td>834.2</td>
<td>0.012</td>
<td>0.003</td>
<td>0.009</td>
<td>0.051</td>
</tr>
<tr>
<td>Aged Z, x=20 mm</td>
<td>306.8</td>
<td>314.2</td>
<td>881.8</td>
<td>834.8</td>
<td>0.025</td>
<td>0.031</td>
<td>0.009</td>
<td>0.082</td>
</tr>
<tr>
<td>Aged Z, x=28 mm</td>
<td>307.4</td>
<td>n.d.</td>
<td>n.d.</td>
<td>834.6</td>
<td>0.012</td>
<td>0.000</td>
<td>0.000</td>
<td>0.073</td>
</tr>
</tbody>
</table>

*a* The BE values presented for the Ce(3d) spectra correspond to the marking \( v \) according to the nomenclature set forward by Burroughs et al. [106]. Also, peaks with \( v''' \) and \( u''' \) markings were found at 899 and 916 eV indicating that ceria is present as CeO_{2} [105, 106].
On the aged sample Z, there were slight differences in the peak energies at the various positions on the monolith samples. As seen in Table 13, most elements remained in the same state except for rhodium. For rhodium, lower binding energies were registered, in the range of 306.6-307.4 eV, associated with metallic rhodium [105]. Hence, a possible phase transition from Rh$^{3+}$ to Rh$^{0}$ occurs on the surface of the catalyst during ATR. Also, the XPS analysis showed evidence of initial partial oxidation followed by steam reforming occurring in situ. As seen in Table 13, for catalyst Z in comparison to fresh powder samples, lower Rh/Al, Pt/Al and La/Al ratios are detected at sampling point x=1 mm in the bimetallic washcoat indicating losses of noble metals and promoters to be occurring, possibly due to sintering effects. However, for ceria, a higher Ce/La ratio is noted at x=1 mm. These results suggest that oxidation reactions such as partial and total oxidation occur initially. The exothermic reactions result in higher surface temperatures, which cause migration and sintering of the active metals. Theses trends confirm the Spaci MS data where T peaks are noted at the front of the monolith, as shown in Fig. 17. At sampling points x=9, 20 and 28 mm the Rh/Al, Pt/Al and La/Al ratios were higher than at x=1 mm. Also, the Ce/Al ratio remained intact at 0.009 similar to that of the fresh powder samples. Hence, these results indicate less sintering is taking place along the length of the catalyst. A possible explanation is the occurrence of endothermic steam reforming which lowers the surface temperature resulting in less particle migration and agglomeration. Again, this reaction trend can also be seen in the Spaci MS data in Fig. 17. Finally, the XPS analysis also showed evidence of Pt migration as some Pt was noted to reach the second washcoat.
6.4 Summarizing Paper IV

In Paper IV, IW-prepared catalysts consisting of 1 wt% Rh and 1 wt% Pt supported on delta alumina, ceria-zirconia (17.5 wt% ceria), silica and titania were tested for ATR of diesel at bench-scale. Promoters in the form of MgO, Y₂O₃, La₂O₃, CeO₂ and ZrO₂, ranging from 4 to 10 wt%, were also added on the supports to detect differences in catalyst activity. In general, the addition of promoters had an insignificant as well as negative impact on the catalyst performance in most cases except for the alumina-promoted sample. The addition of 10 wt% La₂O₃ on RhPt/Al₂O₃ was found to enhance the diesel conversion, hydrogen productivity as well lower the ethylene concentration. The improved activity was believed to be the result of higher reducibility of Rh₉O₆ species, at T~250°C, as shown in the H₂-TPR profile, Fig. 20. Other groups have reported similar results [110-112]. In this thesis, the Paper IV results presented in the following sections will be on the unpromoted samples.

![Fig. 20. TPR profiles of RhPt alumina-supported samples](image)

6.4.1 Characterization of fresh supported RhPt catalysts

The surface and porosity data of the different supports obtained from the N₂ sorption measurements are presented in Table 14. As seen in the table, the addition of the noble metals on the supports, along with a final calcination temperature of 800°C for 3 h, resulted in a decrease in surface area and pore volume. For the alumina samples, the delta alumina support had an initial surface area of 105 m²/g. The BET surface area for RhPt/Al₂O₃ was 94 m²/g. Hence, only a small degree of the initial surface area loss was lost, which is characteristic for alumina [57]. For the other supports more significant drops in surface area were observed. For instance, for ceria-zirconia, the support had the initial surface area of 173 m²/g while for the impregnated sample RhPt/CeO₂-ZrO₂ the surface area was reduced to almost 1/3. Similar trends were noted for the silica and titania samples. For silica, the surface area of RhPt/SiO₂ was 137 m²/g, which is the highest surface area of all samples. Similar surface area trend of the supports using N₂-BET has been reported by others [72, 113].
Table 14. Washcoat properties of fresh IW prepared RhPt-supported catalyst. The surface area and porosity were measured by N$_2$-BET while the crystallite size of Pt was determined by XRD. The Pt crystallite size was measured at 2θ=81.5° using the Scherrer equation.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition$^a$</th>
<th>Surface area [m$^2$/g]</th>
<th>Pore volume [cm$^3$/g]</th>
<th>Pore diameter [Å]</th>
<th>d$_p$(Pt) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ-Al$_2$O$_3$</td>
<td>Rh(1.0)Pt(1.0)/Al$_2$O$_3$</td>
<td>94</td>
<td>0.59</td>
<td>250</td>
<td>30</td>
</tr>
<tr>
<td>CeO$_2$-ZrO$_2$$^b$</td>
<td>Rh(1.0)Pt(1.0)/CeO$_2$-ZrO$_2$</td>
<td>64</td>
<td>0.22</td>
<td>136</td>
<td>n.d.</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Rh(1.0)Pt(1.0)/SiO$_2$</td>
<td>137</td>
<td>0.30</td>
<td>87</td>
<td>46</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Rh(1.0)Pt(1.0)/TiO$_2$</td>
<td>217</td>
<td>0.33</td>
<td>n.a.</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ The nominal weight loadings of the metals and the promoters on the supports are given in the parentheses.

