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Rational Catalyst Design for Direct Conversion of CH4 and CO2

Vesna Havran Mueller
Washington University in St. Louis

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Rational Catalyst Design for Direct Conversion of CH$_4$ and CO$_2$

by

Vesna Havran Mueller

A dissertation presented to the Graduate School of Arts and Sciences Of Washington University in partial fulfillment of the Requirements for the degree of Doctor of Philosophy

August 2013
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Possibilities for mitigation of carbon dioxide and methane levels in the atmosphere are of major global interest. One of the alternatives that attracts much scientific attention is their chemical utilization, especially because both of these gases are components of the natural gas, and rapid and extensive shale gas development makes them abundant raw materials. Development of an effective catalytic process that could be scaled-up for industrial purposes remains a great challenge for catalysis. Understanding of the mechanisms of molecular activation as well as of the reaction pathways over active centers on heterogeneous catalysts needs to be advanced. To that end this work focused on initiating the development of a bifunctional catalyst for low-temperature (200°C - 450°C) direct conversion of methane and carbon dioxide by tailoring the structure of each active component using the insights from molecular modeling.

Pt nanoparticles supported on ceria support have been selected based on molecular modeling and density functional theory analysis that provided the guidance for the catalyst structure optimization. Tetrahedral Pt nanoclusters, with a high fraction of edge and corner sites that would supposedly promote methane activation, were prepared by carefully adjusting the concentration ratio between Pt
precursor and the capping polymer. Ceria nanorods, exhibiting more reducible facets that would activate carbon dioxide, were prepared by hydrothermal method. Conventional incipient wetness and modified polyol method were also used for the preparation of supported round shape Pt samples, for the comparison. Catalyst activity was evaluated by studying the H₂ evolution rates during the exposure of the catalyst to the methane flow, in a small packed bed reactor, at the atmospheric pressure and temperatures up to 450°C. Insights into the structure of the adsorbed carbonaceous species, formed during methane chemisorption, were gained from temperature programmed reduction profiles. The effects of catalyst structure, reaction temperature, CH₄ partial pressure and the Pt loading on the methane activation were outlined. Results revealed that a strong metal-support interaction, characteristic for the ceria supported samples, had a pronounced impact not only on the total amount of chemisorbed CH₄, but also on the structure of the adsorbed carbonaceous film. This has been attributed to the high concentrations of oxygen vacancies at the interface between ceria and Pt. The promoting effect of ceria was further confirmed in the experiments involving supported tetrahedral Pt nanoclusters. However, the application of these nanoparticles was limited by the instability of their shapes under reaction conditions. New synthesis methods that would increase the catalyst stability and prevent reconstruction of cluster shapes need to be developed. Further studies of the reactivity of the adsorbed carbonaceous species with the carbon dioxide and the selectivity towards desired oxygenates are needed.

An integrated method involving both experimental and modeling efforts could enable more rational design of new materials with improved activity and selectivity and could potentially cut the costs and duration of extensive “trial-and-error” approach commonly practiced in industry. The possibility of tailoring catalyst activity and selectivity through shape and size- control could lead to the more efficient catalyst utilization.
1. Introduction and motivation

1.1. Introduction

Methane and carbon dioxide are greenhouse gases. Although the amounts of methane in the atmosphere are lower than carbon dioxide, methane’s global warming potential (GWP) is approximately 25 times higher than that of CO₂ (Yuliati and Yoshida, 2008). The abundance of these two gases creates a potential for their use as starting materials in chemical synthesis. Large amounts of methane are widely available in nature in the form of natural gas while substantial amounts of carbon dioxide are man-generated. Both of these gases are components of the natural gas. Currently, the proven world natural gas reserves are estimated at 6,300 trillion cubic feet or around 177 trillion cubic meters according to the latest reports (Figure 1, EIA (January, 2009)).

![Figure 1. World proven reserves of natural gas (x 10^{12} m^{3}, EIA (January, 2009))]
Although the presence of natural gas in the shale layers of sedimentary rock formations that were deposited in ancient seas has been known for many years, due to the difficulty in extracting the gas from these rocks it was considered uneconomical. However, new developments in the extraction technologies, the directional drilling, which is drilling at an angle other than vertical, and hydraulic fracturing, which uses pressurized liquids to crack subsurface rock, have caused a boom in the shale gas production. As a result hundreds of trillions of cubic feet of gas that previously couldn't be economically produced became recoverable (U.S. Department of Energy (DOE)). US Energy Information Administration (EIA) projects that shale gas production will rise to 13.6 trillion cubic feet by 2035, representing nearly half of all U.S. natural gas production.

However, large amounts of natural gas are mainly found in remote areas (Table 1) thus hindering its full exploitation due to cost ineffective gas transportation. Natural gas liquefied by refrigeration can be transported by pipelines. However, to distribute the gas by these pipelines compression to ca. 80 bars is needed (Crabtree, 1995). and sometimes a pipeline may not be available for distant markets (Lunsford, 2000). This challenge increases the desirability for onsite gas to liquids conversion (Crabtree, 1995; Fox, 1993; Lunsford, 2000; York et al., 2007; Holmen, 2009). Chemical conversion of CH₄ and CO₂ at mild conditions to highly valuable chemicals and/or clean fuels is the subject of great importance in C1 chemistry. Developing an effective process for such a conversion would help address environmental issues, by lowering the levels of CO₂, and would also reduce the need for indirect routes of fuel production from methane via synthesis gas. Due to strong intra-molecular bonds both molecules are quite chemically inert and thermodynamically stable. Consequently, most of their reactions require significant energy inputs as well as properly designed catalytic systems that lower kinetic barriers in their direct conversion. Despite great scientific attention to this issue, no breakthrough technology has
emerged so far. The potential of directly converting methane and carbon dioxide to higher value products, such as liquid hydrocarbon fuels or acetic acid for example, has not been fully realized either.

Table 1. Location of natural gas reserves (x $10^{12}$ m$^3$, York et al., 2007)

<table>
<thead>
<tr>
<th>Type of location</th>
<th>1960</th>
<th>1970</th>
<th>1990</th>
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<tr>
<td>Easy onshore zones</td>
<td>15.8</td>
<td>27.5</td>
<td>60</td>
</tr>
<tr>
<td>Offshore</td>
<td>1.6</td>
<td>4.5</td>
<td>25</td>
</tr>
<tr>
<td>Arctic and Siberia</td>
<td>0.1</td>
<td>7.5</td>
<td>42</td>
</tr>
<tr>
<td>Other difficult onshore</td>
<td>-</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>World</td>
<td>17.5</td>
<td>40.0</td>
<td>129</td>
</tr>
<tr>
<td>Share of difficult zones (%)</td>
<td>10</td>
<td>31</td>
<td>53</td>
</tr>
</tbody>
</table>

The catalytic activation of methane on supported transition metals has been a matter of intense investigation and Pt was shown to be the most active noble metal for these purposes (Wei and Iglesia, 2004a-c). Once methane is activated, it can be used in a variety of industrially relevant reactions (for example, synthesis-gas (syngas) formation, Viñes et al., 2010). However, it is difficult to achieve controlled CH$_4$ dehydrogenation and avoid complete oxidation (Rostrup-Niesen, 1994) and nonselective breaking all for C-H bonds (Yuliati and Yoshida, 2008). Therefore, the key issue with the direct conversion of methane is related to selectivity rather than reactivity (Holmen, 2009). This requires catalysts and proper understanding of pathways on catalytic surfaces. Recent advances in synthetic chemistry, novel in situ/in operando spectroscopy methods, and molecular modeling capabilities, can provide significant insights at atomic scale and help identification of highly selective catalytic structures with high concentrations of desired surface sites. (Christopher and Linic, 2010; Sabbe et al., 2012)
Periodic operation of the catalyst in which gases are alternatively fed into the reactor, has been suggested as an option for overcoming thermodynamic barrier (Huang et al., 2001; Ding, 2007). It is found that upon methane introduction into the reactor, within the first minute a surface reaction (methane dissociation) has been completed and gas flow is then switched to carbon dioxide. Catalyst selectivity and different product distributions over various noble metals, has been explained by differences in the adsorption energies of resulting surface CH$_x$ species and their reactivity with incorporated CO$_2$ molecule. Therefore, molecular modeling analysis can be a powerful tool for guiding the selection of material that could stabilize specific reaction intermediates, yield more of hydrogen rich CH$_x$ species and in that way enable controlled CH$_4$ dehydrogenation and improve selectivity towards desired oxygenates.

It is believed that the CH$_x$ species formed during dissociative CH$_4$ adsorption on a reduced transition metal surface are a function of metal, metal structure, support, metal–support interactions, and operational parameters (residence time, temperature, and pressure). Due to electronic and geometric constraints, the formation of CH$_x$ fragments via CH$_4$ dissociation is structure sensitive (Bradford, 2000) and it is believed that the resultant CH$_x$ surface species typically occupy an adsorption site which completes carbon tetravalency (Bradford and Vannice, 1999). This structure sensitivity has also been shown by dramatic increase in CH$_4$ dehydrogenation over Pt nanoparticles in comparison with extended Pt surfaces (Viñes et al., 2010). This has been explained by the presence of low-coordinated sites, such as edge, corner, and nearby sites on nanoparticles which significantly facilitate the conversion by reducing the energy barriers of every reaction step and stabilize the reaction intermediates. Also, the same reasoning was given for higher turnover rates of CH$_4$ decomposition over smaller Pt clusters that contain more coordinative unsaturated surface Pt atoms than the catalyst samples with lower dispersion (i.e bigger crystallites, Wei and Iglesia, 2004).
Nanocrystals are thermodynamically unstable, and, therefore, need to be stabilized by dispersing them on a support (Barkhuizen et al., 2006). Depositing metals on a support not only requires spreading expensive material and providing necessary mechanical strength but also provides certain geometric (increased surface area and optimization of porosity, crystal and particle size) and chemical functions (improvement of activity, minimization of sintering and poisoning, as well as the effect of spillover, Murzin and Salmi, 2005). Whether the oxide catalyst support is inert or actively participates in the activation of either methane or carbon dioxide is strongly affected by its acidic, basic or redox properties (Ferreira-Aparicio et al., 2000; Fan et al., 2009), which in turn affect the reaction mechanism. In the case of the acidic oxide supports, the CO\textsubscript{2} activation step can take place on active metal sites, but aging due to graphitization of these active sites affects the mechanism. In the case of basic oxides, the support itself, in the vicinity of the metal particle at the metal-support interface, can play a significant role in the reaction (Ferreira-Aparicio et al., 2000; Fan et al., 2009). Under reaction conditions of CO\textsubscript{2} and CH\textsubscript{4}, the mobility of the adsorbed species from the metal active sites to the support and vice versa can be considerable (Ferreira-Aparicio et al., 2000). Furthermore, the nature of the active sites can be strongly affected by the metal-support interaction, especially when noble metal is supported on reducible metal oxides such as CeO\textsubscript{2}, TiO\textsubscript{2}, Nb\textsubscript{2}O\textsubscript{5} and La\textsubscript{2}O\textsubscript{3} (Barrabés et al., 2008).

Ceria is redox oxide support and has been used in a variety of applications in fields such as catalysis, electrochemistry and optics due to its unique properties. CeO\textsubscript{2} is adopted into three-way catalysts (TWCs) for reducing the emission of toxic pollutants (CO, NOx, and hydrocarbons) from automobile exhaust due to its high oxygen storage capacity and facile Ce\textsuperscript{4+}/Ce\textsuperscript{3+} redox cycle. The facile generation of oxygen vacancies forms interfacial active centers over which the reaction takes place (Tang et al., 2004). CeO\textsubscript{2} nanoparticles have significant impact not only due to their considerably small sizes and high surface areas but also due to the general improvements in their material properties with respect to their
microsized or bulklike materials. It is well-known that both surface and bulk oxygen atoms can be utilized in the redox process for nanostructured CeO$_2$ materials, whereas for bulk powders, only surface atoms can be used. This redox property is strongly related to the CO$_2$ adsorption on ceria (Song et al., 2007). Furthermore, certain facets of ceria are more easily reducible than the others. Designing the structure of ceria support that could expose more of these reactive facets could potentially enhance CO$_2$ activation.

Besides actively participating in the CO$_2$ activation, ceria could also strongly affect the state of adsorbed carbon film upon CH$_4$ adsorption on the catalyst surface, through its interaction with Pt. There are no systematic investigations of the effect of ceria on the structure and distribution of adsorbed carbonaceous species at various operating conditions. So far published studies focused only on Pt supported on inert silica (Belgued et al., 1996a, b). Further studies are needed on the effect of ceria structure that might improve reactivity of adsorbed CH$_x$ species with CO$_2$ molecule and enhance selectivity towards desired oxygenates.

The selectivity and activities of Pt particles strongly depend on their sizes and shapes. Independent control of particle size and shape during catalyst preparation could result in the design of highly selective catalysts (Ahmadi et al., 1996; Wang et al., 1997; Lee et al., 2008; Chen et al., 2009). While the effect of Pt cluster size on CH$_4$ activation has been investigated before, there are no detailed studies of the effect of different cluster shapes. Wang et al. (1997) showed that Pt nanoparticles with cubic, tetrahedral and octahedral shapes contain numerous surface steps, edges and kinks which are expected to critically affect catalyst activity and selectivity. Due to several issues associated with these types of syntheses, achieving high yield of metal nanoclusters of desired shape is a challenging task but has been achieved, and a summary of all different shapes of Pt polyhedrons that have been accomplished is given.
in Chen et al. (2009). However, current shape and size-controlled preparation methods are complex and difficult to scale-up (Linic and Christopher, 2010). To obtain high quality shapes and highly dispersed Pt nanoparticles, various operating parameters (concentrations of the metal precursor and other reactants, pH, reducing time etc.) must be carefully adjusted. Furthermore, not only it is very important to maintain well defined shape and prevent sintering in the process of particle deposition on the appropriate support (Lee et al., 2008) but also to access their stability under reaction conditions. Those under-coordinated surface sites may not be the most thermodynamically stable ones, and under reaction conditions might reconstruct into more stable, lower energy structures (Linic and Christopher, 2010). There are no experimental studies of the effect of Pt nanocluster shape on the CH₄ activation yet.

Development of bifunctional catalyst for direct conversion of methane and carbon dioxide by carefully tailoring the structure of each active component has been the main goal of this work. The control of catalytic particles sizes and shapes so that their exhibit high concentration of highly active and selective surface sites not only can improve their selectivity but can also help illucidate the crucial factors that impact process selectivity and reaction mechanisms at a molecular scale (Linic and Christopher, 2010). Thorough literature review (Havrán et al., 2011) and theoretical findings of our collaborators (Cheng et al., 2012; Cheng et al., 2013) provided guidelines for the selection of specific structures of Pt supported on ceria which are chosen as a potential candidate. Cyclic catalytic operation in which methane and carbon dioxide are fed alternatively into the reactor has been suggested as a way of overcoming the thermodynamic limitations. State of the adsorbed carbonaceous species upon exposure to the methane flow can strongly affect the product distribution. It is hypothesized that the presence of more reactive hydrogen rich CHₓ species on the catalyst surface can improve selectivity toward certain oxygenates.
There are currently no reported studies of the effect of ceria support on the state of adsorbed carbonaceous film. Further investigations are needed to evaluate the influence of ceria as a supporting material, at different operating conditions, and compare its performance to the inert silica that has already been studied. Catalytic behavior of Pt/silica catalysts is also studied here for the comparison. There is strong scientific evidence that the shape-controlled catalytic synthesis, that can produce Pt nanoparticles rich in edge and corner sites and ceria support with exposed more easily reducible facets, would facilitate the development of the right catalyst for the envisioned process and is the preferred direction to follow. Not only that metal active center and the support can provide active centers for methane and carbon dioxide activation, but also, the metal-support interaction can significantly affect their performance.

1.2. Motivation for research

Possibilities for mitigation of carbon dioxide and methane levels in the atmosphere are of major global interest. One of the alternatives that attracts much scientific attention is their chemical utilization, which would enable us to close the carbon dioxide cycle. Both of these gases are major components of the natural gas and rapid and extensive shale gas development makes them abundant raw materials. The main issues in their direct conversion are the thermodynamic stability of both molecules and high energy requirements for most of their reactions. For this purpose transition metals deposited on metal oxide support have been studied extensively, but there is still no effective catalyst design that would bring these processes to industrial scale. Understanding of the mechanisms of molecular activation as well as of the reaction pathways over active centers on heterogeneous catalysts needs to be advanced.

The possibility of tailoring catalyst activities and selectivities through careful preparation methods could lead to the more efficient catalyst utilization. Using density functional theory (DFT) as a guideline to
determine the desired catalytic structure and composition from the first principles could provide a powerful tool for creating an integrated method for rational catalyst design. Although first principle simulations cannot yet replace traditional experimental screening and testing, their role and contribution in industrial heterogeneous catalytic reaction engineering will inevitably grow in the foreseeable future (Sabbe et al., 2012). Work of Professor Cynthia Lo and her student Zhuo Cheng (Cheng et al., 2012; 2013) with whom we have closely collaborated, has provided the theoretical background for selection of materials that are chosen for this study. It has been demonstrated that the presence of kinks, edges etc on metal active centers facilitates methane activation (Viñes et al., 2010). Metal particles deposited on different supports by common preparation methods are usually amorphous or round shape (“near spherical”). There are no systematic studies published on the effect of various metal clusters’ shapes (tetrahedral, octahedral etc.) containing numerous kinks and edges on methane activation and its reaction with CO\textsubscript{2}. In addition, there are no studies of the effect of support and operating conditions on the structure and reactivity of adsorbed carbonaceous species on the catalyst surface, formed during methane exposure.

Further investigation of factors that affect conversion and selectivity as well as the stability of deposited clusters is needed and should help in determining the key features required for catalyst design and process development and operation. An integrated method involving both experimental and modeling efforts could enable more rational design of new materials with improved activity and selectivity and could potentially cut the costs and duration of extensive “trial-and-error” approach commonly practiced in industry.
1.3. Research objectives

The main purpose of presented work is to develop a catalytic system that will enhance methane activation and its reaction with the carbon dioxide to obtain higher value products based on the guidelines provided by molecular modeling analysis. The goal is to advance the understanding of the mechanism and site requirements for methane activation on supported Pt catalysts as well as CO$_2$ reduction on different supports, within the available experimental and computational facilities. To meet this goal, the following objectives are set:

- Investigation of the effect of different operational factors (temperature, CH$_4$ partial pressure) and support (ceria vs. silica) on the amount of chemisorbed methane and on the structure and reactivity of adsorbed carbonaceous species formed upon methane chemisorption

- Synthesis and characterization of catalyst samples with well-defined shapes that have been chosen on the basis of molecular modeling studies as potential candidates that might enhance methane activation and carbon dioxide reduction

- Investigation of the effect of Pt nanocluster shapes supported on silica and ceria on methane activation at different temperatures

Taking into account that methane chemisorption is considered to be one of the limiting steps in the process of direct conversion with carbon dioxide, successful catalyst design realized without the understanding of the mechanisms involved in the activation of methane. The work presented in this thesis focus mainly on this part of the process –methane activation. Due to time constraints, no experiments were performed to study the actual reaction with the carbon dioxide and investigate the selectivity towards different oxygenates. However, in the light of the overall objective, recommendations of molecular modeling analysis for the structure of possible catalysts for CO$_2$
activation are included in the Chapter 2, as well as the experimental results of preparation of those samples. Finally, results presented here should contribute to the development of an integrated approach in the catalyst design involving both experimental and theoretical aspects of the studied heterogeneous catalytic reaction.

1.4. Thesis outline

The structure of this thesis is following:

Chapter 1 emphasizes the importance of studying the possibilities for chemical conversion of methane and carbon dioxide and, also, the significance of developing an integrated experimental and theoretical approach in rational catalyst design. This chapter summarizes the main objectives and motivation for this work.

Chapter 2 gives a brief literature review on the processes that have been studied so far that involve direct utilization of methane and carbon dioxide, catalyst design requirements for their catalytic conversion and highlights molecular modeling studies related to chosen reactants and catalysts, further outlining the main guidelines for this work.

Chapter 3 explains, in detail, preparation methods that have been used for synthesis of shaped Pt nanoclusters supported on silica and ceria supports, techniques used for characterization of prepared samples, experimental set up (packed bed reactor) used for testing of the samples, and operating conditions of the gas chromatograph used for product analysis.
Chapter 4 reports the investigation of the support effect and the effect of operating conditions (temperature, CH₄ partial pressure, Pt content) on the amounts of chemisorbed methane and on the structure of the adsorbed carbonaceous species during the short (1 min) exposure of the catalyst to the methane flow. This chapter indicates the conditions that result in the highest amounts of chemisorbed methane and that yield the most of the reactive carbonaceous species.

Chapter 5 discusses the effect of Pt nanocluster shape on methane activation. Catalysts activity is evaluated by comparison of the amounts of H₂ that evolve during catalyst exposure to methane flow at different temperatures. This chapter shows whether hemispherical (traditional) or tetrahedral Pt nanoparticles result in higher H₂ evolution and therefore enhance methane activation.

Chapter 6 presents the conclusions and recommendations for future work related to the catalyst development for methane conversion.
2. Review of possibilities for catalytic conversion of CH₄ and CO₂

2.1. Methane and carbon dioxide conversion to higher value products

The abundance of methane and carbon dioxide, especially in the form of natural gas, creates a potential for their use as starting materials in chemical synthesis. Developing a process that would directly convert these two gases into liquefied value added products would significantly decrease the high cost of gas transportation from remote areas and also allow skipping the energy intensive syngas production step involved in dry reforming process. Despite great scientific attention to this issue, no breakthrough technology has emerged so far.