$^b$ Ceria content in the support, ~17.5 wt% CeO$_2$.

The bulk crystalline measurements using XRD showed the presence of metallic Pt (~30-46 nm) for all impregnated samples except for the ceria-zirconia sample, see Table 14. Also, characteristic crystalline phases ascribed to the supports were detected for the bulk composition of the non-impregnated alumina, ceria-zirconia and titania. The XRD analysis showed the presence of δ-Al$_2$O$_3$, tetragonal ZrO$_2$ and anatase peaks. In contrast, as expected, the XRD pattern of the non-impregnated silica did not exhibit any distinctive sharp diffraction peaks as silica is amorphous. Furthermore, Rh peaks were not detected by XRD for all samples. Hence, in this study, the absence of Rh and Pt peaks in the XRD patterns indicates that the noble metals are finely dispersed on the ceria-zirconia support. The TEM results, see Fig. 22a-d, showed similar trends.

![Fig. 21. TPR profiles of RhPt catalysts.](image-url)
Fig. 22. TEM images of dispersed Rh and Pt particles found in fresh powder samples of a) RhPt/CeO$_2$-ZrO$_2$ and b) RhPt/SiO$_2$ and c-d) RhPt/TiO$_2$.

The TPR analysis (Fig. 21) showed that the reducibility of Rh$_{\text{ox}}$ species, at temperature region 40-250 °C, increased in the following order: RhPt/Al$_2$O$_3$ < RhPt/SiO$_2$ < RhPt/TiO$_2$ < RhPt/CeO$_2$-ZrO$_2$. The peaks at T~450 °C were ascribed to possible hydrogen spillover effect of the supports.

TEM and EDX analysis confirmed the presence of metallic Rh, oxide species Rh$_{\text{ox}}$ and metallic Pt as shown in Fig. 22a-d. In general, the average diameter of the smallest single Rh and Pt particles was approximately 5-20 nm and 5-15 nm, respectively. For RhPt/CeO$_2$-ZrO$_2$, it was difficult to see and confirm if the Pt particles sizes were the smallest of all samples. This was due to multiple layers of ceria and zirconia crystals on top of the Pt particles making it challenging to scrutinize and measure the average Pt sizes and dispersion.
6.4.2 Activity of supported RhPt catalysts

As seen in Table 15, all catalysts were found active and selective for ATR of diesel. The catalyst activity of the unpromoted samples, in terms of diesel conversion, increased in the following order: RhPt/SiO2 < RhPt/TiO2 < RhPt/Al2O3 < RhPt/CeO2-ZrO2. Again this trend in activity confirms the trends noticed in the previous papers that the reforming activity can be correlated with the reducibility of RhOx on the supports rather than e.g. the surface area. In this study, the highest RhOx reducibility was noted for RhPt/CeO2-ZrO2 (Fig. 21) while the highest surface area was noted for RhPt/SiO2 (Table 14). Another interesting trend is that RhPt/Al2O3 exhibited the highest ethylene formation, indicating that a high degree of carbon deposition takes place on the active sites of the catalyst. The latter was confirmed by O2-TPO analysis which is discussed in the following section.

Table 15. Activity results of RhPt-catalysts. The reaction condition for ATR of diesel was T_{feed}=650 °C, H2O/C~2.5, O2/C~0.49, TOS= 3h, GHSV~17700 h⁻¹ and P=1 atm. See Table 14 for catalyst formulation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>X_{diesel} [%]</th>
<th>S_{CO2} [%]</th>
<th>H2 [vol%]</th>
<th>C2H4 [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhPt/Al2O3</td>
<td>94</td>
<td>56.1</td>
<td>24</td>
<td>4000</td>
</tr>
<tr>
<td>RhPt/CeO2-ZrO2</td>
<td>98</td>
<td>53.5</td>
<td>40</td>
<td>1000</td>
</tr>
<tr>
<td>RhPt/SiO2</td>
<td>85</td>
<td>56.1</td>
<td>17</td>
<td>2400</td>
</tr>
<tr>
<td>RhPt/TiO2</td>
<td>92</td>
<td>53.1</td>
<td>29</td>
<td>2100</td>
</tr>
</tbody>
</table>

6.4.3 Characterization of aged RhPt supported catalysts

In Fig. 23a, the TPO profiles of a fresh and aged RhPt/Al2O3 are depicted. As seen in the figure, significant differences are noted, several distinguishable large peaks are present for the aged sample in the temperature interval 40-1000 °C. This indicates that coke species are present and oxidized to form CO and CO2 during TPO.

![Fig. 23. O2-TPO profiles of a) fresh cordierite, fresh and aged RhPt/Al2O3 and b) aged RhPt-supported catalysts. The fresh RhPt/Al2O3 sample was pre-reduced in H2 from room temperature to 1000 °C, 10 °C/min, dwelling at the maximum temperature for 2 h, prior to the TPO analysis.](image-url)
In Fig. 23b, the TPO profiles of all aged RhPt samples are shown. As seen in the figure, the peak intensities increased in the following order: RhPt/SiO₂ < RhPt/CeO₂-ZrO₂ < RhPt/TiO₂ < RhPt/Al₂O₃, indicating that a larger amount of coke deposits are present on alumina and titania than on ceria-zirconia and silica. Similar coke deposit trends have been reported by Mizuno et al. [114]. For ceria-zirconia, in particular ceria’s excellent oxygen storage capacity and WGS activity are known to assist in oxidizing and removing carbon species from the metal surface area of the catalyst during reforming [66, 67]. While silica is an inert and stable material known to exhibit high tolerance towards poisoning effects, e.g. sulfur [4, 57].

6.4.4 Possible correlations between characterization and activity results

In this thesis, the results show the accessibility and reducibility of Rh₅O₃ species plays a major role in the catalyst activity during diesel reforming. The higher reducibility of Rh₅O₃ species noted for RhPt/CeO₂-ZrO₂ at low reduction temperatures in Fig. 21, may be the result of a promoting effect caused by additional supply of oxygen originating from the support. Results from other studies have shown that during calcination, Rh can be sturdily incorporated into the lattice of CeO₂ in the CeO₂-ZrO₂ support [115-117]. Consequently, a strong interaction between Rh and CeO₂ takes place and as a result the oxygen migration from ceria to rhodium is facilitated [115-117]. The latter ceria promotion effect may also explain the improved reducibility of Rh₅O₃ species noted for the Ce-La promoted alumina sample, Rh₃.0Ce₁₀La₁₀/δ-Al₂O₃, shown in Fig. 16.

To summarize, in Paper IV, the higher activity results of RhPt/CeO₂-ZrO₂ for ATR of diesel, compared to other supported catalysts, may be ascribed to the higher reducibility of Rh₅O₃ species as well as the greater dispersion of Rh and Pt on the support. Also, the support contribution, in particular ceria, is believed to promote water-gas shift activity as well as reduce coke deposits on the catalyst surface.
7. Full-scale operations of Rh catalysts (Papers II-III, V-VI)

Within the scope of this thesis, two full-scale reformers were developed and tested to evaluate promising Rh catalysts. Both reformers were horizontally mounted in the reactor set-up and the reactor design was typically cylinder shaped. Also, both reformers were composed of stainless steel.

The first fuel reformer, termed REF1, was used for the reforming experiments reported in Paper V. The second fuel reformer, termed REF2, was used in the full-scale studies described in Papers II-III and VI, respectively. In REF1 a catalyst consisting of 1 wt% Rh on \( \gamma \)-alumina doped with Ce and La was tested full scale (Paper V). In REF 2 the zoned catalyst (Paper II) along with a catalyst consisting of 3 wt% Rh on \( \delta \)-alumina doped with Ce and La (Paper III) were tested in full scale.

7.1 Reactor design REF1 (Paper V)

For REF1, the reactor dimensions were ID=80 mm and L=220 mm. The scheme of the reactor design can be divided into two main zones: a mixing zone and a catalytic zone. As seen in Fig. 24, a single-fluid pressurized-swirl nozzle was used to inject liquid fuel as a fine hollow cone spray into the mixing zone for evaporation and blending with a mixture of superheated air and steam (300 °C) that enters the reformer from perpendicularly arranged injection holes (at L=40 mm). The mixture then enters the catalytic zone where the reforming catalyst is located and hydrogen generation takes place.

Fig. 24 Schematic drawing of REF1 (T# – thermocouple, L – length of reformer) [11].
7.1.1 Full-scale operations using REF1

In Paper V, a monolithic catalyst with a washcoat consisting of 1 wt% Rh on γ-alumina doped with Ce and La with a surface area of 133 m²/g was tested for ATR of diesel (see Fig. 25).

Fig. 25. Cordierite monolith catalyst (400 cpsi, OD=78 mm and l=100 mm) coated with 1 wt% Rh on Ce-La doped γ-alumina. The reactor flange is also shown with the nozzle welded on the centre. The latter is surrounded by 6 thermocouple fittings used to measure the temperatures in the mixing zone.

The parameters used in the study were H₂O/C~2.0, O₂/C~0.4 (λ~0.27), GHSV~8 700 h⁻¹ and P=1 atm. Commercial Swedish diesel MK1 was used as fuel for the reforming experiments (see Table 6). The diesel flow rate was kept at 12 g fuel/min estimated to generate an electrical power output of 3 kWₑ for PEFC-APU operation. The reactor set-up for the full-scale experiments can be seen in Fig. 26.

Fig. 26. Full-scale reactor set-up for testing of Rh-based diesel-reforming catalysts (MFC=mass flow controller).
7.1.2 Activity results and discussion using REF1

The activity results showed that the catalyst was active and selective for diesel reforming. The diesel conversion was ~96% and the hydrogen concentration in the reformate was ~30 vol%. Also, no coke deposits were observed inside the reformer or on the catalyst after the experiments were completed. The temperatures measured inside the reactor prior to and after catalyst at H2O/C~2.0, O2/C~0.4 are shown in Fig. 27.