The methane molecule is very stable and symmetrical, without any functional group, magnetic moment or polar distribution that would assist chemical attacks and enhance its reactivity (Holmen, 2009). It has a tetrahedral geometry with four equivalent C-H bonds which are very strong - 434 kJ/mol. The activation of this C-H bond requires high temperatures, at which free radical reactions in the gas phase are dominating (Holmen, 2009). Most of the reactions involving methane are thermodynamically unfavorable. Besides the large amounts of energy that is necessary, a suitable catalyst that would decrease the activation energy (Yuliati and Yoshida, 2008) and help overcome reaction potential energy barrier limits has yet to be developed. Since it is difficult to avoid unselective breaking of all four C-H bonds and complete oxidation (Rostrup-Nielsen, 1994), the key issue with the direct conversion of methane is related to selectivity rather than reactivity (Holmen, 2009). Such controlled CH₄ dehydrogenation again requires catalysts and proper understanding of pathways on catalytic surfaces. Despite the considerable research effort in this area, no readily applicable solution has emerged that results in satisfactory yields and/or selectivities. Main routes for methane utilization, its reforming, partial oxidation to syngas, and oxidative and un-oxidative dehydrogenation, have been extensively
reviewed in the literature (Fox, 1993; Crabtree, 1995; Bradford and Vannice, 1999; Lunsford, 2000; Otsuka and Wang, 2001; Yuliati and Yoshida, 2008; Holmen, 2009; Hammond et al., 2012).

Despite the large number of known processes for synthesis of chemicals from carbon dioxide, only a few are actually implemented on a large scale (Aresta, 2003). In chemical manufacturing, the current largest use of CO$_2$ is in the synthesis of urea, a widely used fertilizer, in the production of salicylic acid, which is found in pharmaceuticals, and in cyclic organic carbonates (Table 2). Carbon dioxide has also been used for refrigeration, beverage carbonation, dry cleaning, air conditioners, fire-extinguishers, separation techniques, water treatment, etc. As reported by the International Energy Agency (IEA, 2009), the total anthropogenic CO$_2$ emissions in 2007 were around 29 x 10$^9$ metric tons. The electricity and heat generation combined with transport have been the largest contributors of CO$_2$ creating almost two thirds of global emissions (Figure 2). According to IEA statistics, coal has been the dominant source for world electricity and heat generation at 41 %, while the share of natural gas was 23 %. 

Total amount of carbon dioxide used in industry is approximately 115 x 10$^6$ metric tons per year and major process are listed in Table 2 (Aresta and Dibenedetto, 2007, Ritter, 2007). Its utilization as a carrier fluid, where carbon dioxide is not chemically converted and can be recovered at the end, is estimated at 18 x 10$^6$ metric tons per year (Aresta and Dibenedetto, 2007). The energy needed during CO$_2$ chemical transformations produces large amounts of CO$_2$ and the resulting organic chemicals in which CO$_2$ is incorporated release CO$_2$ at the end (Dai et al., 2010). However, despite the fact that currently the use of CO$_2$ in the chemical industry cannot reduce significantly the global CO$_2$ levels, it is believed that the full potential of the fixation of CO$_2$ into the value added products has not yet been completely explored. Thus, the further development of industrial processes that are utilizing CO$_2$ for high demand products is of great importance (Ritter, 2007, Dai et al., 2010).
Figure 2. World CO₂ emissions by sector for 2007 (IEA, 2009)

Table 2. Use of CO₂ in the chemical industry (Aresta and Dibenedetto, 2007)

<table>
<thead>
<tr>
<th>Industrial processes that utilize CO₂ as raw material</th>
<th>Approximate amount of CO₂ used in the process per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>70 Mt</td>
</tr>
<tr>
<td>Inorganic carbonates and pigments</td>
<td>30 Mt</td>
</tr>
<tr>
<td>Methanol</td>
<td>6 Mt</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>20 kt</td>
</tr>
</tbody>
</table>

In Table 2, the synthesis of urea and salicylic acid are thermal processes, while other processes are catalytic. Environmental concerns as well as the recurring energy crisis have raised enormous scientific interest into this subject and plenty of literature has been devoted to the possibilities of CO₂ conversion (Song, 2002; Aresta, 2003; Centi and Perathoner, 2004; Song, 2006; Aresta and Dibenedetto, 2007; Sakakura, 2007; Centi and Siglinda, 2009) as well as the catalysis for CO₂ conversion (Krylov and Mamedov 1995, Ma et al., 2009; Raudaskoski et al., 2009). The molecule of carbon dioxide is characterized by significant thermodynamic stability. Its structure is linear with bond strength of 532
It’s Gibbs free energy of formation has large negative value ($\Delta G_f = -394.6$ kJ/mol) contributing to the high inertness of CO$_2$ and rendering its reactions energetically unfavorable. Besides requiring high energy inputs, the reduction reactions of CO$_2$ also need an effectively designed catalytic system that lowers the kinetic activation barriers. The review of the current most promising CO$_2$ reduction processes, as well as interactions of CO$_2$ with metal surfaces and its adsorption on metal oxides, has been presented in Aresta’s work (Aresta, 2003). Although much has been learned about the mechanisms of CO reduction, reaction pathways of the CO$_2$ molecule on heterogeneous catalysts still remains a great challenge.

As it has been mentioned earlier, methane and carbon dioxide are both components of the natural gas whose new reserves are being discovered rapidly in the United States. Process that would enable the conversion of natural gas into liquid fuels at the remote extraction sites would cut the extensive costs of gas transportation, as described earlier. One of the possibilities is dry reforming process that has received considerable attention.

It involves the reaction between carbon dioxide and methane in the production of syngas (1), which can be further used for making methanol (2) or Cn hydrocarbons (3):

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 &\rightarrow 2\text{H}_2 + 2\text{CO} & \Delta H_{298}^{\circ} = 247 \text{ kJ/mol} & \Delta G_{298}^{\circ} = 170.8 \text{ kJ/mol} \quad (1) \\
\text{CO} + 2\text{H}_2 &\rightarrow \text{CH}_3\text{OH} & \Delta H_{298}^{\circ} = -128.6 \text{kJ/mol} & \Delta G_{298}^{\circ} = -29.1 \text{kJ/mol} \quad (2) \\
n\text{CO} + 2n\text{H}_2 &\rightarrow (\text{CH}_2)n + n(\text{H}_2\text{O}) 
\end{align*}
\]

Publications dealing with various aspects of this reaction are numerous (Edwards and Maitra, 1995, Bradford and Vannice, 1999, Stagg-Williams, 2000, Hu and Ruckenstein, 2002, Chen et al., 2005, York et
al., 2007, Moon, 2008, Guo et al., 2009, Ma et al., 2009). Reaction (1) is limited by thermodynamics and even with the help of catalysts can take place only at high temperatures (> 730°C, Yuliati and Yoshida, 2008). The first step of this process involves a highly endothermic reaction ($\Delta H_{298} = 247$ kJ/mol) and the overall process may produce even more unwanted CO$_2$ via the water-gas shift reaction:

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298} = -41.1 \text{ kJ/mol} \quad \Delta G_{298}^0 = -28.6 \text{ kJ/mol} \quad (4)$$

Noble metals, such as Ru, Rh, Pd, Pt, Ir have been investigated extensively for the dry reforming reaction, but their high cost and limited availability hindered the commercialization of the process (Moon, 2008). Due to its fast turnover rates, long-term stability and lower cost, nickel-based catalyst has been considered as the most suitable (York et al., 2007). However, the nickel catalyst is prone to deactivation by carbon deposition. In order to realize the process at an industrial scale, an effective catalyst that minimizes the coke deposition should be developed. Recently, a Ni-Ce-ZrO$_2$ catalyst was reported to give high conversions of reactants (97%) and provide high resistance to catalyst deactivation but still required a high temperature of 800°C (Yuliati and Yoshida, 2008). Dry reforming suffers from the high energy requirements and inherent carbon deposition at such high temperatures, but it gives a lower ratio of H$_2$/CO suitable for the Fischer–Tropsch synthesis of long-chain hydrocarbons (Hu and Ruckenstein, 2002). Developing a process that would directly convert these two gases into liquid commodities would be a great advantage compared to indirect route of syngas synthesis.

### 2.1.1. Catalytic routes for direct reaction of CH$_4$ and CO$_2$

Both homogeneous as well as heterogeneous catalytic systems have been investigated for possible direct conversion of methane and carbon dioxide to oxygenates. Most studies, however, have been devoted to the low temperature production of acetic acid from methane and carbon dioxide. Currently,
Acetic acid is mainly produced from CH\textsubscript{4} through a multistep process, in which syngas and then methanol are produced first. The stoichiometry of the methanol carbonylation is the following:

\begin{equation}
\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}
\end{equation}

(5)

It is believed that the direct reaction of CH\textsubscript{4} and CO\textsubscript{2}, if made possible, would be a much more attractive way to produce acetic acid, decreasing the production costs as well as potential environmental risks of the indirect route (Huang et al., 2004; Ding et al., 2007):

\begin{equation}
\text{CO}_2 + \text{CH}_4 \leftrightarrow \text{CH}_3\text{COOH} \quad \Delta H^{\circ}_{298} = 36.4 \text{ kJ/mol} \quad \Delta G^{\circ}_{298} = 71.1 \text{ kJ/mol}
\end{equation}

(6)

Such direct conversion of CH\textsubscript{4} and CO\textsubscript{2} to acetic acid is an example of maximum atomic efficiency. If successfully accomplished, it would eliminate the need for the intermediate step of syngas production. However, due to large positive values of Gibbs free energy, the reaction is thermodynamically unfavorable, and effective ways of moving the equilibrium towards the production of acetic acid have yet to be found.

Several research groups (Huang et al., 2001; Wilcox et al., 2003; Huang et al., 2004; Ding et al., 2007) have investigated the different methods of acetic acid production by direct conversion of CH\textsubscript{4} and CO\textsubscript{2}. Only a few have investigated the use of homogeneous catalysts. Kurioka and co-workers (1995) first reported the formation of acetic acid from CH\textsubscript{4} and CO\textsubscript{2} in Pd(OAc)\textsubscript{2}/Cu(OAc)\textsubscript{2}/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/CF\textsubscript{3}COOH catalytic system. Later, Taniguchi et al. (1998) found that this reaction can proceed in an aqueous solution of a vanadium catalyst, VO(acetylacetonate)\textsubscript{2}, in which also oxidant peroxydisulfate (K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) and trifluoroacetic acid (CF\textsubscript{3}COOH) solvent were used. However, some studies indicated that the solvent is not inert in this reaction system at the given experimental conditions (Wilcox et al., 2003). Moreover, since trifluoroacetic acid is expensive and difficult to handle, it would be desirable to find a more
convenient solvent (Holmen, 2009). Similar findings were reported in the US patent No. 6960682 (Bell et al., 2005), in which acetic acid is produced by contacting methane and carbon dioxide at 85°C in a high pressure autoclave. The reaction took place in the presence of K₂S₂O₈ as an initiator and VO(acac)₂ as a catalyst, which were both dissolved in an anhydrous acid and corresponding anhydride. These authors also mention a 1924 British patent (226248GB) by Dreyfus, in which the synthesis of acetic acid from methane and carbon dioxide over nickel carbonate as a catalyst was described. Furthermore, patent WO96/05163 of Hoechst A.G. was also cited in which the catalyst used contained metals from VIA, VIIA and/or VIIIA group and high selectivities were claimed (70-95%).

Several studies of direct low-temperature conversion of CH₄-CO₂ on heterogeneous catalysts have been reported (Huang et al., 2001; Wilcox et al., 2003; Huang et al., 2004; Ding et al., 2007). Huang et al. (2001) applied periodic operation of the catalyst as a new and promising way to overcome thermodynamic limitations in this reaction system. The catalyst used in their experiments was a copper-cobalt based catalyst, otherwise used for hydrogenation of CO₂. Experiments were run at different Cu/Co ratios, from 0.3 to 6, and at different temperatures (100-400°C). Different distribution of products was observed depending on whether the gases were fed alternatively, the reactor was swept with hydrogen between the cycles, no hydrogen sweep was applied, or the gases were introduced simultaneously (Table 3). Reported rates of formation of acetic and formic acids were 7-43 µmol/(gcat·h) and 6-25 µmol/(gcat·h), respectively. The temperature of 250°C and Cu/Co ratio of 5 were the optimum conditions for the production of acetic acid.
Table 3. Product selectivities as a result of different gas feed (Huang et al., 2001)

<table>
<thead>
<tr>
<th>Type of gas feed</th>
<th>CH₄ and CO₂ fed alternatively with H₂ sweeping between the cycles</th>
<th>CH₄ and CO₂ fed alternatively without H₂ sweeping between the cycles</th>
<th>CH₄ and CO₂ fed simultaneously</th>
</tr>
</thead>
</table>
| Product selectivity (%) | 48% C₁–C₄ alcohols
44% two cyclopentane derivatives
5.6% acetic acid etc. | 36% formic acid
28% acetic acid
21% methanol
5.5% methyl furan
3.4% cyclopentane derivative
2.4% butanone etc. | 68% formaldehyde
21% cyclopentane derivative
12% acetic acid etc. |

The same group continued their investigation by studying the reaction on a catalyst containing noble metals (Ding et al., 2007). The same step-wise approach was used, but this time on 1% and 2% Pd/SiO₂ and Rh/SiO₂ catalysts. Experiments were run isothermally at different temperatures from 170-400°C. The authors consider the methyl radical formation from methane and insertion of the CO₂ molecule into the intermediate as two steps that limit the overall process (Figure 3). The results showed that the best catalyst among those investigated is 2% Pd/SiO₂ at 200°C. Again, quantitative results were presented for the formation rates of acetic acid which ranged from 2.5-38 μmol/(gcat·h). It has been claimed that the good catalyst for this reaction should promote selective formation of methyl radicals and also should insert CO₂ readily. From that point of view, higher catalytic reactivity of Pd compared to Rh was not surprising. The dominant intermediate specie on the Pd surface is desirable CH₃ form whereas on Rh surface besides CH₃ there are also CH₂ groups (Ding et al., 2007).
Figure 3. Schematic presentation of step-wise conversion of CH₄ and CO₂ to acetic acid (Ding et al., 2007)

Table 4. Adsorption energies (eV) of CHₓ species with transition metals Ru, Rh and Pd (Ding et al., 2007)

<table>
<thead>
<tr>
<th>Species</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>-2.70</td>
<td>-2.58</td>
<td>-2.20</td>
</tr>
<tr>
<td>CH₂</td>
<td>-4.07</td>
<td>-3.77</td>
<td>-2.93</td>
</tr>
<tr>
<td>CH</td>
<td>-5.64</td>
<td>-5.45</td>
<td>-4.46</td>
</tr>
<tr>
<td>C</td>
<td>-5.51</td>
<td>-5.47</td>
<td>-4.47</td>
</tr>
</tbody>
</table>
Additionally, the adsorption energies of CH₄ species indicate that the second step, insertion of CO₂ molecule into the intermediate, is more favorable on the Pd surface (Table 4). Different energetic of CH₄ dehydrogenation over Pd and Rh metal clusters, as well as different adsorption strengths of CH₄ species, are responsible for differences in catalyst selectivities and therefore product distribution, by enabling controlled CH₄ dehydrogenation over Pd and formation of desirable active M-CH₃ species. Analysis of surface CH₄ species was strictly theoretical; there was no experimental evidence of structure and distribution of adsorbed carbon species on the catalyst surface.

Finding catalyst that could chemisorb CH₄ and yield more of these hydrogen reach carbonaceous species would be a direction for improved selectivity towards certain oxygenates and molecular modeling tools, such as DFT analysis, could provide guidance in the selection of successful materials. Ding et al. (2007) also found that, based on the maximum of H₂ evolution rates as a result of CH₄ chemisorption, best duration of the exposure to CH₄ flow is around 1 minute. During that time surface reaction has completed and CO₂ could be introduced.

Huang et al. (2004) also tried to introduce oxygen into the reaction and, in that way, overcome thermodynamic limits:

\[
\text{CH}_4 + 0.5\text{CO}_2 + 0.5\text{O}_2 \rightarrow 0.75\text{CH}_3\text{COOH} + 0.5\text{H}_2\text{O} \quad \Delta G^{°}_{298} = -146.89 \text{ kJ/mol} \quad (7)
\]

This time, they used V₂O₅-PdCl₂/Al₂O₃ as a catalyst. It was noticed that the catalyst activity increased with reaction time and the highest formation rates were around 30 μmol/(gcat·h) for given experimental conditions. Although these values are still low, no significant byproducts were observed. Wilcox et al. (2003) examined the synthesis of acetic acid by diffuse-reflectance FTIR when methane and
carbon dioxide were introduced as equimolar mixture over 5% Pd/carbon and 5% Pt/Al$_2$O$_3$ catalysts. During the temperature programmed reaction (from 100 to 400°C), the estimated yield of acetic acid was ca. 1.5·10$^{-6}$. Formation of acetic acid was observed only above 350°C for Pd/carbon catalyst and above 200°C for Pt/Al$_2$O$_3$ catalyst; no by-products were recorded. Very low yields were reported and no mechanism for possible reaction pathways was suggested.

2.1.2. Alternative methods for CH$_4$ and CO$_2$ direct conversion

Several papers published recently by the group of Eliasson (Liu et al., 2001, Zhang et al., 2001, Eliasson et al., 2002, Li et al., 2002, Zhang et al., 2002) raise attention to a novel and quite interesting technique of dielectric barrier discharges (Figure 4). It was mainly applied for production of syngas, but in one paper various distributions of products, including acetic acid and different alcohols, were examined as a function of variable feed conditions and different reactor configurations. As the authors claim, one of the main advantages of this reactor system is that reactions can be operated at low gas temperature and still achieve notably high methane conversion. The thermodynamic barrier has been overcome by formation of high energy electrons (10000°C-100000°C) that initiate the dissociation of reactant molecules. It has been assumed that the main mechanism is by free radical reactions. However, a more fundamental investigation is necessary because the reaction mechanism and kinetics are not yet fully understood.
One of alternative recent approaches to overcoming thermodynamic limitations of some unfavorable reactions at mild conditions is the use of UV photo energy. A description of possibilities for photo-catalytic conversion of methane can be found in Yuliati and Yoshida (2001). Shi et al. (2004) reported production of acetone from methane and CO\(_2\) over Cu/CdS-TiO\(_2\)/SiO\(_2\) catalyst. Despite significantly high selectivities (92.3% for acetone), conversion of methane was very low. Teramura et al. (2004) investigated the reduction of CO\(_2\) to CO in the presence of CH\(_4\) over MgO and ZrO\(_2\). It was reported that methane participated in the formation of surface acetate and formate. Resulting yields are still very low emphasizing the need for further improvement of the photo-catalytic system. The major hurdles for industrial application are the low yields and variable and intermittent nature of the solar light.

**Summary**

Considering possible future industrial production of higher value products by direct conversion of methane and carbon dioxide, it seems more desirable to develop a heterogeneous catalytic system that would enable acceptable yields and selectivity at lower temperatures (< 400°C). A detailed literature review (Havran et al., 2011) indicates that the development of an effective catalyst that would lower the kinetic barriers and enhance methane conversion (and its reaction with CO\(_2\)) still remains the most
challenging task. The review also showed that neither has a detailed mechanism has been suggested nor has the knowledge of what is actually happening on the surface of the catalyst significantly improved.

Periodic operation of the catalyst has been suggested as a way to overcome the thermodynamic barrier. In this step-wise process, catalyst would alternatively be exposed to the methane flow first and then to carbon dioxide flow, and so on in cycles. It has been found that the optimum duration of exposure to the methane flow is around 1 minute during which the surface reaction (methane dissociation to surface carbonaceous species) has been completed. Catalyst selectivity and product distribution depend on different energetic of CH₄ dehydrogenation over different metals and the structure of the resulting adsorbed carbonaceous species. Molecular modeling analysis could provide guidance for selecting materials that could enhance CH₄ chemisorption and yield more of hydrogen reach carbonaceous species (CHₓ) and hence improve selectivity towards certain oxygenates.

2.2. Structure and site requirements for catalytic activation of CH₄ and CO₂

2.2.1. Methane activation on Pt

The limiting step in methane reaction with carbon dioxide is the methane activation and successful catalyst design for direct conversion of these two gases cannot be realized without the understanding of the activation of methane and structural requirements of the catalytic active site that could possibly enhance it. It has been suggested that transition metal centers play a particularly important role in the controlled activation of the C-H bond of methane in both homogeneous and heterogeneous catalysis (Xu et al., 2003).

It has already been shown that various metals can chemisorb CH₄ at moderate temperature and decompose it to carbonaceous adspecies and hydrogen at higher temperatures (Belgued et al. 1996,
Martins et al., 2007). During methane activation on a metal surface, depending on the exposure temperature and duration, several events can take place: dissociative chemisorption with CH\textsubscript{3} and H ad-species; dissociative chemisorption with simultaneous H\textsubscript{2} gas evolution and the formation of CH\textsubscript{x} ad-species with lower H content; formation of surface or bulk carbide as well as dissolved interstitial carbon and three dimensional carbon deposits, differing in their morphologies and reactivity (Martins et al., 2007). It is believed that elemental carbon is favored at higher temperatures since the stability of CH\textsubscript{x} species is questionable above 130°C (Belgued et al., 1996). Generally, those different forms of carbon are referred to as C\textsubscript{α}, C\textsubscript{β} and unreactive graphitic C\textsubscript{γ} and can be distinguished by the temperature at which they react with H\textsubscript{2} (Xu et al., 2003). Finding conditions that result in the formation of more reactive CH\textsubscript{x} and carbon species, and avoiding formation of graphitic unreactive carbon, is of great importance in methane catalysis.