As seen in the figure, the temperatures in the mixing section ranged from 475 °C before the steam/air inlet holes (x/L=0.05) to 585 °C at the catalyst inlet (x/L=0.4). After the catalyst outlet (x/L=0.9) the temperature was higher, ~650 °C, indicating oxidation reactions taking place inside the monolithic channels. Also, major differences were noted in the radial temperature measurements at x/L=0.9, with a gradient of ~100 °C. The large gradient may have been the result of disturbance in the flow pattern, for instance due to poor reactant mixing. The latter trend was seen in temperature measurements in the mixing zone during continuous operation; these readings showed the existence of occasional local temperature rises caused by hot-spot formation as a result of stagnant zones of recirculated reactants. Furthermore, the achieved reaction temperature was too low to generate complete fuel conversion, the latter most likely limited by the reactor design (such as thermal insulation and geometry) rather than catalyst design. For instance, during the experiments, higher O2/C ratios than 0.4, in order to increase the reaction temperature, often resulted in total oxidation and unsteady reactions owing to reactor design limitations. The incomplete diesel conversion, the existence of radial temperature gradients and hot-spot formations noted in this paper may have been caused by poor mixing and nonfunctional reactor design. The results derived from this study indicated that improved turbulence, fuel dispersion and reactant mixing were needed to enhance and stabilize the reformer’s overall performance. Based on these results a new catalytic reformer, REF2, was developed where adjustments were made to the reactor design with the aim to improve the operating efficiency.
7.2 Reactor design REF2 (Paper VI)

Fig. 28 shows a side view image of the upgraded catalytic reformer, REF2. The interior of the reactor can be seen in Fig. 29. As seen in the figures, the lengths of the mixing zone and catalytic zone, respectively, for REF2 were extended in comparison to REF1. Also, the reactor was slightly widened in the radial direction. The reactor dimensions for REF2 are ID=84 mm and L=400 mm. The reactor design improvements for REF2 were the following:

- a new single-fluid pressurized-swirl nozzle was installed to further atomize and disperse the fuel into fine micro-sized droplets (<10μm).
- the air-steam injection holes were repositioned further upstream in the mixing zone to improve the reactant mixing with the fuel and to prevent the occurrence of stagnant zones
- an alumina foam disc was placed in the mixing zone to improve the mixing and to protect the catalysts in case of auto-ignition incidents of the fuel
- the catalytic zone was extended by including two reforming catalysts to prevent diesel slip
- a total of 14 K-type thermocouples were placed in different radial and axial positions inside the reactor for temperature measurements, four of these were placed inside the monoliths for in-situ temperature measurements
- a heat-resistant packaging mat was inserted as an insulator, to cover the inside of the reactor in order to hold the foam and the monoliths in place, and to minimize leakages and heat losses.

![Fig. 28. Side view image of REF2 including arrowed descriptions.](image-url)
7.2.1 Full-scale operations using REF2 – testing of zoned catalyst (Paper II)

In Paper II, the zone-coated monolith catalyst was tested full-scale for validation using the upgraded reformer, REF2. The reaction conditions in the study were \( \text{H}_2\text{O}/\text{C}=2.5, \; \text{O}_2=0.49 \; (\lambda=0.33), \; \text{GHSV}=10800 \; \text{h}^{-1} \) (measured for both catalysts) and \( P=1\text{atm}. \) Commercial diesel MK1 was used as fuel for the reforming experiments (see Table 6). The diesel flow rate was kept at 19.5 g fuel/min estimated to generate an electrical power output of 5 kW\(_e\) for PEFC-APU operation. The same reactor set-up, as shown in Fig. 26, was used for the experiments. The catalyst candidates tested, \( Z \) and \( R_{3.0B} \), respectively, are depicted schematically in Fig. 29. See Tables 10 and 12 for catalyst formulations.

![Diagram](image)

**Fig. 29.** Interior design of REF2 showing the location of the air/steam injection holes, the foam and catalysts \( Z \) and \( R_{3.0B} \). See Table 10 and 12 for catalyst formulations. Catalyst dimensions: OD=80.3 mm, l=76.2 mm.

7.2.2 Activity results and discussion using REF2 – validation of zoned catalyst

A stable and steady-state operation was achieved with REF2. For instance, no hot-spot formations were noted in the mixing zone throughout all experiments. Regarding mixing zone temperatures; in the beginning of all reforming experiments a temperature increase was noted in the mixing zone, in which a customary homogeneous ignition (aka “light-off temperature”), took place raising the temperature of the reactant mixture from 300 to 400 °C before reaching equilibrium. The typical
temperatures measured in the mixing zone at \( \text{H}_2\text{O/C}=2.5, \text{O}_2/\text{C}=0.49 \) ranged from 450 (at \( l=10 \text{ mm} \)) to 490°C (at \( l=100 \text{ mm} \)), as shown in Fig. 30. Also, as depicted in the figure, the temperature gradients were much smaller (≤ 50°C) compared to REF1, indicating that the mixing and reforming reactions were superior. Also, reforming temperatures exceeding 700 °C were manageable while increasing the \( \text{O}_2/\text{C} \) ratio.

In this study, the temperature measurements and analyzed product gases established that the sequence of the main reactions taking place for ATR of diesel were primarily partial oxidation followed by steam reforming. As mentioned previously, Fig. 30 shows the temperature profile for diesel MK1 at steady state at \( \text{H}_2\text{O/C}=2.5, \text{O}_2/\text{C}=0.49 \). This profile is typical for ATR as it displays an initial maximum followed by a decrease of the temperature measured in the axial direction in the catalytic zone (distance between the front of Z, \( l=170 \text{ mm} \), and the back of \( \text{R}_\text{3.0B}, l=350 \text{ mm} \)). The initial increase of the average temperature noted inside the first catalyst (∼760 °C) is believed to be the result of exothermic partial oxidation reactions. The decreases noted in the average outlet temperatures of both catalysts, ∼722 and 690°C, measured at \( l=260 \) and 370 mm, respectively, indicate that subsequent endothermic steam reforming reactions are taking place along the reactor length.

![Temperature profile](image)

**Fig. 30.** Axial temperature measurements along reactor length, at full-scale, for ATR of diesel MK1 over catalysts Z and \( \text{R}_\text{3.0B} \). FOAM=inert zirconia-treated alumina foam. See Tables 10 and 12, respectively, for catalyst formulations.

In this study PO and sequential SR trends were also noted in the product gas measurements. For instance, the GC analysis showed that all oxygen was consumed after the first catalyst, Z. In addition, the FTIR analysis showed that the steam concentration in the outlet stream of the second catalyst, in comparison to the first catalyst, decreased by an average of ∼0.3 vol% for all samples.
collected. Again, these O\textsubscript{2} and H\textsubscript{2}O trends confirm the Spaci-MS data tendencies reported by Michael et al. [42] as shown in Fig. 17.

The activity results showed that the zone-coated catalyst was active and selective for diesel reforming. As seen in Table 16, the diesel conversion was close to complete and the hydrogen concentration in the reformate was \(\sim 31\ \text{vol}\%\). The main alkane product was methane, \(\sim 9500\ \text{ppm}\), indicating that the conversion was good. Also, the ethylene level was very low, approximately 4 ppm. Finally, no signs of deactivation were noted for both catalysts after a total of 40 hours time on stream. Also, no coke deposits were observed inside the reformer or on the catalysts after the experiments were completed.

**Table 16.** ATR of diesel MK1 over catalyst Z and R\textsubscript{3.0B} at H\textsubscript{2}O/C=2.5, O\textsubscript{2}/C=0.49 The gas samples were analyzed after 40 hours of steady state operation. See Tables 10 and 12, respectively, for catalyst formulation.

<table>
<thead>
<tr>
<th></th>
<th>Z</th>
<th>R\textsubscript{3.0B}</th>
</tr>
</thead>
<tbody>
<tr>
<td>T\textsubscript{CAT} [°C]</td>
<td>760</td>
<td>718</td>
</tr>
<tr>
<td>X\textsubscript{Diesel} [%]</td>
<td>99.3</td>
<td>99.4</td>
</tr>
<tr>
<td>S\textsubscript{CO2} [%]</td>
<td>33</td>
<td>34</td>
</tr>
<tr>
<td>H\textsubscript{2} [vol%]</td>
<td>31.3</td>
<td>31.9</td>
</tr>
<tr>
<td>CH\textsubscript{4} [ppm]</td>
<td>9500</td>
<td>15400</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{6} [ppm]</td>
<td>48</td>
<td>16</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{4} [ppm]</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{8} [ppm]</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
7.2.3 Full-scale operations using REF2 – testing of uniformly coated Rh catalysts (Paper III)
This paper provides a deeper understanding regarding possible reaction mechanisms occurring during ATR of diesel at full-scale that can be correlated to the fuel properties and operating parameters H2O/C and O2/C. In this study, two cordierite monolithic catalysts (CAT1 and CAT2) with the same washcoat composition Rh3.0Ce10La10δ-Al2O3 were prepared and incorporated in REF2. The fuel candidates tested were diesel surrogate n-tetradecane, and commercial low-sulfur and FT diesel fuels (see Table 6 for fuel properties). The reaction conditions tested are listed in Table 17.

Table 17. Operating parameters for the fuels used in the full-scale ATR experiments.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Flow rate [g fuel/min]</th>
<th>Pth [kWth]</th>
<th>Pe [kWe]</th>
<th>O2/C</th>
<th>λ</th>
<th>H2O/C</th>
<th>GHSV [h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-tetradecane</td>
<td>19.0</td>
<td>14.0</td>
<td>5.0</td>
<td>0.37-0.51</td>
<td>0.30-0.33</td>
<td>2.0/2.5/3.0</td>
<td>9300-12400</td>
</tr>
<tr>
<td>Diesel MK1</td>
<td>19.0</td>
<td>13.5</td>
<td>5.0</td>
<td>0.37-0.50</td>
<td>0.29-0.33</td>
<td>2.0/2.5/3.2</td>
<td>9500-12400</td>
</tr>
<tr>
<td>FT diesel</td>
<td>19.0</td>
<td>13.7</td>
<td>5.0</td>
<td>0.39-0.40</td>
<td>0.25-0.26</td>
<td>2.5/3.2</td>
<td>10200-11100</td>
</tr>
</tbody>
</table>

a Pth = thermal power output.
b Pe = electrical power output estimated for an APU system based on PEFC technology.
c λ = actual-to-stoichiometric air/fuel ratio.
d Total GHSV measured for both catalysts in the reactor.