It has been suggested that CH\textsubscript{x} surface fragments tend to preferentially occupy adsorption sites that complete carbon tetravalency (Bradford and Vannice, 1999, Bradford, 2000). Bradford and Vannice (1999) described the multistep decomposition of methane on metal surfaces in the following way:

\[
\begin{align*}
\text{CH}_4 + 2\text{M} & \leftrightarrow \text{CH}_3\text{-M} + \text{H-M} \quad (8) \\
\text{CH}_3\text{-M} + 2\text{M} & \leftrightarrow \text{CH}_2\text{-M}_2 + \text{H-M} \quad (9) \\
\text{CH}_2\text{-M}_2 + 2\text{M} & \leftrightarrow \text{CH-M}_3 + \text{H-M} \quad (10) \\
\text{CH-M}_3 + 2\text{M} & \leftrightarrow \text{C-M}_4 + \text{H-M} \quad (11)
\end{align*}
\]

where M\textsubscript{n} represents an ensemble of n surface metal atoms. The above equations make the formation of CH\textsubscript{x} species structure sensitive. It has already been known that C-H bond activation in alkanes is structure sensitive on well defined surfaces; as well as that coordinatively unsaturated surface atoms
lead to higher methane sticking and dissociation rates than atoms on close-packed surfaces (Wei and Iglesia, 2004a). Wei and Iglesia (2004a, b, c) studied thoroughly the mechanism and site requirements for activation and chemical conversion of methane on noble metal - Pt, Ir, Rh, Ru clusters supported on various metal oxides (ZrO$_2$, γ-Al$_2$O$_3$, ZrO$_2$-CeO$_2$). The results of their investigation of the kinetics of three different reactions of methane (methane decomposition, methane reforming with H$_2$O and so called “dry reforming” – with CO$_2$) showed no significant difference between turnover rates, rate constants and activation energies for these three reactions. This kinetic insensitivity to co-reactants and the first order CH$_4$ kinetic rate dependence lead to the main conclusion that C-H bond activation is the only kinetically relevant step and that reactions of CO$_2$ or H$_2$O with methane derived chemisorbed carbon species are fast and kinetically irrelevant.

Furthermore, since methane turnover rates increased with increasing Pt dispersion, Wei and Iglesia (2004a) confirmed that coordinatively unsaturated Pt surface atoms, prevailing in small crystallites, are indeed more active than atoms on the low-index surfaces prevalent in larger crystallites. Those surface atoms with fewer Pt neighbors, by binding CH$_x$ and H species more strongly and by stabilizing the activated complexes involved in the formation of these intermediates, lower C-H bond activation energies (Wei and Iglesia, 2004). Results also showed that methane reaction rates depend only on the size of Pt clusters and not on the identity of the support, implying the irrelevance of the effect of the support on the overall methane reaction rates. Since their work showed that the only kinetically relevant step in all three reactions has been the C-H bond activation, activation of the co-reactant- CO$_2$ or H$_2$O over the support has not been considered an important issue. Additionally, of all investigated noble metals, Pt exhibits the highest activity for any cluster size used (Wei and Iglesia, 2004).
Rasko and Solymosi (1997, 1998) examined the reactivity of adsorbed CH₃ radicals, produced by the high temperature pyrolysis of azomethane, towards CO₂ on a Rh/SiO₂ and TiO₂ catalyst. Their results strongly support the idea that during the dry reforming of methane over supported Rh, the CH₃ fragments formed in the decomposition of methane do not decompose to carbon, but rather react with CO₂.

2.2.2. Carbon dioxide activation on ceria

As a well-known functional rare earth metal oxide, fluorite cubic structured ceria has been extensively studied and employed in various applications including solid-state fuel cells, catalysts, UV blockers and polishing materials. In three-way catalyst (TWCs), ceria acts as an oxygen buffer by absorbing and releasing oxygen through a fast Ce³⁺/Ce⁴⁺ cycles simultaneously promoting CO oxidation to CO₂ by engaging the lattice oxygen species (Tana et al., 2009). This unique ability of CeO₂ to absorb and release oxygen under fuel-lean and fuel-rich conditions is described by the oxygen storage capacity (OSC) and it is strongly related to the formation and migration of oxygen vacancies in ceria (Yang et al., 2004, Song et al., 2007, Tana et al., 2009). The presence of these vacancies and availability of quasi-free electrons in the non-stoichiometric materials were anticipated for the enhanced catalytic activity (Fierro, 2006). Oxygen vacancies can be formed on the oxide surface or in the bulk and can significantly affect the electronic and catalytic properties of the oxide (Yang et al., 2004). Both surface and bulk oxygen atoms could be utilized in the redox process for nanostructured materials, but for bulk powders only surface ones could be used (Mai et al., 2005).

It is generally accepted that the low temperature reduction (400 -550°C) is due to the removal of surface oxygen and the high-temperature reduction (above 700°C) is related to the oxygen species in bulk ceria (Tana et al., 2009). Several phenomena may occur during the surface reduction, such as release of surface carbonates, reduction of Ce⁴⁺ to Ce³⁺ and formation of bridging OH groups. It is considered that
the addition of Pt onto the ceria promotes the surface reduction step, most probably by reduction of Pt and spillover of hydrogen from the metal to the surface of the oxide that forms the bridging OH groups. (Barrabés et al., 2008)

It has been found that CO₂ activation on partially reduced CeO₂₋ₓ is possible through formation of carbonate, carboxylate, or bicarbonate, as well as direct dissociation of CO₂ on metal loaded ceria (Staudt et al., 2010). A strong relationship has been found between the adsorption behavior of CO₂ and the oxidations states of cerium at various temperatures (Song et al, 2007). However, there is a lot of ambiguity regarding the mechanism of this process and the literature mainly is focused on surface science approach. Accordingly, Staudt et al. (2010) have shown that partial reoxidation of CeO₂₋ₓ by CO₂ occurs even at room temperatures, in absence of any noble metal co-catalysts and in the absence of surface hydroxyl groups or water. Their experiments were performed under ultra-high vacuum on well-defined CeO₂₋ₓ thin film on Cu(111). Song et al. (2007) found in pulse experiments in a TAP reactor (at 10⁻²–10⁻³Pa) that CO₂ can be adsorbed on the oxidized ceria and Pt-Rh/CeO₂, at low temperatures forming a carbonate species. For samples reduced by H₂, CO₂ adsorption is strongly related to the reduced Ce³⁺ sites (O vacancies), and formed carbonate species are more thermally stable than those formed on the Ce⁴⁺ site - even at higher temperature of 500°C. Their experiments showed that the ceria support was exclusively responsible for the formation of carbon residuals. Reduction has been more easily achieved on Pt-Rh/ceria than on pure ceria due to the so-called H₂-spillover effect; H₂ is activated over the metal center at lower temperature and then migrates to the support to react with surface lattice oxygen of ceria (Song et al., 2007).

An important finding is the experimental confirmation that the adsorption of CO₂ is proportional to the amount of O vacancies on the reduced ceria samples. Determining structures of ceria support that are
more easily reducible and have higher OSC could lead to improving CO$_2$ activation under reducing conditions. It is considered that OSC is mainly dependent on the size of ceria particles and the morphology through exposed crystalline planes (Tana et al., 2009). Generally, ceria materials with smaller particle size and consequently higher specific surface area tend to have more crystal edges and corners which produce higher concentration of surface oxygen species. However, surface areas of samples are not stable under redox cycling and can decrease significantly after only one cycle (Zhou et al., 2005). For three low-index crystalline surfaces present in ceria fluorite cubic structure, it is well known that \{111\} has the lowest surface energy and is the most stable plane, whereas \{110\} and \{100\} are less stable (Yang et al., 2004; Mai et al., 2005; Zhou et al., 2005). Ceria nanoparticles are typically represented as octahedrons with eight \{111\} exposed planes or truncated octahedrons with eight \{111\} and six \{100\} planes (Figure 5). On the other hand, it has been shown that rod-shaped nanostructures, which predominantly expose less stable surfaces, typically four \{110\} and two \{100\}, as shown in Figure 5, exhibit higher OSC and enhanced reactivity despite the smaller specific surface area than that of nanoparticles (Mai et al., 2005; Zhou et al., 2005; Tana et al., 2009).

Moreover, experimentally determined OSC values of nanorods were up to two times greater than those calculated for specific surfaces, implying that oxygen storage takes place not only at the surface but also...
in the bulk and that \{100\}/\{110\} dominated structures significantly enhance the lattice oxygen migration from bulk to surface compared to \{111\}-dominated ones.

As already mentioned previously, the extent of CO$_2$ adsorption is strongly related to the ceria redox capability (Song et al., 2007). Therefore, utilizing structures that have higher OSC and can be reduced to a higher extent creating higher amounts of O vacancies could in that way lead to increase in the concentration of the active sites for CO$_2$ activation. Hence, by controlling the morphology of ceria nanostructures, redox properties could be significantly enhanced and ultimately reducibility and CO$_2$ adsorption facilitated. However, stability of these faceted nanostructures under reaction conditions would need to be considered.

**Summary**

Methane activation over metal centers has been described as dissociative chemisorptions resulting in H$_2$ evolution and adsorbed CH$_x$ species (where x=0, 1, 2 or 3) whose structure and reactivity depends on the nature of the metal, metal structure, support, metal–support interactions, and operational parameters. Above 130°C, dehydrogenation of CH$_x$ species becomes fast and that elemental carbon is more stable forming stronger bonds with the metal surface. Three forms of deposited carbon can exist on the metal surface: C$_\alpha$-reactive, mobile or chemisorbed carbon, C$_\beta$-surface amorphous carbon and C$_\gamma$-inactive, strongly bonded graphitic carbon (Amariglio et al., 1995). Methane chemisorptions is structure sensitive process. Low-coordinate Pt surface atoms with fewer Pt neighbors, by binding CH$_x$ and H species more strongly and by stabilizing these intermediates, lower C-H bond activation energies (Wei and Iglesia, 2004a). It has been found that CO$_2$ activation on partially reduced CeO$_{2-x}$ is possible through formation of carbonate, carboxylate, or bicarbonate, as well as direct dissociation of CO$_2$ on metal loaded ceria. O$^{3+}$ vacancies on reduced ceria act as active sites for CO$_2$ adsorption. Applying
faceted ceria structures that could be more easily reducible could enhance CO$_2$ activation under reducing conditions.

### 2.3. Theoretical considerations

#### 2.3.1. Density Functional Theory (DTF) in heterogeneous catalysis

Almost all heterogeneous catalysts used nowadays in industry were developed by trial-and-error experimental approaches (Yates and Johnson, 2007). However, developing concepts that are useful in understanding which properties determine the activity and selectivity of a catalyst and being able to use calculations to search for new catalyst would be a better approach to catalyst design (Norskov et al., 2011). In that sense, molecular modeling is becoming a powerful tool that helps to better understand the basic physics controlling the reaction rates on the catalyst and it can also provide information that cannot be readily obtained, or at all, from experiments (Yates and Johnson, 2007). An integrated method involving both experimental and modeling efforts could enable more rational design of new materials rather than costly and time consuming empirical methods.

Density functional theory (DFT) is used in heterogeneous catalysis to routinely study adsorption and reaction of molecules on metal surface; it can be used to compute adsorption energies, geometries, electronic properties, reaction pathways, transition states and activation energies for simple reactions on metal surfaces (Yates and Johnson, 2007). The main goal of quantum mechanical modeling is to compute the relevant physical properties of systems containing many atoms by solving the Schrodinger equation, which cannot be solved analytically for any system containing three or more particles. Quantum mechanical approaches, which determine the electronic structure based on wave functions, have very high computational costs that prevent their use in heterogeneous catalysis. Instead of solving the Schrodinger equation to find the high-dimensional wave function of the system, DTF takes the
approach of solving “an approximate equation exactly” without loss of relevant information. It uses different sets of equations that describe properties of atoms and/or molecules as a function of the three-dimensional electron density. The energy of the ground state is expressed as a function of the electron density.

As discussed in detail in Sabbe et al. (2012) and illustrated in Figure 6, there are currently three main first-principles approaches to model the catalyst at the atomic level: cluster approaches, embedded cluster approaches and periodic models.

Cluster approaches are fast, useful for covalently bound surfaces and very well suited to describe finite atomic clusters in nanocatalysis. Embedded clusters lessen the edge effects and are applied for studying ideal and defective ionic surfaces and supported finite clusters as well. Periodic slabs within supercell geometries, model infinitely extended surfaces and, by reliably capturing delocalized metallic bonding, facilitate metal surface calculations. Computational parameters, such as the number of atoms in a cluster model, the number of slab layers or the “vacuum thickness” in periodic models, all strongly affect the simulation results. A real-world catalyst under working conditions is far from ideal defect-free
surfaces or regular structures. To accurately describe the real catalysts these models should take into account surface defects, multifaceted surfaces (including possible structure sensitivity of the reaction), support effects on the active phase, possible spillover effects, catalytically acting supports, the presence of dopant atoms and additives, and surface restructuring (Sabbe et al., 2012). In current computational practice, usually only one of these aspects is assumed to be the most relevant for the given system and is included into the study.

At present, in majority of computational studies the effects of catalytic support are completely ignored (Yates and Johnson, 2007; Sabbe et al., 2012). Interaction of the catalytic particle with the support can strongly influence its bonding properties due to charge transfer or strain effects (Sabbe et al., 2012). Current models that involve the support effect employ either several layers of the active phase or finite clusters deposited on a periodically modeled support. Although the first approach requires only small unit cells, its results may strongly be affected by a strain caused by the lattice mismatch between active phase and the support, as well as electrostatic effect between periodic images. The cluster-on-periodic support approach allows for a full relaxation of the catalyst structure. However, in order to prevent false interactions between the cluster and its periodic images, large surface unit cell models are necessary. Due to these computational costs, only very small sub-nanometer metal clusters containing less than 15 atoms can be modeled. The issue that arises is that such clusters often have very different catalytic properties compared to larger nanoparticles.

Big challenges in obtaining accurate electronic energies are spurious electron delocalization due to self-interaction error, which can cause underestimation of band gaps and reaction barriers and the lack of van der Waals (vdW) interactions (Sabbe et al., 2012). One more important limitation of DFT is that the reaction rates, computed from DFT through transition state theory, are usually not very accurate when
compared with experimentally measured rates (Yates and Johnson, 2007). Relative reactivities between different catalysts can, on the other hand, be predicted with good accuracy. In that way, DFT can be used for evaluation of different materials, finding trends in their performance and consequently provide guidance in the catalyst selection.

In order to define the right model for the catalytic system of interest, accurate knowledge of the catalyst structure and composition under reaction conditions is critical (Norskov et al., 2011; Sabbe et al., 2012). This is where novel in situ/in operando spectroscopy methods can provide significant insights at atomic scale as input to the first principle modeling. Performing the first-principles studies on the wrong surface models will neither give the right information nor advance the understanding of the real system. An integrated approach between molecular modeling and refined experimentation can lead to improved mechanistic insights into the reaction pathways, structure-reactivity dependencies, and, consequently, to a rational design of novel catalysts with improved activity, selectivity and durability as opposed to commonly used “trial-and error” approach.

2.3.2. CH₄ adsorption on unsupported Pt clusters

Viñes et al. (2010) emphasized the critical role of edge and corner sites of Pt nanoparticles in methane activation (Figure 7). Results of their DFT calculations as well as experimental observations showed that the usage of Pt nanoparticles (Pt₇₉ clusters) instead of Pt surfaces (111) significantly facilitated the kinetics of methane dehydrogenation. They also explained this behavior by the presence of low-coordinated sites (edge, corner and nearby sites) in Pt nanoparticles, whose role is to reduce the energy barriers of individual reaction steps and stabilize the reaction intermediates.
Viñes et al. (2010) experimentally confirmed their theoretical predictions by investigating methane decomposition on Pt nanoparticles supported on an ordered CeO$_2$ film on Cu (111) and comparing their observations with previous experiments on Pt (111). It was shown that on supported Pt nanoparticles dehydrogenation of CH$_3$ to CH and C species already takes place at -$153^\circ$C while on the Pt (111) surface CH$_3$ species remains stable up to -$33^\circ$C. This indicates that on the Pt nanoparticles, the activation barrier for dehydrogenation has been significantly reduced. One should point out that the decrease in activation barriers is bigger for Pt nanoparticles depending on their size than for Ni (111) surface when compared with Pt (111) surface! This brings forth a very important notion that the effect of particle-specific sites on the activation barriers might be substantially larger than the effect of choosing different transition metals (Viñes et al., 2010).

Cheng et al. (2012) studied the effect of Pt nanocluster shape on methane dehydrogenation by means of DFT and VASP software. They focused on two platinum clusters roughly 1 nanometer in diameter: a 21-atom hemisphere and a 20-atom tetrahedron (with exposed Pt (111) facets, Figure 8) and calculated the thermodynamics of all four carbon hydrogen bond scission steps in methane dehydrogenation to form a methyl group (CH$_3$), methylene (CH$_2$), methylidyne (CH), and carbon atom (C), successively. The
A hemispherical cluster is chosen to mimic the shape of a spherical cluster upon deposition onto a support, thus creating a flat interface. The tetrahedral nanocluster has higher percentage of edge and corner sites (Table 5), which were shown before to improve methane activation (Vinés et al, 2010). In order to isolate the effect of Pt nanocluster shape, their model didn’t include supports.

![Figure 8. Models for hemispherical Pt21 and tetrahedral Pt20 nanoclusters](image)

**Table 5. The statistics of surface atoms and sites (Van Hardeveld and Hartog, 1969)**

<table>
<thead>
<tr>
<th></th>
<th>Hemispherical cluster</th>
<th>Tetrahedral cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cluster size</td>
<td>~ 1 nm</td>
<td>~ 1 nm</td>
</tr>
<tr>
<td>Total number of atoms</td>
<td>21</td>
<td>20</td>
</tr>
<tr>
<td>Number of surface atoms</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>Percentage of edge and corner atoms in total number of atoms</td>
<td>57%</td>
<td>80%</td>
</tr>
<tr>
<td>Percentage of edge and corner atoms in total number of surface atoms</td>
<td>75%</td>
<td>84%</td>
</tr>
</tbody>
</table>
Their results showed that methane adsorbs more strongly on a tetrahedral cluster ($E_{\text{ads}} = -0.17$ eV or -16.7 kJ/mol) than on a hemispherical cluster ($E_{\text{ads}} = -0.10$ eV or -9.5 kJ/mol). CH$_4$ adsorbed preferentially to a vertex top site on the tetrahedron confirming the role of low-coordinated sites which favor Pt-C bond formation to donate excess electron density to the adsorbate. They furthermore located transition states and calculated the energies of activation by mapping out the minimum energy paths for each step of the dehydrogenation steps on both Pt nanoclusters. These results are depicted in Figures 9 and 10.

Figure 9. Schematic of methane dehydrogenation pathway on hemispherical Pt$_{21}$ nanocluster

Figure 10. Schematic of methane dehydrogenation pathway on tetrahedral Pt$_{20}$ nanocluster
Table 6. Comparison of the energies of activation (eV) for the successive dehydrogenation of methane on metal catalyst

<table>
<thead>
<tr>
<th>Dehydrogenation step</th>
<th>Hemisphere</th>
<th>Tetrahedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ → CH₃ + H</td>
<td>0.39</td>
<td>0.36</td>
</tr>
<tr>
<td>CH₃ → CH₂ + 2H</td>
<td>0.45</td>
<td>0.20</td>
</tr>
<tr>
<td>CH₂ → CH + 3H</td>
<td>0.59</td>
<td>0.71</td>
</tr>
<tr>
<td>CH → C + 4H</td>
<td>1.04</td>
<td>0.59</td>
</tr>
</tbody>
</table>

By comparing energies of activation summarized in Table 6, there is very little effect of the catalyst shape on the scission of the first C-H bond. However, the tetrahedral cluster lowers the energy of activation for the scission of the second C-H bond (lower by 0.25 eV). Furthermore, energy of activation for the scission of the third C-H bond on tetrahedron is much higher than on a hemisphere, which is attributed to the stability of methylene (CH₂) intermediate on the tetrahedron. This indicates that shaped catalysts might offer the possibility of selective C-H bond scission and affect the structure of the chemisorbed film of adsorbed CHₓ species on the catalyst surface.

2.3.3. CH₄ adsorption on supported Pt clusters of different shapes

Cheng et al. (2012) further investigated CH₄ adsorption and its dehydrogenation over Pt clusters supported onto two different oxides: silica and ceria. In reality, Pt nanoparticles are usually deposited onto a certain metal oxide support, which provides it with the mechanical and structural stability. However, sometimes certain supports can also participate in the chemical reactions by changing the electronic structure at the metal-metal oxide interface and in that way affect the catalytic activity and selectivity. As explained earlier, silica is commonly used non-active support, while ceria has received a
lot of attention due to its reducibility. Cheng et al. (2012) again considered two Pt nanocluster shapes – hemispherical and tetrahedral. Model supports were β-cristobalite (110) and ceria (110). β-cristobalite is chosen due to its structural similarity to the amorphous silica support commonly used in catalysis (as determined by neutron diffraction and these two phases have very similar densities and refractive indices). Although the ceria (111) surface is more thermodynamically stable, the (110) surface is more easily reducible and the presence of oxygen vacancies might affect its catalytic activity on CH$_4$ adsorption. Studies were done on both the stoichiometric and reduced (111) surface.

When compared with unsupported clusters no changes in the energies of adsorption for Pt clusters supported on β-silica are predicted. However, it was found that both stoichiometric (CeO$_2$) and reduced ceria (CeO$_{2-x}$) enhance methane adsorption and dehydrogenation. Moreover, the energetics of CH$_4$ dehydrogenation changed. The first C-H bond scission step is exothermic on unsupported clusters but slightly endothermic on supported clusters. When compared to the unsupported clusters, the energy barrier to activation decreases by approximately 0.06 eV for hemispherical Pt/CeO$_{2-x}$ and 0.12 eV for tetrahedral Pt/CeO$_{2-x}$. These results indicate that ceria (111) surface would be a better support than silica for CH$_4$ activation. When comparing the effect of supported cluster shape, CH$_4$ adsorbs more strongly on tetrahedral Pt clusters than on hemispherical for both supports (Figures 11 and 12). Cheng et al. (2012) proposed that the increased electron density at the low-coordinated Pt sites and oxygen vacancies at the metal-support interface, along with lower activation strain on the supported catalysts, all contribute to the enhanced catalytic activity.
Results on unsupported and supported Pt nanoclusters confirm the critical role of support structure and shape of noble metal cluster in catalytic methane activation and dehydrogenation.