7.2.4 Activity results and discussion using REF2 - the effect of fuel properties
For all fuels tested, the fuel conversion increased with higher reaction temperatures. In Fig. 31, the conversion plot for diesel MK1 is shown as function of temperature. As seen in the figure, the conversion improved with an increase in temperature (due to increase in O2/C ratio). Furthermore, the conversion was higher at lower temperatures after the second catalyst (open symbols). Again, the latter trend confirms the occurrence of endothermic steam-reforming reactions.

Fig. 31. ATR of diesel MK1. Diesel conversion as function of temperature, measured at constant H2O/C~2.5. Filled symbols represent results obtained with CAT1. Open symbols represent CAT2. Both catalysts contain the same washcoat composition: Rh3.0Ce10La10δ-Al2O3. The O2/C ratios were varied to generate the average in-situ temperatures shown on the x-axis. The in-situ temperatures of the catalysts were measured at reactor l=180 and 290 mm, respectively (see also Fig. 30).
As seen in Table 18, the optimal O₂/C ratios for diesel MK1 and tetradecane were 0.49 and 0.5, respectively, both reaching a reaction temperature of 750 °C.

For FT-diesel, unsteady-state operations took place throughout all reforming experiments making it difficult to determine the optimal O₂/C ratio. For instance, temperature gradients in the mixing zone and inside the catalyst were found to slowly increase after 2 hours of operation. Hence, only few gas samples were collected and analyzed in detail within this limited time period. It was difficult to comprehend what caused these unfavorable reactions. A possible explanation was that ignition of light fractions in the fuel may have caused the registered temperature gradients.

Table 18. ATR of n-tetradecane, low-sulfur and FT diesel over catalyst Rh₃.⁶Ce₁₀La₁₀/δ-Al₂O₃ at constant H₂O/C~2.5. The analyzed gas samples were collected from the outlet of CAT2. The average in-situ temperature of the catalyst, T_CAT2, presented in the table was measured at reactor l=290 mm (see also Fig. 30).

<table>
<thead>
<tr>
<th></th>
<th>MK1</th>
<th>C₁₄H₃₀</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_CAT2</td>
<td>~750</td>
<td>~750</td>
<td>~700</td>
</tr>
<tr>
<td>Xₐₚₚₖ</td>
<td>~100</td>
<td>~100</td>
<td>90</td>
</tr>
<tr>
<td>S_CO₂</td>
<td>30</td>
<td>33</td>
<td>51</td>
</tr>
<tr>
<td>H₂ [vol%]</td>
<td>30.3</td>
<td>29.9</td>
<td>32.8</td>
</tr>
<tr>
<td>CH₄ [ppm]</td>
<td>4773</td>
<td>8573</td>
<td>2236</td>
</tr>
</tbody>
</table>

As seen in Table 18, fuel properties have a clear effect on the catalyst performance. In general, as seen in Fig. 32a-b, the fuels containing less aromatics and sulfur (n-tetradecane and FT-diesel) were found to result in less carbon monoxide and ethylene formation. Similar results have been reported by others [39, 118]. Also, as seen in Fig. 32b, the ethylene formation was reduced to almost zero at temperatures near 800 °C. This result is in line with what has been reported by others [48, 119].

![Fig. 32. ATR of diesel MK1, n-tetradecane and FT-diesel at constant H₂O/C~2.5. The effect of oxygen-to-carbon ratio on CO a) and C₂H₄ b). The O₂/C ratios were varied to generate average in-situ temperatures for CAT2 (measured at reactor l=290 mm, see also Fig. 30) in the range of 600-800 °C, as seen on the x-axis.](image-url)
7.2.5 Activity results and discussion using REF2 - the effect of H\textsubscript{2}O and O\textsubscript{2}/C

The choice of H\textsubscript{2}O/C and O\textsubscript{2}/C ratios had a clear effect on the product gas distribution. The same trends were noted for all fuels employed. In general, increasing the O\textsubscript{2}/C ratio decreased the H\textsubscript{2}, CO and C\textsubscript{2}H\textsubscript{4} production. Increasing the H\textsubscript{2}O/C ratio slightly increased the H\textsubscript{2} production and decreased the CO and C\textsubscript{2}H\textsubscript{4} formation. The latter CO-trend can be seen in Fig. 33. As seen in the figure, adding a surplus of steam into the feedstock to achieve high ratios of H\textsubscript{2}O/C is advantageous in order to suppress CO formation. However, it should be emphasized that vaporizing water in order to generate higher loads of steam for the reformer would require extra energy for heating purposes and in addition add extra cost to the operation of the APU system. Also, it may require additional heaters for steam generation, thus increasing the volume and weight of the whole APU system [11, 24].

![Figure 33](image.png)

**Fig. 33.** ATR of diesel MK1. The effect of steam-to-carbon ratio on CO formation as function of temperature.

For all fuels tested in the full-scale experiments, no catalyst deactivation e.g. carbon deposition and sulfur poisoning were noted during the ongoing experiments, during shutdown of the reactor and during visual examination of the catalysts. The total time on stream for each fuel tested was approximately 40 h. The same activity results were obtained when the reaction conditions were repeated.
8. Concluding remarks

The main objective of the work presented in this thesis has been to address the challenges of catalytically reforming diesel fuels using Rh-based washcoated cordierite monoliths. The aim is to catalytically fragmentize diesel, by autothermal reforming, into a hydrogen-rich gas mixture that can be fed to a PEFC auxiliary power unit working in the range of 5-10 kW_e. The results and discussion presented in this thesis can provide deeper understanding regarding catalytic diesel reforming, hopefully serving as basis for future studies.

One of the main objectives of the thesis is to bridge the gap of knowledge between the role of the Rh-containing washcoats and the catalyst activity. The hypothesis was to keep the Rh metal loading at a minimum without losing any significant reforming activity. Pt addition, different promoters and supports were tested for the Rh catalysts. Also, different Rh washcoats were coated on specific parts on the cordierite monolith (zone coating) and tested for diesel reforming. In Papers I-IV the physicochemical properties of fresh and aged Rh catalysts were closely investigated and correlated with the catalyst activity from the bench-scale operations. The activity was expressed in terms of diesel conversion, CO_2 selectivity, and hydrogen and ethylene production.

In Paper I, the activity results showed that IW-prepared samples with low nominal weight loadings of Rh and RhPt on γ-Al_2O_3 were all highly active and selective for diesel reforming. However, further improvements of the washcoats were needed as none of the samples tested provided complete fuel conversion at the tested reaction conditions. Furthermore, the bimetallic sample was found least active in terms of diesel conversion. Also, the ethylene formation was the highest among the tested samples.

In Papers II-III, upgrading of the washcoats was carried out using δ-alumina as support material and applying Ce-La as promoters. The unpromoted samples of Rh and RhPt showed similar results in activity as observed in Paper I. The catalyst activity was improved with increase of Rh loading which can be considered positive, however resulting in a more expensive catalyst. Interestingly, the activity results showed significant enhancement in catalyst activity with the addition of Ce-La to the support. In Paper II, a zoned catalyst was also tested in which two washcoats Rh_{1.0}Pt_{1.0}Ce_{10}La_{10}/δ-Al_2O_3 and Rh_{3.0}Ce_{10}La_{10}/δ-Al_2O_3 were coated on specific parts in the axial direction of the cordierite monoliths. The results showed that the zoned catalyst had the highest overall activity compared to the uniformly coated monoliths.

In Paper IV, IW-prepared catalysts consisting of RhPt supported on alumina, ceria-zirconia, silica and titania were tested for ATR of diesel. The catalyst activity of the unpromoted samples, in terms of diesel conversion, increased in the following order: RhPt/SiO_2 < RhPt/TiO_2 < RhPt/Al_2O_3 <
RhPt/CeO₂-ZrO₂. The activity results showed that the nearly all diesel fuel was converted using RhPt/CeO₂-ZrO₂.

The characterization results from the fresh samples taken from the experiments described in Papers I-IV, provided valuable information that may be correlated with the activity results. One of the main conclusions is that Rh₃O₅ is strongly believed to be one of the main active phases for diesel reforming. The extent of accessible and reducible Rh₃O₅ species on the support governs the catalytic activity. In Paper I, the TPR analysis showed that the addition of Pt lowered the reducibility of Rh₃O₅ species, hence resulting in lower reforming activity. The latter observation was confirmed by TEM analysis in which a high number of RhPt alloys were found on the alumina support. In Papers II and III, TPR analysis showed that the addition of Ce-La had a significant positive effect on raising the reducibility of the Rh₃O₅ species. In Paper IV, TPR analysis showed that the reducibility of Rh₃O₅ species was the highest for sample RhPt/CeO₂-ZrO₂. Also, in the same paper, the addition of La on RhPt/Al₂O₃ was found to increase the hydrogen uptake of the Rh₃O₅ species.

The characterization results from the fresh samples also provided valuable information regarding the bulk and surface states as well as the dispersion of the active components in the washcoats. Most of the characterization studies were done on Rh and Pt. Regarding Rh, H₂ chemisorption, XRD and TEM analyses on Rh samples showed that the Rh particles were finely dispersed on all employed supports. Also, the particle sizes of Rh were similar on all tested supports, in the range of ~5-20 nm, Regarding Pt, it was difficult to conclude the role of Pt in diesel reforming from the results derived from Papers I-V. XRD and TEM analyses showed the presence of agglomerated metallic Pt particles with average crystallite sizes up to 45 nm being present on most of the supports except for ceria-zirconia (Papers I and IV). This suggests that the higher activity noted for RhPt/CeO₂-ZrO₂ could be the result of improved Pt dispersion on ceria-zirconia. Similar results concerning Pt-Ce interactions were noted for the Ce-La promoted and alumina-supported RhPt sample (Paper II).