2.3.4. CO$_2$ adsorption on reduced ceria

Cheng et al. (2013) further modeled possibilities for CO$_2$ adsorption on ceria support using DFT by exploring various adsorption sites and configurations for CO$_2$ molecule on stoichiometric and reduced CeO$_2$ (110). Ceria has been used in oxidation of CO molecule to CO$_2$ due to its ability to easily and reversibly convert between Ce$^{4+}$ and Ce$^{3+}$ upon release and storage of oxygen. On the other hand, oxygen vacancies, created under reducing conditions, might be the active sites for the opposite reaction: activation of CO$_2$ molecule and its reduction. As mentioned earlier in this chapter, ceria (110) is not the most thermodynamically stable surface of ceria, but creation of oxygen vacancies on its surface requires the least amount of energy.

Results of Cheng et al. (2013) showed that CO$_2$ adsorption on reduced CeO$_2$ (110), shown in Figure 14, is thermodynamically favored ($E_{\text{ads}} = -1.233$ eV) over the corresponding adsorption on stoichiometric CeO$_2$ (110) surface ($E_{\text{ads}} = -0.262$ eV) shown in Figure 13. A molecule of CO$_2$ adsorbs near the site of the oxygen vacancy on reduced (110) ceria surface forming a unidentate carbonate, as opposed to the bidentate carbonate found by other researchers for CO adsorption to stoichiometric CeO$_2$ [Cheng et al.,
These different intermediate species indicate that the oxidation of CO on ceria and the reduction of CO$_2$ are not the same processes happening from different sides. The first step in CO$_2$ activation is the charge transfer from reduced surface Ce$^{3+}$ ions to the adsorbate to form carbonate anion.

Previous studies pointed out the importance of the interaction between metal nanoparticle and ceria as support and the possibility of oxygen cycling between the support and the adsorbed CO$_2$ species. Mechanism of these interactions is still not clear and needs further investigation on a molecular level. The next step for DFT analysis of this process would be to set up the model for the activation of CO$_2$ at the interface of metal (Pt) nanoparticle with the ceria support.

2.3.5. Summary of DFT findings

DFT analysis (Vinés et al., 2010; Cheng et al., 2012) has confirmed that the role of undercoordinated edge and corner Pt active sites in methane activation is critical. Furthermore, Cheng et al. (2012) showed that the shape of the Pt nanocluster also plays an important role in CH$_4$ adsorption and that it may affect
the distribution of CH₄ species on the catalyst surface upon CH₄ dissociation by stabilizing specific intermediates. They also showed that model ceria surface (110) is a better support than silica model surface (β-cristobalite (110)) for CH₄ adsorption on supported Pt nanoclusters. Regarding CO₂ adsorption, their model points out the possibility for CO₂ activation on oxygen vacancies of reduced CeO₂ (110).

Models presented by Cheng et al. (2012, 2013) provided the guidelines for experimental work in this thesis. Synthesis of Pt nanoclusters of various shapes is not trivial but has been achieved previously (Chen et al., 2009). Model Pt nanoclusters are around 1 nm in size which is also not easy to make experimentally. Another issue is the stability of these clusters under reaction conditions and exposure to high temperature. Model supports used in DFT are flat surfaces which are not common in packed bed reactors at atmospheric pressure because they do not provide enough surface area to result in measurable catalyst activity (famous pressure-material gap). The models also do not take into account the effect of temperature or pressure. As illustrated in the Figures 2-7, modeling involves one gas molecule without taking into account its interactions with other surrounding gas molecules. To be comparable with the theoretical findings, experiments should be conducted under high vacuum conditions and using more advanced facilities that could detect changes happening at the molecular scale.

Despite these limitations, DFT analysis holds promise as a powerful tool in guiding the rational design of heterogeneous catalysts. It can indicate the structure of active sites that can enhance catalyst activity and selectivity and increase the understanding of the processes at the molecular scale.
2.4. Overall summary

Considering possible future industrial production of higher value products by direct conversion of methane and carbon dioxide, and carefully reviewing alternative processes for their utilization, it is concluded that developing a heterogeneous catalytic system that would enable acceptable yields and selectivity at lower temperatures (< 400°C) still remains very attractive but the most challenging task. The review also showed that neither has a detailed mechanism been suggested nor has the knowledge of what is actually happening on the surface of the catalyst significantly improved. Periodic operation in which the catalyst would first be exposed to methane flow and then to carbon dioxide flow has been suggested as a solution to overcome the thermodynamic limitations and also control the selectivities towards different oxygenates. It has been suggested that duration of exposure to the methane flow should be around 1 minute after what time carbon dioxide could be introduced to react with carbonaceous species remaining on the catalyst surface upon methane chemisorption.

Methane dissociative chemisorption results in H₂ evolution and adsorbed CHₓ species (where x=0, 1, 2 or 3) whose structure and reactivity depends on of metal structure, support, metal–support interactions, and operational parameters (residence time, temperature, and pressure). Optimizing catalyst structure and finding operating conditions that would yield higher amounts of more reactive hydrogen rich CHₓ species and in that way enable controlled CH₄ dehydrogenation, is critical in controlling the selectivity towards desired oxygenates. So far, studies of the structure of adsorbed carbonaceous film upon exposure to CH₄ flow have been dealing with various noble metals supported on inert supports such as silica. There are no studies of the CH₄ activation and the structure of the surface carbonaceous species over Pt supported on ceria. DFT analysis has also shown that ceria would be a better support than silica because it lowers the energy barrier for CH₄ activation. On the other hand, CO₂ adsorption is proportional to the concentration of the O³⁺ vacancies on the ceria support. Using ceria nanorods that
expose more easily reducible (110) and (100) facets, as a support for Pt nanoparticles, could help improve CO$_2$ activation under reducing conditions.

Methane activation is structure sensitive reaction and is facilitated by the presence of low-coordinated sites on transitional metal nanoclusters that reduce the energy barriers for breaking the C-H bond step and stabilize certain reaction intermediates (CH$_x$ species). Platinum has been shown to be very active in breaking the C-H bond but the high price limits its application. By rationally tailoring the structure of the Pt nanoparticles so that they contain higher fraction of low-coordinated sites, catalyst activity and its selectivity towards desired products could be significantly improved. In that way, more efficient utilization of the expensive catalytic materials could be achieved. DFT studies (Cheng et al., 2012) have also shown that controlling the shape of Pt nanoclusters could also lead to enhanced methane activation. Tetrahedral Pt nanocluster containing higher fraction of low coordinated Pt sites than the hemispherical Pt nanoclusters of the same size, adsorbs CH$_4$ more strongly. There are no experimental studies of CH$_4$ activation over supported tetrahedral Pt nanoclusters so far.

Further investigation is needed on how these shaped nanoparticles affect conversion and selectivities and in which way redox properties of ceria support can enhance CO$_2$ activation. Although there is no clear mechanism proposed, it is assumed that methyl radicals from methane and carbonate species from carbon dioxide would be desirable reactive intermediates for the synthesis of oxygenates (acetic acid, for example). Finding materials and operating conditions that would lower the barrier for methane activation, form higher amounts of more reactive hydrogen rich CH$_x$ species and prevent formation of the unreactive graphitic coke, is of critical importance. Thus, any new findings in this field would be a significant contribution for the development of scale-up methodology between theory and modeling on one hand and practical catalysis on the other hand.
3. Experimental

3.1. Shape controlled synthesis

3.1.1. Wet chemical preparation

Design and synthesis of highly reactive/selective catalysts has been a challenge in heterogeneous catalysis due to their unique shape-dependent material properties and their promising applications in catalysis, optoelectronics, microelectronics, magnetics, and biology. Controlling the nanoparticle size and shape is of great importance because achieving a high surface-to-volume ratio of nanomaterials would provide high amounts of active sites per metal mass and because of significant dependency of numerous catalytic reaction rates on metal surface characteristics. Consequently, making stable nanoparticles with adjusted crystallographic surface structure could result in enhanced activities and selectivities for desired products and could possibly bridge the “material gap” and “pressure gap” between single crystal studies and real catalytic systems (Jia and Schüth, 2011).

In general, colloidal metal particles can be prepared by two different ways: “top-down” method by subdividing bulk metal by physical methods or “bottom-up” approach by growing of particles starting from metal atoms in a gas phase or in a solution. Although large quantities of nanocrystals can be produced by physical methods, achieving nanoparticles’ uniformity and control of their size is very difficult (Jia and Schüth, 2011). On the other hand, uniform nanoparticles with controlled size and shape have been successfully fabricated by wet chemical synthesis.

Wet chemical preparation of nanoparticulate metal colloids, although a rather complex method, can be realized by various methods and the three most prevalent are chemical reduction of metal salts, electrochemical synthesis, or the controlled decomposition of metastable organometallic complexes (Bönnemann and Richards, 2001; Chen et al., 2009; Jia and Schüth, 2011). Various stabilizers (polymers,
surfactants etc.) are then used to control the growth of the initially formed nanoclusters and to prevent their agglomeration (Bönnemann and Richards, 2001; Jia and Schüth, 2011).

The first reproducible synthesis by chemical reduction of metal salt precursor was done by Turkevich and coworkers who proposed a mechanism for the stepwise formation of nanoparticles based on nucleation, growth and agglomeration (Figure 15, Bönnemann and Richards, 2001; Jia and Schüth, 2011). Now, this is the most common method for making metal nanoparticles, and can be described as:

\[ \text{xM}^{m+} + \text{nxe}^- + \text{stabilizer} \rightarrow \text{M}^n \text{ (cluster)} \]  \hspace{1cm} (12)
The reducing agent (hydrogen, alcohol, hydrazine or borohydride) is mixed with metal precursor salt in the presence of stabilizing agents (ligands, polymers or surfactants). According to the proposed mechanism, the formation of nanoclusters (Figure 15) starts with the reduction of the metal salt to zero-valent metal atoms. These metal atoms can collide in solution with metal ions, metal atoms, or clusters to form the “seed” of stable metal nuclei (Bönnemann and Richards, 2001). Strength of the metal-metal bonds as well as the difference between the redox potentials of the metal salt and the reducing agent applied strongly influence the size of these seed nuclei. Finally, in order to stabilize formed nanoparticles and to prevent their agglomeration, protective agents are added (Figure 16). The final size and shape of metal nanoparticles depend on many factors such as the type of reducing agent, metal precursor, solvent, concentration, temperature and reaction time (Jia and Schüth, 2011). Detailed review of the mechanisms and steps involved in wet chemical preparation has been given in Bonnemann and Richards (2001).

![Figure 16. Conformation model of PVP stabilization of metal nanoparticle, Jia and Schüth (2011)](image)

Chemical reduction synthesis can be performed not only in aqueous solution but also in organic phase using organically soluble reductants such as superhydride or alcohols. For example, nanoparticles of metals of platinum group have been prepared by reduction of metal salts with high boiling-point alcohols such as diols and ethylene glycol by method known as polyol process (Jia and Schüth, 2011). In
the traditional polyol process, polyvinyl pyrrolidone (PVP) is used as stabilizer and is considered to be an effective method in controlling particle size and distribution (Tang et al., 2004). Its modification, in which no stabilizing agents are used, has also had successful applications for the synthesis of Pt colloidal nanoparticles for supported catalyst (Tang et al., 2004; Zhou et al., 2005).

Since nanoparticles are thermodynamically and kinetically unstable in solution, stabilizing agents that adsorb onto their surface have to be used. Nanoparticle stabilization can happen through different mechanisms: electrostatic (where anionic and cationic remnants in solution form an electrical double layer around particles causing Coulombic repulsion that prevents agglomeration), steric stabilization (by adsorption of large molecules such as polymers or surfactants), or both – referred to as electrosteric stabilization (Figure 17, Jia and Schüth, 2011). Deposition of nanoparticles onto solid supports is also a means of stabilization. Stabilizers can be linear polymers, dendrimers, ligands, etc. The conformation model of polyvinyl-pyrolidone (PVP), linear polymer, stabilization of metal nanoparticles is shown in Figure 17.

![Figure 17. Electrostatic stabilization (top) and steric stabilization (bottom, Jia and Schüth, 2011)](image-url)
3.1.2. Controlling the size and shape of Pt nanoparticles

It has been considered that the size of metal nanoparticles can be regulated by varying the concentration of the polymer; higher polymer concentration causes better stabilization and hence smaller particles (Jia and Schüth, 2011). Size control is important in catalysis because it determines the fractions of atoms on the facets, on edges or corners strongly affecting catalyst activity and selectivity. Most of the conventional preparation methods result in spherical or amorphous shape of metal nanoparticles. Transitional metal nanoparticles of face-center cubic structure are usually represented as cuboctahedrons bounded by a mix of (111) and (100) facets as depicted in Figure 18.

Although challenging, the production of different shapes of metal nanocrystals (Figure 19) has been achieved by using various capping agents as well as by manipulating the reduction conditions (Chen et al., 2009). As can be observed from Figure 19, nanoparticles of different shapes expose different facets. These facets have different fractions of atoms located at corners and edges and exhibit different reactivity in a given reaction (Jia and Schüth, 2011).
In the case of metals with face-centered cubic crystal structures, commonly observed simple model systems are cubes, octahedrons and tetrahedrons which expose predominantly (111) or (100) facets. Variations in both type and concentration of the capping agent affect the surface energies and hence growth rates along different directions (e.g. (111) or (100)). In addition, different morphologies of Pt nanocrystals can be obtained by controlling the kinetics; fast reduction results in thermodynamically favored shape while at slower reduction a capping agent has more influence on the nanocrystal shape (Chen et al., 2009).

Ahmadi et al. (1996) achieved first shape-selective synthesis of f.c.c. Pt nanocubes and nanotetrahedrons by manipulating the concentration ratios between capping polymer, linear polyacrylate, and Pt cation. The stabilizer adsorption mechanism and concentration were believed to determine the final shape of nanoparticles. As shown in Figure 19, all planes of nanocubes are (100), while all four facets of nanotetrahedrons are (111). Ahmadi and coworkers (1996) found that the activity of different nanoparticles in electron transfer reaction increased with the increase in the percentage of
surface atoms at the corner and edge sites (35% for tetrahedrons, 13% for cubic, and 6% for truncated octahedron, Narayanan and El-Sayed, 2005). However, because of the high energy of these edge and corner sites, tetrahedrons and cubes changed their shape under reaction conditions into spherical nanoparticles. Control of the shape of Pt nanoparticles was also achieved by changing the reduction rate of Pt$^{4+}$ ions regardless of the capping agent (PAA or PVP, Jia and Schüth, 2011). Tetrahedral particles enclosed by four (111) planes with the lowest surface energies were dominant in the case of slow reduction by hydrogen, while faster reduction lead to formation of truncated octahedral nuclei.

To sum-up, the crucial factors in controlling both particle shape and size is the concentration ratio between the metal precursor and the capping agent (Lee et al., 2008), and additional factors such as pH and reducing time also must to be chosen carefully to obtain high-quality shapes and well dispersed particles. Colloidal metal nanoparticles in solution have been catalyzed by cross-coupling reactions, electron transfer, hydrogenations and oxidations (Jia and Schüth, 2011). All of these reactions occur at milder temperatures.

3.1.3. Deposition of nanoparticles on supports

Deposition of metal nanoparticles onto the support can be carried out through various methods and can be a challenging task since the desired dispersion must be maintained and the loss of well defined particle size and shape must be prevented. The precursor concept, in which the size, shape and composition of prepared colloidal metal nanoparticles can be tailored independently from the support, has these advantages over other methods such as salt-impregnation (Jia and Schüth, 2011).
In the precursor method, the support is dipped into organic or aqueous media containing the dispersed colloidal particles at room temperature to adsorb the prepared particles. This is followed by centrifugation or filtration, repeated washing and finally drying in air or vacuum. Lee et al. (2008) successfully produced tetrahedral and cubic colloidal Pt nanoparticles following the method of Ahmadi and coworkers (2006) and then deposited them on silica support through three different approaches: in situ reduction of H$_2$PtCl$_6$ in presence of support, in situ sol-gel synthesis of a support, and Pt colloid impregnation, as shown in Figure 20. According to their results this colloid deposition gave the best dispersion and kept the shaped of tetrahedral nanoparticles.

![Figure 20. Methodology used for the preparation of supported platinum catalysts with well defined particle shapes and sizes (Lee et al., 2008)](image)

After drying, catalysts are calcined in order to remove impurities and the capping agent and hence activate the catalyst. It has been observed that the capping agent not only stabilizes nanoparticles in the solution but can also block the active sites and, in that way, lower catalytic activity (Jia and Schüth, 2011). Most of the capping agent needs to be removed so that the catalyst doesn’t lose its activity, but on the other hand, calcinations at higher temperatures should be avoided. Lee et al. (2008) observed small changes in the particles’ shape already at 100°C, but the particles did not lose their original shape.
and became rounded until 300°C. Zhang et al. (2010) showed that the capping polymer PVP has a dual function: it stabilizes Pt colloidal nanoparticles by the coordination of Pt atoms with the N and O atoms of PVP, and it helps anchor these nanoparticles onto the ZnO nanowires through unbounded residual N and O atoms of PVP that coordinate with Zn$^{2+}$, as depicted in Figure 21. In the control experiment without any PVP, no Pt nanoparticles were introduced onto the surfaces of nanowires. The calcination step is important for two main reasons: removal of the linker PVP and fixing the nanoparticles onto the surfaces of ZnO nanowires. In samples that were not calcined at 400°C for 1 h, some particles dissociated from the nanowires.

![Figure 21. A schematic illustration of Pt nanoparticles-ZnO nanowires preparation (Zhang et al., 2010)](image)

In summary, mild immobilization methods and gentle calcinations temperatures are necessary in order to preserve metal particle’s shape and size. Consequently, well-shaped metal nanoparticles supported on metal oxides have been used mainly for reactions at milder temperatures. Tetrahedral and cubic Pt nanoparticles on silica support were tested by Lee et al. (2008) for promotion of carbon–carbon double bond cis-trans isomerization reactions in 2-butene at 100°C. After reaction, there was no significant surface reconstruction and particles preserved their shape. Yoo et al. (2003) tested truncated octahedral Pt nanoparticles supported on alumina for the hydrogenation of propene at 30-80°C and noticed that above 50°C high reactivity of surface atoms led to surface poisoning due to side reactions.
However, there are no studies in the literature that investigate well-shaped Pt nanoparticles on ceria support.

### 3.1.4. Preparation of faceted ceria nanorods

Ceria nanorods exposing more reactive \( \{110\} \) and \( \{100\} \) surfaces have been synthesized previously by simple hydrothermal method (Zhou et al., 2005; Tana et al., 2009) without the use of any surfactants. Usually \( \text{Ce(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) has been used as cerium resource, and it has been mixed with a precipitant such as \( \text{NaOH} \) (Mai et al., 2005; Zhou et al, 2005), \( \text{KOH} \) (Huang et al., 2005) or \( \text{Na}_3\text{PO}_4\cdot6\text{H}_2\text{O} \) (Yan et al., 2008). The mixture is then transferred into an autoclave, sealed and heated under autogeneous pressure. Although the exact mechanism of nanorod formation has not yet been clarified, key factors that have been shown to strongly affect the morphology of the product are the concentration of the mineralizer in the autoclave, hydrothermal temperature, and time (Mai et al., 2005). By tuning these parameters, the morphology evolution between the nanoparticles and nanorods has been achieved (Yan et al., 2008). The hydrothermal process has been governed by the dissolution/recrystallization mechanism as schematically described in Figure 22 (Mai et al., 2005). The increase in the base concentration and temperature caused the acceleration of dissolution/recrystallization process and formation of nanorods. In hydrothermal synthesis, where no templates or capping agents are being used, it is difficult for \( \text{CeO}_2 \) to grow anisotropically due to its isotropic structure (Mai et al., 2005).
Mai et al. (2005) suggested that the formation of anisotropic intermediate species - hexagonal Ce(OH)$_3$ facilitated the formation of the nanorods. After drying, white Ce(OH)$_3$ nanocrystals transformed into yellow CeO$_2$·nH$_2$O by oxidation in air without shape change. However, Huang et al. (2005) didn’t observe any hexagonal Ce(OH)$_3$ impurities, which is in agreement with the claim that Ce$^{3+}$ oxidation state is unstable as compared with the Ce$^{4+}$ oxidation state in alkaline solution and in the presence of air. They described the synthesis of CeO$_2$ nanorods by the following expressions:

\[
4\text{Ce}^{3+} + 12\text{OH}^- + \text{O}_2 + (4n-6)\text{H}_2\text{O} \rightarrow 4(\text{CeO}_2\cdot n\text{H}_2\text{O}) \quad (13)
\]

\[
\text{CeO}_2\cdot n\text{H}_2\text{O} \rightarrow \text{CeO}_2 + n\text{H}_2\text{O} \quad (14)
\]
where CeO$_2$·nH$_2$O are ceria nanoparticles. As they suggest, structure transformation from the polycrystalline CeO$_2$·1.1 H$_2$O nanoparticles to the single crystalline CeO$_2$ nanorods proceeds by Ostwald ripening in which larger crystallites grow at the expense of smaller dissolving crystallites. That the OH$^-$ concentration could be the key factor controlling the growth rate of different crystal faces and formation of nanorods is also confirmed in their studies.

In summary, by tuning base concentration and hydrothermal process temperatures, high purity nanorods exposing more reactive surfaces {110} and {100} and exhibiting higher OSC can be prepared. This enhanced redox capabilities are presumed to improve reducibility of ceria samples and facilitate CO$_2$ adsorption. Carbonate species formed by CO$_2$ activation on ceria would then readily react with methyl radicals from methane dissociation on Pt clusters.

### 3.2. Catalyst characterization techniques

#### 3.2.1. Pt nanoparticle size distribution - Transmission electron microscopy (TEM)

Electron microscopy is a widely used technique to determine the size and shape of supported particles. Transmission electron microscopy (TEM) uses an electron beam of high energy and high intensity to bombard the thin sample (Figure 23). The electrons are then either transmitted through atoms or backscattered. The attenuation depends on the density and the thickness of the sample (Chorkendorff and Niemantsverdriet, 2003). The scattering of electrons occurs as a result of the Coulomb interaction with the positively charged nucleus and with the negatively charged electron cloud and is proportional to the atomic number. A detector below the sample is used to detect transmitted electrons. In the resulting image, the areas of transmitted electrons are light in color and areas of backscatter are dark.
In general, detection of supported particles is possible if there is sufficient contrast between particles and support which may be an issue on highly dispersed supported oxides (Chorkendorff and Niemantsverdriet, 2003; Perkas et al., 2006). This method is also difficult to use on a system when both the active phase and the support contains atoms of high atomic number (Ryberg, 2010). It has been reported that it is difficult to observe precious metal particles on CeO2 containing support by TEM, since the dark CeO2 contrast makes the profile of precious metal particle obscure (Takeguchi et al., 2005; Perkas et al., 2006). Perkas et al. (2006) overcame this by using high resolution TEM (HRTEM). Also, analyzed samples must to have a thickness less than 200 nm (Wachs, 1992) so that the electron beam can penetrate the material. This places the limitation on the size of support particles that could be used in our experiments.

![Figure 23. Principle of TEM](image)

By analyzing a certain number of TEM images taken from different regions of the sample, particle size and shape distribution can be obtained. However, image analysis depends on the assumption that the size of the imaged particle is truly proportional to the size of the actual particle and that the detection
probability is the same for all particles, independent of their dimensions. (Chorkendorff and Niemantsverdriet, 2003)

Size and shape distribution of both colloidal and deposited metal nanoparticles have been determined by transmission electron microscope FEI Tecnai G² Spirit operated at 120 kV with line resolution of 0.2 nm. Samples containing ceria were very hard to analyze by regular TEM, and the size and shape of those Pt supported particles could not be determined by TEM. Other samples were first dissolved in distilled water, sonicated, and then a droplet of the solution was deposited on a Cu grid covered with carbon film for TEM analysis. Size and shape distribution were obtained based on measurements of at least 100 randomly chosen nanoparticles from several TEM images from various regions of the sample.

### 3.2.2. Temperature Programmed Reduction (TPR)

Temperature programmed techniques record the effect of linear increase of temperature on surface reactions while the catalyst is exposed to different gases. The principal reactions involve desorptions (TPD), reductions (TPR), oxidations (TPO) and surface reactions (TPSR). The response of the system to the continuous temperature increase is monitored either by measuring the consumed gas concentration (TPR/TPO); or the evolved gas concentration (TPD or TPSR). The temperature programmed reduction provides information about the reduction kinetics of metal oxides, while temperature programmed surface reaction provides insight in reaction kinetics and mechanisms of surface intermediates (Wachs, 1992). Quantities desorbed at specific temperature during TPD provide information about the number, strength and heterogeneity of the adsorption sites (Webb, 2003). TPD and TPSR employed in our studies are described in detail later in the Chapter 4.
TPR is a method used for studying reducible phases in a catalyst and their stability to reduction. Prior to performing the reduction analysis, the catalyst is degassed in an inert atmosphere to remove any adsorbed water or impurities that may interfere in the reduction analyses. After cooling down to room temperature, a reducing gas mixture, such as hydrogen diluted in an inert gas, flows over a sample at a slow temperature ramping rate (normally $\leq 10 \, ^\circ\text{C/min}$). Hydrogen consumption is detected by TCD (thermal conductivity detector). If there are several different oxides species present in the catalyst, there will be several reduction peaks at various temperatures that can be detected during the temperature ramp (Webb, 2003).

TPR analysis of our samples were performed by Quantachrome Instruments laboratory in order to find the temperatures at which catalyst samples are reduced so that all Pt ions from precursor Pt salt is converted to atomic Pt$^0$. Our samples were first degassed in helium flow at 200$^\circ\text{C}$ for 1 hour. Then TPR was performed by reducing the catalyst by 5% H$_2$ in argon flow of 50 ml/min at the heating rate of 10$^\circ$ C/min.

3.2.3. Pt dispersion – Chemisorption

Chemisorption is a simple and very informative characterization technique that involves measuring the quantity of gas required to form an adsorbed monolayer on a metal surface. Unlike the Brunauer-Emmet-Teller (BET) method for measuring surface areas, in which the gas is weakly and nonselectively adsorbed on all surfaces, here the adsorbed gas is chemically bonded to only the metal’s surface. Chemisorption is used to measure dispersion, which is defined as the ratio of the surface metal atoms to total metal atoms in a sample. It is very important to know what fraction of the active metal atoms is exposed because only those atoms participate in surface reaction. Catalyst is more efficient if it has higher dispersion and more exposed metal atoms (Quantachrome manual). Dispersion is determined as:
\[ D = \frac{N_m \cdot S \cdot M \cdot 100}{L} \]  

where \( M \) is the molecular weight of supported metal (gram of metal per mol), \( L \) is the metal percentage in the sample, \( S \) is the adsorption stoichiometry or the number of molecule of adsorbate per surface metal atom, and \( N_m \) is the amount of adsorbed gas (mol) per gram of sample. Multiplying the dispersion by 100 gives a value referred to as the percent exposed or percent dispersion. The number of total metal atoms can be determined based on the amount (weight loading) of metal in the sample. The number of surface atoms is calculated directly from the amount of adsorbed gas (\( N_m \)).

This method requires the knowledge of the conditions under which gases adsorb on metals with known stoichiometry. The most common gases used for determination of dispersion for supported Pt catalysts are \( \text{H}_2 \), \( \text{O}_2 \) and \( \text{CO} \). Hydrogen and oxygen dissociate on metals and are atomically adsorbed (Wachs, 1992). One potential issue is the hydrogen spillover onto the support of the catalyst when adsorbed hydrogen atoms migrate from the metal surface into the interstitial volume of the support and are replaced on the metal by more hydrogen adsorbed from the atmosphere surrounding the catalyst (Augustine, 1996). However, under standard chemisorptions conditions, during low temperature \( \text{H}_2 \) adsorption, the effect of spillover is avoided.

Knowing the exact stoichiometry of the adsorbed species with individual metal atoms on the catalyst surface is critical and sometimes cannot be easily determined (Augustine, 1996). Generally, a 1:1 \( \text{H}:\text{Pt} \) and \( \text{CO}:\text{Pt} \) is used for calculating the metal dispersion. However, difficulty with CO arises due to the formation of many different carbonyl species in their interaction with metal surface. Furthermore, for some metals, the adsorption stoichiometry for hydrogen and CO exceeds 1:1 for extremely small clusters because of multiple adsorption on the low-coordinated metal atoms that dominate the surface
The accuracy of CO chemisorptions measurement is the one most often questioned (Wachs, 1992).

The quantity of gas required to form a monolayer of chemisorbed gas on an active surface can be determined by a dynamic volumetric method (pulse method) or a static volumetric method. In both cases, catalyst samples first have to be cleaned from any contamination before the start of the analysis. The sample is heated; the metal is reduced in H₂, and then the sample is evacuated while still hot enough for the hydrogen to rapidly desorb from its metal surfaces. In the pulse technique, a known amount of catalyst is placed in a flow reactor under a stream of inert gas into which pulses of a known amount of adsorbing gas are injected. The thermal conductivity detector (TCD) at the exit of the reactor monitors the quantity of adsorbing gas that is not taken up by active metal. Pulses of adsorbing gas are injected until the sample is saturated. The chemisorption uptake of the sample is obtained by subtracting the total quantity of gas that was detected on TCD from a known injected quantity of gas from a series of pulses. (Wachs, 1992; Webb, 2003)

In the static volumetric method, the pressure of a known volume of gas is measured; then the gas is expanded into an evacuated known volume that contains the catalyst, and the pressure is measured again. Generally, several measurements are done with progressively increasing pressures up to 30 kPa. The measured uptakes define an isotherm curve that relates adsorbed quantity and pressure data at a constant temperature.

Some of the gas adsorbs weakly (reversibly) on the metals and support, so the catalyst is usually evacuated at the end of the first series of measurements, and the measurements are then repeated. Consequently, two isotherms are generated: one representing the total uptake of the gas which includes
both strongly and reversibly adsorbed hydrogen, and the other reflecting the amount of gas that was only weakly bonded to the surface. Subtracting the quantity reversibly adsorbed from the combined isotherm at each pressure yields an isotherm of irreversible adsorption. Finally, the monolayer uptake is determined by extrapolation of the linear part of this isotherm back to zero pressure.

Our samples were analyzed by static volumetric method in the Quantachrome lab on an Autosorb-1 instrument. Samples were first heated to 200°C at 10°C/min heating rate under helium flow to remove impurities. Pretreatment was continued by cooling down the sample to 40°C and then reducing it in H₂ flow while heating it back up to 400°C at the same heating rate. After keeping the samples at this temperature for two hours under H₂ flow, they were evacuated to remove adsorbed H₂ and cooled to 40°C. Isotherms were created at 40°C by measuring adsorbed volume at 10 increasing pressures in the range from 80 – 800 Torr.

Monolayer uptake is expressed in micromols of hydrogen per gram of sample; that is

\[ N_m = 44.61 \cdot V_m \] (16)

where \( N_m \) is \( \mu \text{mol/g} \) and \( V_m \) is in cc(STP)/g

Active metal surface area is determined as:

\[ SA = \frac{N_m \cdot S \cdot A_m}{166} \] (17)

where \( SA \) is in m² per gram of sample.
Average metal (crystallite) size can also be estimated from chemisorptions studies by assuming certain geometry (hemispherical, cubical or etc.) and that all particles have the same shape:

\[ d = \frac{100 \cdot L \cdot f}{SA \cdot \rho} \]  

(18)

where \( f \) is the particle shape factor (6 for hemispherical particles).

### 3.2.4. Pt loading

Elemental analysis of catalysts is another important characterization technique that is employed to investigate the composition of elements in the catalyst. The metal loading of each of the catalysts was determined by Inductively Coupled Plasma Spectroscopy (ICP) or X-ray photoemission spectroscopy (XRF).

#### 3.2.4.1. Inductively Coupled Plasma Spectroscopy (ICP-MS)

ICP-MS is a powerful technique for evaluating the composition of a material. The method uses inductively coupled plasma to ionize the samples that are subsequently analyzed by a mass spectrometer. There are five major parts of the instrument: the sample injection part, ICP part, interfacing, mass separation, and detection (Figure 24). The sample injection parts, designed to introduce liquids, are usually composed of a nebulizer and sample chamber. When solid samples need to be analyzed they have first to be digested into solution (in strong acid, for example) prior to the analysis. A radio frequency field causes collisions between the argon atoms generating high energy plasma, which instantaneously causes atomization and immediate ionization of the sample. The analyte ions are focused by a series of ion lenses into the quadrupole mass spectrometer, where they are
separated based on mass/charge ratio. A wide range of elements can be detected within ppt to ppm concentration levels.

Figure 24. Scheme of ICP

The metal loading of each of the catalyst was determined by an Agilent 7500ce ICP-MS. The platinum was removed from the support by refluxing a catalyst sample in Aqua Regia (HNO₃:HCl = 1:3) on a hot plate at 90°C for three hours (Wilcox, 2004). In the case of silica samples, it was apparent when all the metal was removed from the supports, as the color of the solid changed from black/grey to light yellow. All solutions were then diluted with DI water to 15 ml. In order to achieve acceptable concentration range for ICP analysis, solutions were diluted 100 times with 2% H₂NO₃ acid. The final solution then underwent the ICP testing. Final platinum loading was determined from ICP concentrations (in ppb) by following expression:

\[
Pt\, (\%) = \frac{c_{ICP} \left( \frac{\mu g}{L} \right) \cdot \frac{1 \, mg}{1000 \, \mu g} \cdot \frac{10 \, ml}{0.1 \, ml} \cdot V(ml) \cdot \frac{1 \, L}{1000 \, ml} \cdot 100\%}{m_{catalyst}(g) \cdot \frac{1000 \, mg}{1 \, g}}
\]  

(19)

where \(c_{ICP}\) is the ICP measurement of the concentration of Pt in the solution, \(\frac{\mu g}{L}\), \(V\) is the volume of initial solution, \(ml\), and \(m_{catalyst}\) is the mass of catalyst sample, \(g\).
The total error of ICP-MS analysis has to account for not only ICP instrument error but also errors associated with each operation: weighing (± 0.00002 g), dilution (± 1.25 ml) and pipetting (± 0.05 ml). For the ceria samples, not all of the solid powder turned yellow indicating that not all Pt was removed from the samples and that ICP measurements might be underestimating the real Pt content of original catalyst samples. Those liquid samples were also then analyzed by XRF.

3.2.4.2. X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) analysis is a method commonly used for determination of almost all elements present in a sample. When high energy photons, emitted from an X-ray source, irradiate a material, they induce ionization of inner shell electrons and create electron vacancies in inner shells (K, L, M). Fast transition of outer shell electrons into these vacancies (within 100 fs) causes the emission of characteristic X-ray fluorescence radiation. The family of characteristic X-rays from each element including all transitions serves as a fingerprint and allows the identification of the element. The fluorescent radiation is diffracted by a crystal at different angles to separate the X-ray wavelengths and therefore to identify the elements; concentrations are determined from the peak intensities (Wach, 1992). It is a very powerful technique that allows qualitative and quantitative analysis of all elements in an unknown sample with high precision and accuracy.

Our samples were analyzed at the Earth and Planetary Sciences Department at Washington University in St. Louis. Sample were finely ground with a mortar and pestle, and dried overnight at 115°C. The samples were diluted and mixed with reagent Al₂O₃ and CeO₂. Depending on the sample composition, the final proportions were 75% Al₂O₃, 25% CeO₂ or 67.5% Al₂O₃, 7.5% SiO₂, 25% CeO₂. The samples were then thoroughly mixed with 2.5% of an organic binder (polyvinyl pyrrolidone, applied in 10% methylene
chloride solution), and pressed into pellets at 110 Pa. Standards with similar compositions were prepared from reagent Al₂O₃ and CeO₂. A commercial atomic absorption standard solution (Alfa Aesar #88086) was added, and the samples were dried. The calibration was also checked with a platinum bar as a standard, with correction for X-ray absorption. The corrected background-subtracted intensities of the Pt Lα and Lβ peaks were analyzed with a Siemens SRS-300 spectrometer with a rhodium tube at 55kV; after correction for absorption, the intensities were plotted against concentration.

3.3. Reactor set up

The reactor set up is shown in Figure 25. All samples were tested in a U-shape, stainless steel, packed bed reactor of 4 mm i.d., 6 mm o.d. and 44 cm (18 in.) total length. 0.2 g of sample was packed between two pieces of quartz wool to prevent the catalyst powder from escaping. The flow of gases entering the reactor was controlled by two Brooks flow meters. Flow meters were first calibrated for specific gases by bubble flow meter Gilian Gilibrator-2. The gases used (N₂, H₂ and CH₄) were all ultra high purity grade (Airgas USA, LLC). Their preheating and homogeneous concentrations were achieved by passing them first through a coiled stainless steel tube (1/8” diameter) connected to the entrance of the reactor and placed together with the reactor in the furnace. The temperature of the cylindrical furnace was controlled by the temperature controller from Quantachrome Instruments. One K-type thermocouple was placed in the reactor with its tip touching the catalyst bed and the other thermocouple was in the furnace bottom. PID settings of the temperature controller for achieving a desired heating rate were determined by running the blank experiments without the catalyst with gas flowing through the reactor. Gasses exiting the reactor were sent to gas chromatograph SRI 8610C for separation and analysis. For methane chemisorption experiment (Chapter 4) two ball valves were placed before and after the reactor to stop the flow of methane. All experiments were carried out at atmospheric pressure.
3.4. Product analysis - Gas Chromatograph

An SRI 8610C gas chromatograph was used for analysis of the reaction products. Gases exiting the reactor were injected into the GC through the multiport gas valve, with two modes: “load” when sample gas is flowing through the sample loop, and “inject” when the sample from the sample loop carried by a carrier gas stream is injected into the GC column. The volume of the sampling loop was 1 ml. The sample is passed through the analytical column that separates molecules based on their strength of adsorption to the column packing. The gases used in the experiments that needed to be separated were CH₄, H₂ and N₂. The column used in experiments, which track H₂ evolution, described in Chapter 5, is HP Molesieve (Agilent, 30 m long x 0.53 mm diameter and 25 μm film thickness). The same column could be used in the experiments measuring CH₄ chemisorption because same gases were involved. However,
due to another unresolved issue (a ghost peak on FID signal), this column was replaced with stainless steel, Molesieve column (SRI Instruments, 0.91 m length, 0.32 cm thickness, 13x 80/100 molecular sieve). Upon exiting the column, the eluting components are directed to flow over detectors.

The instrument is equipped with two detectors connected in series: a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD was used for tracking H₂ and N₂ signals, while the FID was used for detection of the CH₄ signal. The TCD detector has the Wheatstone bridge with four tungsten-rhenium heated wire filaments. Two of the filaments are exposed to the carrier gas carrying the sample while the other two are exposed to the clean carrier gas. Differences in thermal conductivity between the sample and the reference gas disturb the balance of the bridge current and in that way create the actual chromatographic signal. The detection limit of the TCD detector is approximately 100 ppm (SRI Manual). The TCD detector block with filaments is placed within a temperature-controlled oven for high stability. Since our experiments required detection of H₂ concentration on the TCD, argon was used as a carrier gas instead of less expensive and more commonly used helium, which has very similar thermal conductivity as H₂ and, therefore, would impede the detection on the TCD. When using argon as a carrier gas, TCD filaments would burn more easily, and during the work had to be replaced a few times. For the same reason, the temperature of the TCD cell had to be lowered (100°C instead of 250°C). Also, the current for the TCD filaments was set to low. These are all very important details that one needs to pay attention to when using argon as a carrier gas.

The flame ionization detector (FID) can be used for detection of any molecule with a carbon-hydrogen bond, and it is widely used for general hydrocarbon analysis. After exiting the column and flowing over the TCD filaments, sample molecules are inserted and burned in the flame of hydrogen and air, which causes molecule ionization. Negative ions are then collected by a positively-charged collector electrode,
and the electrical current produced by the passing of each component is carried to the electrometer/amplifier for processing to the data system. Its detection limit is around 0.1 ppm and the response is linear (SRI manual). The ratio of air to hydrogen in the combustion mixture should be approximately 10:1 and can be adjusted using electronic pressure controllers. The FID’s response is stable from day to day, and, unlike other detectors, is not susceptible to contamination from dirty samples or column bleed. Our instrument has built-in air compressor. The current for the FID was set on high during the experiments. The standard GC operating conditions are shown in Table 7.

Table 7. Standard GC operating conditions

<p>| | |</p>
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of the oven</td>
<td>30°C</td>
</tr>
<tr>
<td>Flow of H₂ (FID)</td>
<td>30 ml/min</td>
</tr>
<tr>
<td>Flow of air (FID)</td>
<td>8 ml/min</td>
</tr>
<tr>
<td>Flow of carrier gas (Ar)</td>
<td>20 ml/min</td>
</tr>
<tr>
<td>Temperature of TCD cell</td>
<td>100°C</td>
</tr>
</tbody>
</table>

The main part of the GC is the separation column. Before experiment, operating conditions (carrier gas flows, temperature of oven) were tuned so that the optimal conditions are found (Table 7). In order to achieve complete separation of H₂, N₂ and CH₄ gases, a very low temperature of the oven had to be used. Velocity of the carrier gas also had to be increased so that all analyzed gases could come out of the column as fast as possible. Experiments required short analysis time so that several samples could be obtained within 15 minutes of exposure to CH₄. All gases were of ultrahigh purity and obtained from Airgas.
4. The role of metal-support interaction on methane activation

4.1. Introduction

Besides the development of new catalytic materials, in order to overcome the thermodynamic barrier in methane reaction with carbon dioxide, a suggestion has been made to do step-wise introduction of gases (Huang et al., 2001) by first exposing the catalyst to the methane flow and then introducing carbon dioxide to react with the adsorbed carbonaceous species as described earlier in Chapter 2.1.1. Their experiments have shown that different pretreatments and duration of exposure strongly affect the product distribution (Table 3 in Chapter 2). Differences in the selectivities achieved with various noble metals were attributed to the calculated adsorption energies of the resulting surface CH$_x$ species, their hydrogen content and reactivity with incorporated CO$_2$ molecule (Table 4 in Chapter 2). The structures of those adsorbed carbonaceous species have not been confirmed experimentally.

In methane pretreatment of the surface methane dissociatively chemisorbs over metal surface resulting in simultaneous H$_2$ evolution and adsorbed CH$_x$ species (where x=0, 1, 2 or 3) whose structure depends on the nature of the metal, its surface structure, support, metal–support interactions, and operational parameters (exposure time, temperature, and pressure). It has been reported that above 130°C, the dehydrogenation of CH$_x$ species becomes fast and that elemental carbon is more stable forming stronger bonds with the metal surface (Belgued et al., 1996a). Studies have shown that, depending on the temperature, three forms of deposited carbon can exist on the metal surface: C$_\alpha$-reactive, mobile or chemisorbed carbon, C$_\beta$-surface amorphous carbon and C$_\gamma$-inactive, strongly bonded graphitic carbon (Belgued et al., 1996a).
In reactions involving methane, it is of great importance to avoid formation of the inactive, graphitic carbon which causes catalyst deactivation. It is also believed that finding catalysts and operating conditions that would increase the concentration of hydrogen rich CH₅ species could improve catalyst’s selectivity towards certain oxygenates (CH₃ species for acetic acid, for example) (Huang et al., 2001). Accordingly, determining the structure and reactivity of these carbon species at the end of the methane adsorption step would be critical in comparing and finding the right materials and operating conditions for this process.