The characterization results from the aged samples taken from Papers I-IV provided some interesting answers regarding deactivation mechanisms e.g. sintering and coke deposition effects, and possible phase transition of the active metals and promoters that take place in the employed catalysts. O₂-TPO analysis on aged samples shows that the addition of Pt on alumina increased the coke deposition on the catalyst (Paper I). The addition of Ce-La had the opposite effect (Paper II). The extent of coke deposition was most profound on the alumina support (Paper IV). XPS analysis on the aged zoned catalyst showed major sintering effects and Pt migration taking place on the front washcoat of the monolithic catalyst (Paper II). These effects were less prominent on the final half of the catalyst. Hence, the latter observation confirms the main reaction sequence of ATR, exothermic
PO occurs initially followed by endothermic SR. XPS also showed that phase transition takes place. The results showed that rhodium switched oxidation state from e.g. \( \text{Rh}^{3+} \) to \( \text{Rh}^0 \) while Pt remained in the metallic state (Paper II). Similar transitions were seen in the TEM analysis on the aged sample RhPt/Al\(_2\)O\(_3\) (Paper I). These observations suggest that SR is the predominant reaction in ATR which may cause the phase transitions of the rhodium oxide particles.

The final main aim of this thesis is to address the development and testing of full-scale reformers at various realistic operating conditions using promising Rh catalysts (Papers II-III, V-VI). Two full-scale diesel reformers, REF1 and REF2, were successfully developed and found capable of providing high fuel conversion and hydrogen production from commercial diesel over selected Rh catalysts (Papers V-VI). For REF2, major improvements were made in the reactor design to enhance the fuel dispersion, reactant mixing and fuel conversion (Paper VI). The activity results showed that the upgrading had an overall positive effect on REF2 performance. For instance, stable and steady-state operations were achieved as no hot spot formations were noted in the mixing zone with increased time on stream. Also, for REF2, the activity results showed that the zone-coated catalyst was active and selective for diesel reforming at full-scale as well (Paper II). In addition, for REF2, the diesel fuels n-tetradecane, diesel MK1 and FT diesel were tested for ATR of diesel over Rh\(_{1.0}\)Ce\(_{10}\)La\(_{10/6}\)-Al\(_2\)O\(_3\) (Paper III). In general, the fuels containing less aromatics and sulfur (n-tetradecane and FT diesel) were found to result in less carbon monoxide and ethylene formation. Finally, the effects of H\(_2\)O and O\(_2\)/C ratios were studied. In general, increasing the H\(_2\)O/C ratio improved the H\(_2\) production and decreased the CO and C\(_2\)H\(_4\) formation. Increasing the O\(_2\)/C ratio resulted in a decline of H\(_2\), CO and C\(_2\)H\(_4\) production.

Future work, according to the author’s opinion, should be to conduct further research and development on the zone-coated catalyst and the bimetallic sample RhPt/CeO\(_2\)-ZrO\(_2\). Regarding the zoned catalyst, improvements have to be made on the front washcoat to enhance the thermal stability due to initial PO reactions. There are several options: for instance, high temperature-stable hexaaluminate can be used as support. The latter material is often used for catalysts designed and employed for catalytic combustion with reaction temperatures up to 1500 °C [60]. Another solution would be to include a higher load of noble metals on the front washcoat (like in the case of zoned TWC catalyst) in order to sustain the durability of the catalyst, compensating activity losses occurring due to sintering. Also, multilayer and radial coating designs should also be considered for future studies. Regarding RhPt/CeO\(_2\)-ZrO\(_2\), testing at full-scale using the upgraded reformer, REF2, would be the next logical step. Different weight ratios of CeO\(_2\) on CeO\(_2\)-ZrO\(_2\) should also be tested. Moreover, further research has to be carried out to find promising promoters. Finally, the potential reforming activity of Pt has to be clarified for RhPt/CeO\(_2\)-ZrO\(_2\).
Acknowledgements

There have been many people and organizations helping me making this thesis possible. To whom this may concern, I give you my deepest gratitude. It has been a challenging, exhausting and tortuous journey but at the same time exciting, memorable and a truly rewarding experience.

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Nomenclature

A/C  Air conditioner
a.u.  Arbitrary unit
APU  Auxiliary Power Unit
ATR  Autothermal reforming
BE   Binding energy
BET  Brunauer-Emmet-Teller
CI   Compression ignition engine
CFD  Computational fluid dynamics
cpsi Cells per square inch
EDX  Energy dispersive X-ray spectroscopy
F    Molar flow
FC   Fuel cell
FIT  Fuel inlet temperature
FID  Flame ionization detector
FT   Fischer-Tropsch
FTIR Fourier-transform infrared
GC   Gas chromatography
GHSV Gas hourly space velocity
HT-PEFC High-temperature polymer electrolyte fuel cell
H2O/C Steam-to-carbon ratio
ICE  Internal combustion engine
IW   Incipient wetness
LHV  Lower heating value
ME   Micro emulsion
NDIR Non-dispersive infrared
NOx  Nitrogen oxide gases, i.e. NO and NO2
O2/C Oxygen to carbon ratio
Pe   Electric power output
Pth  Thermal power output
PEFC Polymer electrolyte fuel cell
PEMFC Proton exchange membrane fuel cell
PO   Partial oxidation
PM   Particulate matter
PrOx Preferential oxidation
REF1 Reformer, full-scale, used in Paper V
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>REF2</td>
<td>Upgraded reformer, full-scale, used in Papers II-III and VI</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction, dN0x unit</td>
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<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
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<tr>
<td>SR</td>
<td>Steam reforming</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TOS</td>
<td>Time on stream</td>
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<tr>
<td>TPO</td>
<td>Temperature-programmed oxidation</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature-programmed reduction</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>WGS</td>
<td>Water-gas shift</td>
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References