Belgued and al. (1996a,b) designed a two step experiment that provides an insight into the structure of adsorbed carbonaceous species after Pt/silica catalyst exposure to methane flow. Although their main goal was to investigate the conditions that can improve non-oxydative coupling of methane and C-C bond formation between neighboring CH₅ species, their findings are highly pertinent to our task too. Their protocol can be used to find the total amount of chemisorbed CH₄ at different conditions, study the state of the adsorbed layer after the CH₄ chemisorption step and determine the optimal operating conditions that would result in more reactive carbon species.

After exposure of the catalyst to methane flow, the reactor is closed, cooled to room temperature to prevent any further reaction, and then exposed to the inert gas flow during Temperature Programmed Desorption (TPD). During this step, there is back-formation of methane that involves the hydrogen bonded to the metal (Pt, Ru) surface or withdrawn from neighboring CₙHₙ ad-species (Pareja et al., 1998). Catalyst is again cooled to the room temperature and then hydrogenated with H₂ flow during Temperature Programmed Surface Reaction (TPSR). Since the shapes of TPD and TPSR profiles are very sensitive to the conditions of the exposure, they constitute a fingerprint of the carbon ad-species at the end of the adsorption step (Belgued et al., 1996a). Not only do these TPD and TPSR spectra give the total
amount of methane chemisorbed but they also indicate the reactivity of the adsorbed species and the strength of their bonding to the catalyst surface. Immediate exposure of carbonaceous species to the H₂ flow, without first exposing it to the flowing N₂, would cause coupling of the surface CₙHₙ species and formation of the longer hydrocarbons whose long analysis on gas chromatograph would hinder the whole process. That is the main reason for first exposing the catalyst to the nitrogen flow and splitting the analysis in two temperature programmed parts.

Amariglio’s group demonstrated that methane activation is possible over Pt/silica catalyst (EUROPT-1, Belgued et al. 1996a, b), Ru/SiO₂ (Amariglio et al., 1998) Rh-CeO₂/SiO₂ (Pareja et al., 1998) at moderate temperatures (150 – 320°C), although with low reactivity. Adsorption of methane was achieved at lower temperatures on Ru and Rh than on Pt (Pareja et al., 1998). For all catalysts studied, the increase in temperature and in duration of exposure to the CH₄ flow in the first step did not significantly affect the amount of CH₄ desorbed within TPD; they do cause the increase in the amount of CH₄ desorbed in TPSR and, hence, in the overall amount of chemisorbed CH₄. Higher CH₄ partial pressure in the first step also caused an overall increase in the total amount of chemisorbed CH₄ in the case of Pt catalyst. The amount of CH₄ desorbed during TPD is an indicator of the quantity of hydrogen that is available on the surface, bonded to the Pt after the adsorption step. Methane desorbed in TPD appeared in two main peaks at different temperatures for all investigated catalysts. However, the position of these peaks was different for each metal indicating differences in the bond strength. Both TPD desorption peaks occurred at lower temperatures on Pt metal than on Rh and Ru. The first peak has been attributed to the associative desorption of little dehydrogenated CH₄ adspecies and hydrogen – occurring at temperatures lower than 100°C. According to Belgued et al. (1996) the second peak is associated with the breaking of various C₂+ ad-species, and it occurred in the temperature range 160 – 250°C, depending on the metal and conditions of exposure. Differences between metals were also noticed in the TPSR profiles. In the case
of Pt, no more reactive C1 species remained after TPD, only some strongly H-deficient carbonaceous fragments stayed on the Pt surface. H-deficiency of these ad-species increased with the temperature and exposure time to CH₄ flow. All methane desorbed in one peak at 350°C, irrespective of the temperature of initial exposure. On the other hand, for both Ru and Rh they noticed a quick and immediate release of CH₄ at room temperature indicating the presence of fresh carbon deposits. They also noticed, for all investigated metals, the evolution of H₂ at temperatures above 100-150°C as well as C₂H₆ (at the order of magnitude lower rate than the rate of formation of H₂).

The maximum in H₂ evolution occurred within the first minute of exposure to CH₄ flow; the same as in the studies by Ding et al. (2007) who, based on those findings, recommended 1 minute as an optimal time for the exposure to the CH₄ flow in the cyclic operation of the catalyst.

Studying methane activation over three different Pt supported catalysts – silica, alumina and zirconia, Martins et al. (2007) did not notice any major effect of the supports. Hydrogenation of C ad-species was very difficult for all samples. However, they found that when Pt/silica and Pt/alumina were mixed with MoO₃, the hydrogenation of C ad-species was enhanced. The presence of MoO₃ improved the mobility of CH₄ ad-species, favoring the C-C nucleation and, as reported earlier, Mo suppressed the formation of nonreactive adsorbed graphitic layers during the dissociative adsorption of CH₄ (Martins et al., 2007). Mechanism for enhanced activity has not been explained; whether this effect is due to Mo or different bonding energies between oxygen and Mo, and oxygen and Si, Al, and Zr remains unclear.

It has been shown before that the activation of methane over Pt clusters is size sensitive (Eswaramoorthy et al., 2000). As described earlier in Chapter 2.2.1, coordinatively unsaturated Pt surface atoms, prevailing in small Pt crystallites, binding CH₄ and H species more strongly. They stabilize
the activated complexes involved in the formation of these intermediates, lower C-H bond activation energies\textsuperscript{10} and are consequently more active than atoms on the low-index surfaces prevalent in larger Pt crystallites. Eswaramoorthy et al. (2000) claim that methane, being a weak acid, will adsorb more favorably on electron-rich platinum. This is in accordance with the DFT analysis of CH\textsubscript{4} adsorption over Pt nanoclusters of different shapes supported on silica and ceria (Cheng et al., 2013). Cheng et al. (2013) proposed that increased electron density at the low-coordinated Pt sites and oxygen vacancies at the metal-support interface (present in Pt-ceria), along with lower activation strain on the supported catalysts, all contribute to the enhanced catalytic activity. In their study of H\textsubscript{2} production from natural gas (Odier et al., 2001) attributed the huge difference in the activity of Pt/silica and Pt/ceria to the large spillover of H\textsubscript{2} and carbonyls to ceria support that liberates the Pt sites for further methane activation. If no spillover of carbon to the support is possible, the Pt surface becomes quickly blocked by coke and no further methane activation takes place (Odier et al., 2001).

There have not been any thorough investigations of the state of the surface species after methane chemisorptions on ceria based catalysts. The identification of surface intermediates is an important step in determining the mechanism of a reaction and in developing an in-depth understanding of a catalytic process. Finding the optimal catalyst design and operating conditions that could increase the concentration of hydrogen rich CH\textsubscript{x} species and prevent formation of deactivating graphitic carbon and, in that way achieve controlled CH\textsubscript{4} dehydrogenation, could result in the improvement of the selectivity towards desired products (various oxygenates). Studying the effect of the catalyst structure (support, Pt loading), and the operating conditions (temperature, CH\textsubscript{4} partial pressure) on the amounts of chemisorbed CH\textsubscript{4} and on the structure and the reactivity of adsorbed carbonaceous film is of critical importance in advancing the knowledge about methane activation and rational catalyst design.
4.2. Experimental

4.2.1. Catalyst preparations

Supported Pt catalysts were prepared by incipient wetness method. Ceria support was synthesized by precipitation from Ce(NO$_3$)$_3$ x 6H$_2$O (Sigma-Aldrich) aqueous solution while adding NH$_3$xH$_2$O solution under vigorous stirring at 60$^\circ$C until the pH of the mixture was greater than 9. The precipitate was then aged in the mother liquid for 4 h and washed with DI water three times. The solid obtained by centrifugation was dried at 100$^\circ$C overnight and calcined at 450$^\circ$C for 4 h in air. Davicat SI 1301 (Grace Davison) was used as the bare silica support.

In the incipient wetness method of preparation, it was first necessary to determine the amount of solution needed to just wet the bare support. For 1 g of ceria powder it was 1 ml of DI water and for silica 3 ml of DI water. Accordingly, 0.02 g and 0.105 g of Pt(NH$_3$)$_4$(NO$_3$)$_2$ salt (Sigma-Aldrich) were dissolved in 1 ml (for ceria support) and 0.034 g for 3 ml (for silica) of DI water. Actual Pt content was determined by XRF. Samples were dried overnight at 100$^\circ$C.

4.2.2. Catalyst characterizations

The actual loading of the Pt on catalyst samples was determined using elemental chemical analysis on a Siemens SRS-300 X-ray fluorescence (XRF) spectrometer with a rhodium tube at 55 kV described in detail in Chapter 3. The specific surface area was determined by BET method, using N$_2$ adsorption measurements at liquid nitrogen temperature, using a Quantachrome Autosorb 1-C apparatus. Before analysis, the samples were degassed for 24 h at 100$^\circ$C in vacuum. Pt dispersion was determined by H$_2$ chemisorption at 40$^\circ$C and assuming stoichiometry of 2 (Pt:H$_2$ = 2) in Quantachrome Autosorb 1-C apparatus.
Temperature programmed reduction experiments were performed over preoxidized catalysts; around 200 mg of 1.7% Pt/ceria and 100 mg of 1.7% Pt/silica. Samples were first degassed under helium flow at 200°C for 1 h. Reduction was done under a flow of a 5% H₂/Ar mixture (50 ml/min) using a heating rate of 10°C/min. Both dispersion and TPR measurement were done by Quantachrome Instruments.

4.2.3. Apparatus

The catalyst samples (0.2 g) were sandwiched between quartz wool in the U-shape stainless steel packed bed reactor of 4 mm i.d., 6 mm o.d. and 44 cm total length. The gas flows were controlled by two Brooks flowmeters. The gases used were all ultra high purity N₂, H₂ and CH₄ (Airgas USA, LLC). The gases were preheated by flowing first through the stainless steel coiled tube (0.25 cm diameter) that was placed in the furnace together with the reactor and connected with it. Temperature of the catalyst bed was controlled by the temperature controller from Quantachrome Autosorb 1-C apparatus. A K-type thermocouple was placed in the reactor with its tip touching the catalyst bed. Gasses exiting the reactor were sent to gas chromatograph (SRI 8610C) equipped with stainless steel Molesieve column (0.91 m length, 0.32 cm thickness, 13x 80/100 molecular sieve) and two detectors, TCD and FID, connected in series. More experimental details are given in Chapter 3.

4.2.4. Procedures

4.2.4.1. Pretreatment of the catalyst

Each sample (0.2 g) was first exposed to N₂ flow (50 ml/min) up to 100°C at the heating rate of 6°C/min and then to H₂ flow (50 ml/min) up to 450°C at the same heating rate. Reduction was continued by keeping the sample at 450°C for 15 h under the same H₂ flow. Adsorbed H₂ was removed by a N₂ purge, and the sample was then cooled to the reaction temperature also under N₂ flow. The sample was then
exposed to CH₄ flow. Between the experimental runs, the sample was always heated up at the same rate to 100°C under N₂ flow (50 ml/min) and then H₂ flow (50 ml/min) up to 450°C, where it was kept for 30 min. This was enough to ensure there were no carbonaceous species on the surface before the new exposure to methane. The sample was always purged with N₂ to remove the adsorbed H₂ before the reaction step and exposure to CH₄ (Belgued et al., 1996a).

4.2.4.2. Determination of the amount of chemisorbed CH₄

The amount of chemisorbed CH₄ was determined by following a slightly modified protocol described in Belgued et al. (1996a). Catalyst is first exposed to the CH₄ flow of 200 ml/min for 1 minute, as that has been reported as optimal duration within which surface dissociation of CH₄ has been completed (Ding et al., 2007). After exposure of the catalyst sample to CH₄ flow, the reactor was closed and cooled in less than 1 min to around 15°C by immersing the reactor into the water with ice, and then purged of any remaining CH₄ in the reactor by introducing N₂ flow. In that way, CH₄ already present in the reactor (from the gas phase) can be distinguished from the methane formed by hydrogenation of carbonaceous species on the catalyst surface (Belgued et al., 1996a). If the catalyst is then exposed immediately to the H₂ flow, the formation of higher alkanes would hinder the product analysis. That is the reason that the catalyst was first exposed to N₂ flow (80 ml/min) under temperature ramp up to 300°C at heating rate of 6°C/min. It was kept at this temperature until the CH₄ signal on the GC dropped to the baseline. In that way, the most reactive carbonaceous species with the available hydrogen from the catalyst surface form CH₄, which then desorbs in the N₂ flow. After that, the reactor was again cooled to around 15°C and then exposed to H₂ (80 ml/min) for temperature programmed surface reaction (TPSR) at the same heating rate up to 450°C. Sample was kept at this temperature until there was no more CH₄ formation. Keeping the sample at the end of temperature programmed operations at constant temperature is the only
modification to the protocol of Belgued et al. (1996a). As described in their work (Belgued et al., 1996a) this procedure helps determine the state of carbonaceous species at the end of exposure to CH₄.

Integration of the peak that elutes from the GC column gives the concentration of the CH₄ in the exit flow from the reactor at that specific temperature (moment) during temperature programmed process. The integrated values of CH₄ when plotted over time form the curve that describes the release of CH₄ from the catalyst surface with respect to time (temperature ramp). The area under this curve gives the total amount of CH₄ desorbed over the whole temperature range (first during TPD and then TPSR). The sum of areas under these desorption curves (TPD and TPSR) corresponds to the total amount of chemisorbed CH₄.

The position of desorption peaks (temperature of maximum desorption) provides information on the bond strength of the desorption species. Presence of multiple peaks would indicate that there are carbonaceous species that are bonded with different strength. Hydrogen-rich carbonaceous species (CH₃, CH₂, CH) would desorb at lower temperatures (below 130°C) than different types of carbon (reactive α-carbon, β-carbon or graphitic γ-carbon). One of the major goals is to identify catalyst structure and operating conditions that give higher amounts of these more reactive carbonaceous species without forming unreactive graphitic carbon.

The investigated factors that might affect the distribution of surface species on the catalyst are: temperature, Pt loading, support and CH₄ partial pressure.
4.3. Results

4.3.1. Catalyst characterization

Specific surface area of ceria support, obtained by BET measurement, is 67.5 m$^2$/g, and specific surface of silica support is 320 m$^2$/g. Results of XRF measurement of Pt content and H$_2$ chemisorption measurement of Pt dispersion are shown in Table 8.

Table 8. Results of catalyst characterization

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pt content (% wt)</th>
<th>H$_2$ uptake (µmol/g)</th>
<th>Pt dispersion (%)</th>
<th>Pt size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/ceria</td>
<td>1.71</td>
<td>19.4</td>
<td>44.3</td>
<td>2.56</td>
</tr>
<tr>
<td>Pt/ceria</td>
<td>0.34</td>
<td>5.17</td>
<td>59.3</td>
<td>1.91</td>
</tr>
<tr>
<td>Pt/silica</td>
<td>1.75</td>
<td>18.6</td>
<td>42.8</td>
<td>2.65</td>
</tr>
<tr>
<td>Pt/silica</td>
<td>0.3</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

H$_2$ uptake was used to determine the amount of surface Pt atoms available on the sample assuming that 1 molecule of H$_2$ adsorbs on 2 Pt atoms. For 1.7% wt Pt/ceria it was 7.76 µmol/g and for 1.7% wt Pt/silica it is 7.45 µmol/g.

Assuming that all carbons are bonded to Pt atoms and that 1 C adsorbs on 1 Pt, adsorbed methane data are converted into corresponding surface coverages.

Results for TPR studies and corresponding H$_2$ consumption curves are shown in Figure 26. Comparison between the positions of the peak maxima of two curves indicates obvious differences in the nature of Pt species on the surface of these catalysts. The TPR curve corresponding to the 1.7% Pt/ceria (Figure 26) shows low temperature peak around 130°C, medium temperature peak at around 190°C and very broad high temperature peak above 700°C. Low temperature peak (< 150°C) is attributed to the reduction of the PtO$_x$ species formed during the pre-oxidation step (Panagiotopoulou et al., 2007). The
medium temperature peak, at around 200°C, has been attributed to reduction of ceria in the vicinity of Pt crystallites (Panagiotopoulou et al., 2007). The high, broad peak (> 700°C) is due to reduction of the bulk ceria (Panagiotopoulou et al., 2007, Barrabes et al., 2008).

Figure 26. TPR profile of 1.7% Pt/CeO₂ and 1.7% Pt/SiO₂ catalyst

TPR curve for 1.7% Pt/silica, presented in Figure 26, shows peaks around 170°C, 215°C, 260°C and broad peak around 410°C. All these multiple peaks can be attributed to the reduction of various oxidized Pt species to metallic Pt (Jiao and Regalbuto, 2008). Also, broader peaks can indicate a non-uniform size distribution of Pt nanoparticles (Jiao and Regalbuto, 2008).

It is generally considered that the reduction of bare ceria occurs in two stages: starting with the surface reduction of the outermost layer of Ce⁴⁺ (around 400 - 500°C) leading to the bulk reduction of the inner Ce⁴⁺ layers which begins at temperatures higher than 700°C (Barrabés et al., 2008). Addition of Pt onto
ceria support facilitates the surface shell reduction step and causes the shift of the first reduction peak to lower temperatures by reduction of Pt and H₂ spillover from the metal to the surface of ceria (Gaillard, 2004; Takeguchi et al., 2005), resulting in the formation of bridging OH groups (Barrabes, 2008). This interaction between ceria support and Pt nanoclusters is evident from Figure 26. The peak attributed to the reduction of ceria surrounding the Pt, at around 200°C, is significant and is order of magnitude bigger than the peak on silica (at 215°C) that corresponds to the reduction of oxidized Pt species. Therefore, the existence of strong metal-support interaction is evident, and the results of studies of its role in the CH₄ activation are discussed next.

4.3.2. Studies in packed bed reactor

Results below illustrate the effects of different operating conditions, as well as the catalyst support, on the methane chemisorption. In all performed experiments only CH₄ is detected; no other species have been observed. If any coupling of CHₓ species on the catalyst surface occurred it was below detection limits of our FID detector.

4.3.2.1. Effect of temperature

From desorption peaks shown in Figure 27, it can be seen that the initial temperature of methane adsorption does not have significant effect on the amount of methane desorbed during TPD. The least amount of methane desorbed for reaction at 200°C, and the highest amount at 300°C. Since at this step, only N₂ is introduced, these desorbed amounts of CH₄ are an indication of the amounts of hydrogen available at the catalyst surface after 1 min exposure to the CH₄. Peaks for reactions at 200°C and 300°C are located at slightly lower temperatures (around 270°C and 290°C respectively) compared to the other peaks (around 300°C). This shows that hydrogenaceous carbon species formed during reaction at lower
temperatures (200°C, 300°C) bonded less strongly to the catalyst surface than those carbonaceous species formed at higher temperatures. Multiple peaks are present only for reaction at 200°C where first peak occurs at 269°C and the second peak at the same temperature as for the other peaks, at 300°C. These two peaks can be a sign of either two different bonding strengths or the presence of two kinds of species on the surface. There is no CH₄ formation observed at temperature lower than 130°C indicating the absence of hydrogen rich CH₄ species on the catalyst surface.

Figure 27. TPD profiles following exposure of 1.7% Pt/ceria to CH₄ at various temperatures
Figure 28. Profiles of H₂-TPSR of the adspecies remaining on the Pt surface after TPD corresponding to Figure 27

At the onset of the second part of the experiment, while the catalyst is still at room temperature, big amounts of CH₄ are released (Table 9) from the reactor. In the literature it is referred as reactive carbon (Pareja et al., 1998). Here, the amounts of CH₄ released appear to vary a lot (big standard deviation in measurement) and no clear trends could be observed. Moreover, this reactive carbon was also observed on bare supports, both ceria and silica. Although the measurement protocol was repeated always in the same way, it might be that the current experimental setting can not accurately capture this measurement and that it needs more sensitive detection. Although the gas was sampled always at the same time, it may be that the sampling frequency would have to be increased which was not possible on the available experimental set up. Because of this uncertainty these amounts of CH₄ were not included in the calculation of the total amount of adsorbed CH₄.
Results of TPSR of the remaining carbonaceous species with H\textsubscript{2} for the exposures at different temperatures are shown in Figure 28. The areas under the curve reveal that the amounts of CH\textsubscript{4} desorbed during TPSR increase with the increase of reaction temperature. CH\textsubscript{4} released in this part of experiment originates from hydrogen deficient carbonaceous species. Most of the desorption maxima occur at 413°C, except for the reaction at 200°C which is at slightly lower 395°C indicating that there are no significant effects of the reaction temperature on the type and bonding strength of the remaining hydrogen deprived carbons on the catalyst surface. In addition, the absence of multiple desorption peaks also shows that only one type of carbon species was bonded to the surface. As mentioned earlier there were no species other then CH\textsubscript{4} are observed. CH\textsubscript{4} is the only product of hydrogenation and if any coupling of CH\textsubscript{x} species occurred to produce longer chain hydrocarbons, it was below detection limits of the FID detector.

**Table 9. Molar amounts of CH\textsubscript{4} produced during TPD and H\textsubscript{2}-TPSR after 1 min exposure to CH\textsubscript{4} at atmospheric pressure at various temperatures, for 1.7% Pt/CeO\textsubscript{2}**

<table>
<thead>
<tr>
<th>Temp.</th>
<th>TPD (µmol CH\textsubscript{4}/g cat)</th>
<th>CH\textsubscript{4} released at room temperature (µmol CH\textsubscript{4}/g cat)</th>
<th>TPSR (µmol CH\textsubscript{4}/g cat)</th>
<th>Total = TPD + TPSR (µmol CH\textsubscript{4}/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>1.0 ± 0.1</td>
<td>42.6 ± 59.3</td>
<td>2.0 ± 1.0</td>
<td>3.0 ± 1.1</td>
</tr>
<tr>
<td>300°C</td>
<td>3.4 ± 0.8</td>
<td>94.1 ± 57.2</td>
<td>2.5 ± 0.9</td>
<td>5.9 ± 0.8</td>
</tr>
<tr>
<td>350°C</td>
<td>3.6 ± 0.5</td>
<td>64.9 ± 32.8</td>
<td>11.2 ± 1.1</td>
<td>14.8 ± 1.3</td>
</tr>
<tr>
<td>400°C</td>
<td>2.6 ± 1.6</td>
<td>25.6 ± 15.9</td>
<td>31.7 ± 10.1</td>
<td>34.3 ± 10.9</td>
</tr>
<tr>
<td>450°C</td>
<td>2.5 ± 1.0</td>
<td>23.5 ± 28.7</td>
<td>49.7 ± 7.5</td>
<td>52.2 ± 7.1</td>
</tr>
</tbody>
</table>

Overall amounts of chemisorbed CH\textsubscript{4} increase with the reaction temperature (Table 9).
Figure 29 presents the H$_2$ evolved during the exposure of the catalyst to CH$_4$ flow at three different temperatures. Some H$_2$ was detected at 300°C but those were very low amounts, at the detection limits of the TCD detector.

![Graph showing H$_2$ flow rate vs. exposure time for different temperatures](image)

**Figure 29.** H$_2$ evolved during exposure of 1.7% Pt/ceria to CH$_4$ (200 ml/min) as a function of exposure time for different temperatures, m(cat)=0.2 g

It can be seen that the increase in temperature leads to the higher rates of H$_2$ evolution. From these rates observed and normalized per weight of sample, corresponding amounts of CH$_4$ were calculated assuming that 2 mol of H$_2$ evolve from 1 mol of adsorbed CH$_4$. Those values are shown in Table 10 and compared with the amounts of CH$_4$ desorbed during TPD and TPSR experiments. At 350°C these values match pretty well. However, at 400°C and 450°C, the values estimated from H$_2$ evolution rates are higher than what has been determined by desorptions. The reason for discrepancy might be that not all of the carbon comes off from the catalyst surface in the process of hydrogenation during TPSR, or that
at these higher temperatures, adsorbed CH₄ species on the surface couple and build various longer chain molecules that desorb from the surface but do not get detected in the exit stream on FID detector.

Table 10. Comparison of the amount of chemisorbed CH₄ determined by desorption experiment with the amount estimated from the rate of H₂ evolution, for 1.7% Pt/CeO₂ during 1 minute of CH₄ flow (200 ml/min)

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Total adsorbed CH₄ (μmol CH₄/g cat)</th>
<th>H₂ evolved during 1 min (μmol H₂/g cat)</th>
<th>Estimated CH₄ from the rate of H₂ evolution during 1 min (μmol CH₄/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C</td>
<td>14.8 ± 1.3</td>
<td>24.9 ± 9.5</td>
<td>12.4 ± 4.8</td>
</tr>
<tr>
<td>400°C</td>
<td>34.3 ± 10.9</td>
<td>135.8 ± 33.6</td>
<td>67.9 ± 16.8</td>
</tr>
<tr>
<td>450°C</td>
<td>52.2 ± 7.1</td>
<td>227.4 ± 30.3</td>
<td>113.7 ± 15.1</td>
</tr>
</tbody>
</table>

The amount of surface Pt atoms available on the sample is determined from H₂ uptake (Table 8). From H₂ chemisorption experiment on Quantachrome Autosorb 1C, it was determined that H₂ uptake for 1.7% Pt/ceria was 19.41 μmol/g (Table 8). Since the sample size in the reactor was 0.2 g, H₂ uptake for such sample would be 0.2 g · 19.41 μmol/g = 3.88 μmol. Under assumption that 1 mol of H₂ adsorbs on 2 mol of Pt, total amount of available surface Pt atoms in the sample is 2 · 3.88 μmol = 7.76 μmol. Further assuming that all carbon atoms are bonded to Pt atoms and that 1 C adsorbs on 1 Pt, at maximum coverage, amount of adsorbed carbon would be n_max(C) = 7.76 μmol. Coverage at different conditions has been then determined as:

\[
Coverage \, (%) = \frac{n(CH_4 \, adsorbed, \, \mu mol)}{n_max(C, \, \mu mol)} \cdot 100\% \quad (20)
\]

Corresponding coverages are shown in Figure 30.
As can be seen in Figure 30, the surface coverage with CH₄ species at reaction at 450°C is larger than 100%. This indicates that the carbonaceous species are adsorbing not only on Pt but also on the support. However, as shown later in Figures 31 and 32, there is no CH₄ adsorption on bare support at this temperature. It is thus probable that after Pt deposition onto ceria, due to their strong interaction and high concentration of oxygen vacancies on ceria in the vicinity of Pt crystallites (Figure 26), carbonaceous species adsorb onto the boundary areas between Pt nanoparticles and surrounding ceria rendering our first assumption of all carbon adsorbing only on Pt -invalid.
4.3.2.2. Effect of Pt loading

Figure 31. TPD profiles following exposure of ceria based samples to CH₄ (200 ml/min) at various Pt loadings at 450°C

Figure 32. Profiles of H₂-TPSR of the adspecies remaining on the Pt surface after TPD corresponding to Figure 31
Figures 31 and 32 illustrate the effect of Pt content on the chemisorbed CH₄. CH₄ does not chemisorb on reduced bare ceria support indicating that the oxygen vacancies on ceria do not act as active sites for CH₄ chemisorption on bare ceria. Desorption peak in TPD appeared at the same temperature for both 0.3 and 1.7% wt Pt samples, at 300°C. TPSR desorption maximum for 1.7% wt Pt appeared at slightly lower temperature (415°C) than on 0.3% wt Pt (430°C). Table 11 gives the results of the comparison of the activities of sample of various Pt loadings expressed per gram of sample.

Table 11. Molar amounts of CH₄ produced per g of sample during TPD and H₂-TPSR after 1 min exposure to CH₄ at atmospheric pressure at various Pt loadings, at 450°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>TPD (µmol CH₄/g cat)</th>
<th>CH₄ released at room temperature (µmol CH₄/g cat)</th>
<th>TPSR (µmol CH₄/g cat)</th>
<th>Total = TPD + TPSR (µmol CH₄/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare ceria</td>
<td>no activity</td>
<td>20.4</td>
<td>no activity</td>
<td>-</td>
</tr>
<tr>
<td>0.3% Pt/ceria</td>
<td>1.1</td>
<td>108.4</td>
<td>68.3</td>
<td>69.5</td>
</tr>
<tr>
<td>1.7% Pt/ceria</td>
<td>2.5 ± 1.0</td>
<td>23.5 ± 28.7</td>
<td>49.7 ± 7.5</td>
<td>52.2 ± 7.1</td>
</tr>
</tbody>
</table>

Since the experiments have shown that bare ceria does not adsorb any CH₄ and considering that these samples contain different amounts of Pt, it is more appropriate to compare their activities normalized per gram of the active metal (Pt). Those values are shown in Table 12.

Table 12. Molar amounts of CH₄ produced per g of Pt during TPD and H₂-TPSR after 1 min exposure to CH₄ at atmospheric pressure at various Pt loadings, at 450°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>TPD (µmol CH₄/g Pt)</th>
<th>CH₄ released at room temperature (µmol CH₄/g Pt)</th>
<th>TPSR (µmol CH₄/g Pt)</th>
<th>Total = TPD + TPSR (µmol CH₄/g Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3% Pt/ceria</td>
<td>323.5</td>
<td>31882.4</td>
<td>20088.2</td>
<td>20441.2</td>
</tr>
<tr>
<td>1.7% Pt/ceria</td>
<td>147.1 ± 58.8</td>
<td>1382.4 ± 1688.2</td>
<td>2923.5 ± 441.2</td>
<td>3070.6 ± 417.6</td>
</tr>
</tbody>
</table>
When expressed in that way, per g of Pt, it can be seen that Pt nanoclusters in 0.3% sample are much more active than the Pt nanoclusters for the 1.7% sample, in both parts of the experiment. Overall, 0.3% sample converted almost 7 times more CH$_4$ than the 1.7% sample. From H$_2$-chemisorption analysis given in Table 9, it can be seen that the dispersion of 0.3% Pt/ceria sample is much higher than of 1.7% Pt/ceria indicating also smaller Pt nanoparticle size (1.9 nm for 0.3% vs 2.6 nm for 1.7%, Table 1). Calculated coverage for the activity at 450°C is over 400% indicating that CH$_4$ adsorbs most probably at the interface of Pt and ceria. Due to higher dispersion, there are more of these interfacial areas and probably more of oxygen vacancies in ceria surrounding those small Pt crystallites making the effect of metal-support interaction even more pronounced.

Results show that these smaller Pt particles bond carbon species more strongly (seen from the position of the desorption peak in TPSR) but are more active for the CH$_4$ activation (seen from higher overall amount of chemisorbed CH$_4$).

These results confirm that smaller Pt nanoclusters are more active for CH$_4$ conversion due to the presence of coordinatively unsaturated Pt surface atoms which are responsible for the reduction of C-H bond activation energy (Wei and Iglesia, 2004a). Also, as explained earlier, CH$_4$ being a weak acid would adsorb more favorably on the Pt sites with the increased electron density (Eswaramoorthy, 2000) such as these low coordinative surface atoms.(Cheng et al., 2012)

4.3.2.3. Effect of support

The same experiments are performed on Pt on silica in order to examine the effect of support on CH$_4$ conversion. As described earlier, Pt/silica was already examined by other researchers (Belgued et al., 1996, Martins et al., 2007). However, it was prepared by different technique than the one used in this
work. Here, both ceria and silica based samples have been prepared by the same method, the incipient wetness, as described in the experimental section.

Figure 33 shows the TPD profiles for reactions at different temperatures.

![Figure 33. TPD profiles following exposure of 1.7% Pt/silica to CH\textsubscript{4} at various temperatures](image)

It can be seen that the amount of CH\textsubscript{4} released in this part of experiments are quite low, especially when compared to work of Belgued et al. (1996). Maximum desorption for almost all reaction temperatures occurs at around 250°C. Interestingly, secondary smaller peak can also be observed, at around 140°C. It seems that some hydrogen rich species might remain on the surface, although in very small quantities.

Figure 34 shows the TPSR profile for silica based samples.
Figure 34. Profiles of H₂-TPSR of the adspecies remaining on the Pt surface after TPD corresponding to Figure 33

All TPSR curves (Figure 34) have two desorption peaks indicating the existence of two different bond strengths between adsorbed carbons and the catalyst surface. First peak occurs at around 340 – 380°C, while the second peak occurs at 450°C for all investigated reaction temperatures. The amounts of CH₄ released in the first peak decreases as the temperature of reaction increases. On the contrary, the amount of CH₄ released at 450°C increases with the increase of reaction temperature. Accordingly, ratio of methane released at lower temperatures to the methane released at higher temperature decreases as the reaction temperature (exposure to CH₄) increases. For the reaction temperature of 200°C all CH₄ desorbed exclusively at lower temperature. On the other hand, for the reaction temperature of 450°C, majority of CH₄ was hydrogenated at 450°C. As discussed earlier, it is important to find the operating
conditions that will favor more reactive, loosely bonded carbons that would readily react with the potential co-reactant.

Table 13. Molar amounts of CH\textsubscript{4} produced during TPD and H\textsubscript{2}-TPSR after 1 min exposure to CH\textsubscript{4} at atmospheric pressure at various temperatures for 1.7% Pt/silica, at CH\textsubscript{4} flow = 200 ml/min

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>TPD (µmol CH\textsubscript{4}/g cat)</th>
<th>CH\textsubscript{4} released at room temperature (µmol CH\textsubscript{4}/g cat)</th>
<th>TPSR (µmol CH\textsubscript{4}/g cat)</th>
<th>Total = TPD + TPSR (µmol CH\textsubscript{4}/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>1.1</td>
<td>42.5</td>
<td>1.2</td>
<td>2.3</td>
</tr>
<tr>
<td>300°C</td>
<td>1.3</td>
<td>74.8</td>
<td>2.3</td>
<td>3.6</td>
</tr>
<tr>
<td>400°C</td>
<td>1.4</td>
<td>98.4</td>
<td>5.0</td>
<td>6.4</td>
</tr>
<tr>
<td>450°C</td>
<td>1.2 ± 0.1</td>
<td>74.2 ± 55.2</td>
<td>8.3 ± 1.1</td>
<td>9.5 ± 1.1</td>
</tr>
</tbody>
</table>

Total amount of surface Pt atoms available in the 1.7% Pt/silica sample, derived from the H\textsubscript{2} uptake (Table 8), is 7.45 µmol. That is also the amount of carbon (methane) adsorbed at the maximum coverage. Corresponding coverages are presented in Figure 35.

Figure 35. Total adsorbed CH\textsubscript{4} as a function of reaction temperature, and corresponding coverages with CH\textsubscript{x} species, on the 0.2 g of 1.7% Pt/silica
• **Comparison of supports (ceria vs. silica)**

Integration of TPD profiles for ceria and silica samples (Figures 27 and 33), shows that the amount of CH4 released on ceria is about 4 times higher than on silica samples (Tables 9 and 13). Comparison of desorption peak maxima shows that carbonaceous species on silica samples appear to be more loosely bound to the catalyst surface. Although in smaller concentration, some hydrogenated CHx species remained on the silica samples, which was not the case for ceria samples.

Comparison of TPSR profile is given in Figures 36 – 39.

![Graph depicting CH4 flow over time](image)

*Figure 36. H2-TPSR profiles for ceria and silica supported catalysts, for reaction at 200°C*
Figure 37. H₂-TPSR profiles for ceria and silica supported catalysts, for reaction at 300°C

Figure 38. H₂-TPSR profiles for ceria and silica supported catalysts, for reaction at 400°C
Figure 39. H$_2$-TPSR profiles for ceria and silica supported catalysts, for reaction at 450°C

Existence of multiple peaks on silica samples and the differences in temperatures at which most of the carbon species are being hydrogenated are clear sign of different bonding strengths of adsorbed carbons and ceria and silica support. First, as TPSR plots show, there are two major peaks on silica samples and only one on ceria sample. Position of these peaks is also different. At lower reaction temperatures (200 - 300°C), total amounts of adsorbed CH$_4$ are similar for two supports. However, desorption peaks maxima of silica samples occur at lower temperature meaning that carbon species are less strongly bonded and hence more easily hydrogenated on silica samples. On the other hand, at higher reaction temperatures (400 - 450°C) amounts of adsorbed CH$_4$ are much higher on ceria catalyst. Also, at these higher reaction temperatures, maximum on ceria samples occurs at around 415°C which is lower than the 450°C at which majority of carbon species desorb from silica sample.
These results indicate that at lower reaction temperatures (up to 300°C) silica is better support for methane activation because the adsorbed carbonaceous species are more loosely bound to the catalyst surface and hence more reactive. On the other hand, at higher reaction temperatures (higher than 300°C), ceria is better because not only it adsorbs more methane but also those adsorbed species are less strongly bound to the catalyst surface.

![Figure 40](image.png)

**Figure 40. Comparison of total amounts of adsorbed CH₄ for ceria and silica supported Pt catalysts (1.7%)**

As illustrated in Figure 40, total amounts of adsorbed methane are much higher on ceria-supported samples than on silica based samples at higher reaction temperatures (400°C, 450°C). At lower reaction temperatures, differences in the activity are not so pronounced.
Results of H₂-chemisorption analysis and dispersion measurements, presented in Table 8, show no significant differences between dispersion of ceria and silica supported Pt. Therefore, the differences in the behavior of two supports and the activities of samples cannot be attributed to the differences in dispersion and hence Pt nanocluster sizes (2.56 nm vs. 2.65, Table 8). Higher activity of ceria samples could be explained by a strong metal support interaction and, based on TPR results, high concentration of oxygen vacancies in the vicinity of Pt crystallites. These interfaces might play a critical role in the methane activation due to large spillover of adsorbed C and H species to the ceria support which clears the Pt metal centers for further dehydrogenations (Odier, 2001; Ewasrasmoto, 2001). This effect is more pronounced at higher reaction temperatures (400°C, 450°C).

For both ceria and silica based catalysts, the converted CH₄ represented a very small fraction of the total CH₄ that entered the reactor. Table 9 shows that the quantity of chemisorbed CH₄ ranged from 3 to 53 μmol/gcat or 0.6 to 10.6 μmol per Pt/ceria sample and 0.46 to 1.9 μmol per Pt/silica sample (derived from Table 6, 2.3 to 9.5 μmol/gcat). The amount of CH₄ sent to the catalyst was 200 ml/min, at ambient conditions, which is around 8.2 mmol per 1 minute of exposure. Therefore, CH₄ conversion ranged from 0.07 to 1.3‰ for ceria based sample and 0.06 to 0.23‰ for silica based sample. On the other hand, as mentioned earlier, ceria sample is able to chemisorb maximum 7.76 μmol of CH₄, and silica 7.45 μmol of CH₄, at full coverage assuming C/Pt to be 1. This consumption at maximum coverage gives a limiting yield with respect to CH₄ entering the reactor of 0.95‰ for ceria and 0.91‰ for silica.
4.3.2.4. Effect of CH₄ partial pressure

At constant flow rate of CH₄ (200 ml/min) and reaction temperature of 400°C, partial pressure of CH₄ in the inlet flow was changed from 0.25 atm to 1 atm. From Figure 41, it can be observed that amount of CH₄ released during TPD reaches maximum when inlet partial pressures of CH₄ are 0.5 and 0.75 atm. However, although the desorption peaks for 0.5 and 0.75 atm are bigger, the amounts of desorbed CH₄ which are calculated by integrating these peaks, are not significantly different and are within the experimental error, as shown in Table 14. There is no release of CH₄ below 130°C at any of partial pressures investigated meaning that only hydrogen deprived species are left on the catalyst surface. No multiple desorption peaks are observed, neither the CH₄ partial pressure has any affect on the position of these peaks.

![TPD profiles following exposure of 1.7% Pt/ceria to CH₄ at various partial pressure of CH₄, at total pressure of 1 atm and total flow rate of 200 ml/min](image)

Figure 41. TPD profiles following exposure of 1.7% Pt/ceria to CH₄ at various partial pressure of CH₄, at total pressure of 1 atm and total flow rate of 200 ml/min
Figure 42 illustrates that the increase in the feed CH₄ partial pressure during adsorption results in the increase of the amount of CH₄ released during TPSR. There are no multiple peaks but Figure 42 shows a drift in the temperature of the maxima from 413°C to 450°C as the partial pressure increases from 0.25 atm to 0.75 atm. However, at pure CH₄ flow, it drops again to 413°C.

Table 14 summarizes the results for different pressures of CH₄ in the inlet flow. The increase of the CH₄ partial pressure in the inlet flow increases the total amount of CH₄ chemisorbed.
Table 14. Molar amounts of CH$_4$ produced during TPD and H$_2$-TPSR after 1 min exposure to CH$_4$ at 400°C at various CH$_4$ partial pressures, at total partial pressure of 1 atm, CH$_4$ flow of 200 ml/min, over 1.7% Pt/CeO$_2$

<table>
<thead>
<tr>
<th>Partial pressure of CH$_4$ (atm)</th>
<th>TPD ($\mu$mol CH$_4$/g cat)</th>
<th>CH$_4$ released at room temperature ($\mu$mol CH$_4$/g cat)</th>
<th>TPSR ($\mu$mol CH$_4$/g cat)</th>
<th>Total = TPD + TPSR ($\mu$mol CH$_4$/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.8</td>
<td>4.9</td>
<td>11.8</td>
<td>12.6</td>
</tr>
<tr>
<td>0.5</td>
<td>3.0</td>
<td>0.78</td>
<td>12.2</td>
<td>15.2</td>
</tr>
<tr>
<td>0.75</td>
<td>3.2</td>
<td>1.4</td>
<td>14.7</td>
<td>18.0</td>
</tr>
<tr>
<td>1</td>
<td>2.6 ± 1.6</td>
<td>25.6 ± 15.9</td>
<td>31.7 ± 10.1</td>
<td>34.3 ± 10.9</td>
</tr>
</tbody>
</table>

Figure 43 presents the corresponding coverages calculated by Eq.(20)

Figure 43. Total adsorbed CH$_4$ at various CH$_4$ partial pressures and corresponding coverages with CH$_x$ species, on 0.2 g of 1.7% Pt/ceria

Figures 44 and 45 show the effect of CH$_4$ partial pressure on TPD and TPSR profiles for 1.7% Pt on silica.

It can be seen that the increase in CH$_4$ partial pressure increases the CH$_4$ desorbed in TPD. However, the amounts of CH$_4$ released during TPD are very low and no clear peaks could be distinguished. Similarly,
the amounts of CH\textsubscript{4} desorbed in TPSR increase with the increase in CH\textsubscript{4} partial pressure. At lower CH\textsubscript{4} pressures (0.5 and 0.75 atm) there are no multiple desorption peaks like it appears when flowing pure CH\textsubscript{4}. Under those conditions, most of the carbonaceous species come off from the surface at 450°C.

Figure 44. TPD profiles following exposure of 1.7% Pt/silica to CH\textsubscript{4} at various partial pressure of CH\textsubscript{4}, at total pressure of 1 atm and total flow rate of 200 ml/min
Figure 45. TPSR profiles following exposure of 1.7% Pt/silica to CH₄ at various partial pressure of CH₄, at total pressure of 1 atm and total flow rate of 200 ml/min

Table 15 lists the integrated values for total CH₄ desorbed in each part of experiment. As in the case of ceria, total CH₄ increases with the increase in CH₄ partial pressure in the inlet flow.

Table 15. Molar amounts of CH₄ produced during TPD and H₂-TPSR after 1 min exposure to CH₄ at 450°C at various CH₄ partial pressures, for 1.7% Pt/silica

<table>
<thead>
<tr>
<th>Partial pressure of CH₄ (atm)</th>
<th>TPD (µmol CH₄/g cat)</th>
<th>CH₄ released at room temperature (µmol CH₄/g cat)</th>
<th>TPSR (µmol CH₄/g cat)</th>
<th>Total = TPD + TPSR (µmol CH₄/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.8</td>
<td>1.3</td>
<td>4.0</td>
<td>4.8</td>
</tr>
<tr>
<td>0.75</td>
<td>0.9</td>
<td>25.8</td>
<td>7.5</td>
<td>8.4</td>
</tr>
<tr>
<td>1</td>
<td>1.2 ± 0.1</td>
<td>74.2 ± 55.2</td>
<td>8.3 ± 1.1</td>
<td>9.5 ± 1.1</td>
</tr>
</tbody>
</table>

Figure 46 shows the corresponding coverages.
Figure 46. Total adsorbed CH₄ at various CH₄ partial pressures and corresponding coverages with CH₄ species, on the 0.2 g of 1.7% Pt/silica

4.4. Conclusions

In this chapter, the role of metal – support interaction on the methane conversion was investigated by comparing ceria and silica based Pt catalysts. In addition, the effect of temperature, Pt loading and CH₄ partial pressure on the total amounts of chemisorbed CH₄ and the structure of adsorbed carbonaceous film, were studied, too.

It was found that the strong metal-support interaction, present in ceria based sample, plays important role in the CH₄ conversion. Interfacial areas at the boundaries of Pt and ceria containing high concentrations of oxygen vacancies, by causing the large spillover of adsorbed C and H species from Pt onto ceria, clear the Pt active sites for further CH₄ dehydrogenation. This effect is more pronounced at
higher temperatures (400°C, 450°C), at which the activity of ceria based sample is much higher than the silica sample. At those temperatures, not only the activity of ceria sample is higher, but also the adsorbed hydrogen-deprived carbon species are less strongly bound to ceria than to silica supported catalysts. On the other hand, at lower reaction temperatures, the total amounts of CH₄ converted are similar. However, results indicate that at lower reaction temperatures (up to 300°C) silica is the better support for methane activation because the adsorbed carbonaceous species are more loosely bound to the catalyst surface and hence more reactive.

Increase in the adsorption temperature leads to the increase in the total amounts of CH₄ converted, for both ceria and silica samples. However, the nature of the adsorbed CHₓ species is different between two samples. Upon initial exposure of the catalysts to the CH₄ flow, hydrogen rich CHₓ species remain in very small amounts on the silica catalyst. On ceria, there is none detected, under all operating conditions that were used in this work. For both Pt/ceria and Pt/silica catalysts, the increase in the CH₄ feed partial pressure during adsorption results in the increase of adsorbed CH₄. Change of CH₄ pressure does not affect the structure of the adsorbed carbon film on the surface.

Results also confirmed that smaller Pt nanoparticles are more active for CH₄ conversion. The presence of the low coordinated Pt surface atoms with increased electron density favors CH₄ activation.

Studying the effect of the catalyst structure (support, Pt loading), and the operating conditions (temperature, CH₄ partial pressure) on the amounts of chemisorbed CH₄ and on the structure and the reactivity of adsorbed carbonaceous film is of critical importance in advancing the knowledge about methane activation and rational catalyst design. These findings are useful not only the methane reaction
with carbon dioxide, but also for reactions involving non-oxidative methane activation used for H₂ production for fuel cells, for example. However, H₂ evolution rates obtained in this work give the maximum space time yields of 0.0024 kg/(m³·s) or 8.6 gH₂/l·h at 450°C which is still low for any commercial application.
5. The effect of Pt shape on CH₄ dehydrogenation

5.1. Introduction

The goal of these experiments is to investigate the effect of Pt nanocluster shape and support on methane activation. The selection of Pt cluster shapes and support structure has been guided by molecular modeling and DFT analysis, as explained in Chapter 2 (Cheng et al., 2012; 2013). To test the effect of Pt nanoparticle shape, tetrahedral and “near-spherical” Pt nanoparticles were prepared. To study the effect of support, ceria powder and ceria nanorods were synthesized while premade silica was used as a reference support. Catalysts were tested in a laboratory scale packed bed reactor and their performance in methane activation was compared based on the rates of H₂ evolution during exposure to the CH₄ flow at different temperatures. Tetrahedral Pt clusters deposited onto ceria powder were compared with the round Pt on ceria powder made by modified polyol method and also round Pt on ceria prepared by incipient wetness method (described in detail in Chapter 4).

5.2. Experimental

5.2.1. Catalyst preparation – Shape controlled synthesis

5.2.1.1. Preparation of tetrahedral Pt nanoparticles (NP)

Colloidal tetrahedral Pt nanoparticles were synthesized by mixing H₂PtCl₆·6H₂O and polyvinylpyrroldone (PVP), as a capping agent, in a specific concentration ratio and reducing the mixture with hydrogen gas. Following the recommendations from Lee et al. (2008) a solution of H₂PtCl₆·6H₂O (c= 2·10⁻⁴ M) was prepared and thoroughly mixed with the polyvinylpyrroldone solution (PVP, Mw ≈360 000) so that the concentration ratio [H₂PtCl₆·6H₂O]: [PVP] was 1:0.0005. The pH of the mixture was adjusted to 7.5 by addition of 10% wt NaOH solution. The mixture was then outgassed by bubbling argon at 30 psi for 20 min. For the reduction hydrogen gas at 20 psi was bubbled for 10 minutes. The flask was sealed, wrapped in aluminum foil and stored in the dark for 12 hrs. The whole preparation process was at room
temperature. The solution changed color from pale yellow to dark brown, which indicated a change in light absorption properties and formation of Pt colloidal nanoparticles (Figure 47).

Figure 47. UV-vis absorption spectra of the solution used to prepare tetrahedral Pt colloidal particles at different stages of the synthesis

5.2.1.2. Preparation of ceria supports

Ceria powder was prepared following a common precipitation method as described in Tang et al. (2004). One starts with a 0.1 M Ce(NO$_3$)$_3$·6H$_2$O aqueous solution, as the cerium source, while adding NH$_4$OH solution under vigorous stirring (550 RPM or setting 7 on a magnetic stirring hot plate made by Corning) at T = 60°C until the pH of the mixture is greater than 9. The precipitant is then aged in the mother liquid for 4 hrs, centrifuged and washed several times with distilled water. The obtained solid is dried at 100°C for 10 hrs and then calcined at 450°C for 4 hrs in air.
Synthesis of ceria nanorods was performed as described in Zhou et al. (2005). First, 0.75 g of Ce(NO$_3$)$_3$∙6H$_2$O was dissolved in distilled water. With rigorous stirring for 15 min (550 RPM), 16 ml of 10% wt NaOH solution was added rapidly. Yellow precipitate of the amorphous CeO$_2$ appeared. All the slurry (around 17.5 ml) was transferred into a 25 ml autoclave (Figure 48) and filled with DI water up to 80% of its volume. The final concentration of the NaOH in the autoclave was around 2M.

The system was kept at 100°C for 10 h and then allowed to cool at room temperature. The final product was centrifuged, washed with DI water in order to remove the ionic remnants, dried at 60°C and calcined at 350°C for 4 hrs. A high yield of 94-97 % was achieved.

5.2.1.3. Deposition of tetrahedral Pt NPs onto supports

In the case of supported tetrahedral Pt NPs, the selected support (silica powder, ceria powder or ceria nanorods) was added into the solution of tetrahedral Pt NPs. This solution was left for 24 hours under...
rigorous stirring (550 RPM) in order for nanoparticles to deposit from solution onto the support. Following the Pt nanoparticle adsorption, the solution cleared and the initially light colored powder became dark grey indicating metal deposition (Figure 49). The final product was centrifuged, washed with distilled water and ethanol, dried at 60°C for 10 hrs, and then calcined in air for 1 hr at 200 °C. Mild calcination temperature is applied (200°C for 1 h) so that the metal cluster shape is not damaged.

![Figure 49. Solution cleared indicating deposition Pt NPs onto support](image)

5.2.1.4. Preparation of “near-spherical” supported Pt catalyst

Catalyst containing “near-spherical” Pt nanoparticles was prepared by the modified polyol method described in Tang et al. (2004). 246 mg of H₂PtCl₆·6H₂O were dissolved in 60 ml of ethylene glycol. The amounts of chloroplatinic acid and cerium powder (or nanorods) were adjusted to achieve nominal 3% wt metal loading. The pH of the solution was set to 12 by the addition of NaOH. The mixture was stirred (550 RPM) and maintained at 130°C for 1 h to ensure the complete reduction of Pt. The solution changed color from the light yellow to dark brown. The following one-step mechanism has been proposed for this redox synthesis (Tang et al., 2004):

\[
PtCl₆^{2-} + CH₂OH-CH₂OH → Pt^{0} + CHO-CHO + 4H^{+} + 6Cl^{-} \quad (21)
\]
The obtained particles were washed with hot distilled water until no Cl\(^{-}\) anion could be detected in the filtrate by AgNO\(_3\) solution. After drying overnight at 100°C, the solid was calcined in air at 200°C for 4 h.

The size and shape distribution of both colloidal and deposited metal nanoparticles were then determined by transmission electron microscope (TEM, FEI Tecnai G\(^2\) Spirit) operated at 120 kV. The samples were dissolved in distilled water, sonicated and then a droplet of the solution was deposited on a Cu grid covered with carbon film for TEM analysis. The platinum loading of each of the catalysts was determined by an Inductively Coupled Plasma Mass Spectrometer (Agilent 7500ce ICP-MS).

Round Pt on ceria prepared by incipient wetness method is also used for a comparison (described in detail in Chapter 4).

5.2.2. Apparatus and experimental protocol

Catalyst samples (0.2 g) were sandwiched between two pieces of quartz wool in a laboratory scale packed bed reactor (described in detail in Chapter 3.1). First, Ar was flown through to remove moisture and impurities while heating the catalyst up to 100°C. Then, the sample was reduced in 50 ml/min of H\(_2\) flow for 1 hr at the temperature of the reaction (200°C – 450°C). For tetrahedral Pt samples and samples made by polyol method, Pt is being reduced during preparation while on the other hand, for sample made by incipient wetness method Pt is being reduced in the rector before the reaction (see Chapter 4). Therefore, former two samples did not need long reduction periods.

Then, adsorbed H\(_2\) was removed by flowing Ar for 30 min. The catalyst was then exposed to CH\(_4\) flow of 200 ml/min for 10 min. Simultaneous H\(_2\) evolution was detected on gas chromatograph (described in detail in Chapter 3.2):
\begin{equation}
\text{CH}_4 \rightarrow \text{CH}_x + (4-x)/2\text{H}_2 \quad x = 0, 1, 2, 3
\end{equation}

Between runs, catalyst was regenerated with 50 ml/min of H\textsubscript{2} flow for 30 min at the temperature of reaction. The space velocity per mass of catalyst (60 000 ml/gcat h) was kept constant so that the results could be compared. Such high space velocity ensured the absence of external mass transfer resistance and the small size of used support powders ensured the absence of internal diffusion limitations.

5.3. Results

5.3.1. Catalyst characterization

5.3.1.1. Characterization of tetrahedral Pt nanoparticles (NP)

The size of tetrahedral NPs (triangular in 2-D) was determined from TEM images by measuring the longest side of the triangle for 300 randomly chosen NPs. The resulting shape and size distribution are shown in Figures 50 and 51. The analysis of shape distribution reveals that 65 ± 8 % have tetrahedral shape. The remaining particles are either truncated tetrahedral, “near spherical”, or completely irregular in shapes. For those NPs with tetrahedral shape, the average side length is 7.0 ± 1.3 nm.

Figure 50. TEM images of tetrahedral colloidal Pt NPs c= 2·10^{-4} M a) mag = 67 000; b) mag = 220 000
Figure 51. Size distribution of tetrahedral Pt NPs, based on 300 randomly chosen NPs

5.3.1.2. Characterization of ceria supports

TEM images of the ceria powder are shown in Figures 52a,b. From Figure 52b it can be observed that interplanar distance in crystallites is around 0.31 nm which corresponds to preferential exhibition of the (111) plane.

Figure 52. TEM image of ceria nanopowder a) mag = 110 000; b) mag = 350 000
From the TEM images in Figure 53, the nanorods’ dimensions are around $93 \pm 30 \text{ nm} \times 12 \pm 3 \text{ nm}$, and thus the aspect ratio is approximately 8. In order to more accurately determine the interplanar distances, the exposed planes and the preferred directions of the nanorods’ growth, HRTEM would have to be used to check if these nanorods indeed expose (110) facets.

![Figure 53. TEM image of ceria nanorods a) mag = 42 000; b) mag = 265 000](image)

### 5.3.1.3. Characterization of supported tetrahedral Pt NP

Results from Lee et al. (2008) on silica powder (in our case – silica Davicat SI 1301, BET specific surface area = 320 m$^2$/g) were successfully reproduced and, as can be seen from Figure 54, tetrahedral Pt NPs preserved their shape after deposition and calcinations.
In the case of ceria powder and ceria nanorods, shown in Figures 55 a and b, solutions containing Pt nanoparticles did not become clear after deposition of nanoparticles on support, indicating that some Pt NPs remained in the solution and did not adsorb onto the support. Figure 55 shows that tetrahedrons are just physically mixed, non-uniformly, with the nanorods. It is very difficult to distinguish Pt nanoparticles from the support in TEM images. As discussed in Chapter 3, TEM analysis of Pt particles supported on ceria can be difficult since the dark CeO$_2$ contrast obscures the profile of precious metal particle (Takeguchi et al., 2005, Perkas et al., 2006).
Figure 55. TEM images (mag = 110 000) of a) tetrahedral Pt NPs on ceria nanorods; b) tetrahedral Pt NPs on ceria powder

The difficulty with deposition of tetrahedral Pt nanoparticles onto ceria nanorods might be attributed to the nanorods not being long enough (~93 nm) to “hold”/adsorb Pt tetrahedrons (~7 nm). Possibly longer nanowires could provide increased stability for big Pt tetrahedrons. Tana et al. (2010) reported the preparation of ceria nanowires which exposed more reactive (110) facets. However, their length (around 140 nm) is just slightly longer than the length of nanorods. An attempt was made to follow the protocol of Tana et al. (2010), by changing the operating conditions of the autoclave, in order to increase the length of ceria nanowires. As Figures 56 a and b show, by decreasing the volume of the solution in the autoclave reactor, some increase in the aspect ratio was achieved. However, the size of these nanowires was not uniform. Further fine tuning of the operating conditions would be needed; due to time constraints, it was not pursued in this work.
Figure 56. Ceria nanowires on left - prepared in 80% of the autoclave volume (x 42 000 mag), on right – prepared in 60% of the autoclave volume (x 30 000 mag)

For the above reasons, samples containing nanorods were not tested in the reactor.

5.3.1.4. Characterization of “near-spherical” supported Pt catalyst

Although it was difficult to analyze this sample by TEM, for the previously mentioned reasons, the average Pt nanoparticle size on ceria powder was estimated to be around 2.2 ± 0.4 nm, based on 50 NPs from different TEM images (Figure 57).
The preparation of the catalyst by the modified polyol method was only limitedly successful. During latter attempts, the support powder would adhere and bake on the walls of the beaker despite rigorous mixing. Due to limited amounts of as prepared materials, and due to the difficulties in reproducing the synthesis method, it was not possible to repeat the tests in the reactor.

The metal loading of each of the catalyst was determined by an Inductively Coupled Plasma Mass Spectrometer (Agilent 7500ce ICP-MS) and sample pretreatment was followed as described in Chapter 3.3.4.1.

The results obtained are summarized in Table 16.

<table>
<thead>
<tr>
<th>Sample</th>
<th>tetrahedral Pt/silica</th>
<th>tetrahedral Pt/ceria powder</th>
<th>tetrahedral Pt/ceria nanorods</th>
<th>“near spherical” Pt/ceria powder (PM)</th>
<th>“near spherical” Pt/ceria powder (IW)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt loading (%)</td>
<td>1.67 ± 0.14</td>
<td>1.72 ± 0.14</td>
<td>0.84 ± 0.07</td>
<td>1.27 ± 0.11</td>
<td>1.71</td>
</tr>
</tbody>
</table>
The results show that not all Pt nanoparticles adsorbed onto the supports, as a significant amount stayed in the solution. As mentioned earlier, nominal Pt loading was 3 wt%.

5.3.2. CH$_4$ dehydrogenation – studies in packed bed reactor

H$_2$ evolution was chosen as a basis for performance comparison between different samples in their success in methane activation. Figures 58 and 59 illustrate the effect of temperature on the extent of H$_2$ evolution on tetrahedral Pt supported on ceria and silica powder samples, respectively. Since both samples contained the same amount of adsorbed tetrahedral Pt nanoclusters, activities are plotted in absolute values (μmol/min) without normalization with respect to Pt content.

In cases of both ceria and silica supported Pt nanoparticles, the increase in temperature causes the increase in H$_2$ evolution. This is to be expected since CH$_4$ conversion is a highly endothermic reaction. Also, for both samples, H$_2$ evolution rate drops significantly within first 2 minutes of the exposure to the CH$_4$ flow. This is in accordance with the previous reports from the literature (Belgued et al., 1996; Ding et al., 2007). These results also indicate that, in step-wise operation of the catalyst, 1 minute might be the optimal duration of one cycle (exposure to CH$_4$) since H$_2$ evolution reaches its maximum within that time frame, as recommended by Ding et al. (2007).
Figure 58. The effect of temperature on H$_2$ evolution rate over tetrahedral 1.7% Pt/ceria during the exposure to the CH$_4$ flow (200 ml/min), at 1 atm, 0.2 g of sample.

Figure 59. The effect of temperature on H$_2$ evolution rate over tetrahedral 1.7% Pt/silica during the exposure to the CH$_4$ flow (200 ml/min), at 1 atm, 0.2 g of sample.
Figure 60. The effect of support on the activity of tetrahedral Pt nanoclusters during the exposure to the CH₄ flow (200 ml/min), at 300°C at 1 atm

Figure 61. The effect of support on the activity of tetrahedral Pt nanoclusters during the exposure to the CH₄ flow (200 ml/min), at 350°C at 1 atm
On the ceria supported sample H$_2$ evolution was detected already at 200°C, while on silica at 300°C. This is an indication of higher activity of ceria supported samples which is further confirmed by comparing the H$_2$ evolution rates of two samples as shown in Figures 60 and 61. The H$_2$ flow rates are more than 2 times higher on tetrahedral Pt nanoclusters supported on ceria than on silica. These results are experimental confirmation of the DFT analysis done by Cheng et al. (2012) and explained in detail in the Chapter 2.3.3. Their molecular modeling calculation, over model tetrahedral clusters supported on model ceria and silica surfaces, have shown that ceria support decreases the energy barrier for CH$_4$ activation for 0.12 eV in comparison with the unsupported tetrahedral clusters. On the other hand, no changes in the energies of adsorption for Pt clusters supported on β-silica are predicted. Enhanced catalytic activity of ceria based samples is attributed to the increased electron density at the low-coordinated Pt sites and oxygen vacancies at the metal-support interface, along with lower activation strain on the supported catalysts. Our results for round shape Pt catalysts presented in Chapter 4, have confirmed the presence of strong metal-support interaction between Pt and ceria which promotes CH$_4$ conversion.

Experiments shown in Figures 58 - 61 were repeated 3 times and although no decrease in the activity was observed, tetrahedral Pt nanoclusters lost their shape. Catalyst samples were analyzed by TEM after the reaction. As mentioned earlier, it was very hard to analyze ceria based samples by TEM because the dark CeO$_2$ contrast makes the profile of Pt particle obscure. Therefore, the shape loss, in Figure 62, is shown for Pt nanoclusters supported on silica.
This instability of Pt nanoparticles under reaction conditions possesses a severe limitation for the application of these catalysts in the near future, unless some ways of stabilization are found that would prevent the reconstruction of the shape.

The effect of Pt nanocluster shape on CH$_4$ activation is shown in Figure 63. H$_2$ evolution rates (per gram of Pt) are compared between tetrahedral Pt supported on ceria and two round Pt catalysts samples prepared by different methods (incipient wetness (IW) and polyol method (PM)).

Results show that at 350°C round Pt nanoparticles are more active than the tetrahedral Pt nanoparticles. However, differences between tetrahedral Pt and round Pt prepared by incipient wetness method are not that significant and are within the experimental error. Moreover, on the sample with tetrahedral nanoparticles H$_2$ evolution could be detected already at 200°C (Figure 58), while on round
particles (IW) H$_2$ did not appear until 300°C, and that was not consistent until 350°C; therefore only results for 350°C and above are shown (Figure 29 in Chapter 4).

![Figure 63. The effect of Pt nanocluster shape on H$_2$ evolution rates during exposure to the CH$_4$ flow (200 ml/min), at 350°C and 1 atm (catalyst prepared by IW – incipient wetness or PM – polyol method)](image)

On the other hand, results shown for sample made by polyol method are only the initial activity, from the first experimental run. Activity of this sample drops for almost 40% after 3 runs as shown in Figure 64.
This fast loss of activity is probably due to the sintering of small Pt nanoparticles. As described in experimental section, the rough average size was 2.2 nm. Time constraints prevented further sample analysis and TEM imaging, which could show if nanoparticle aggregation was the cause for deactivation.

One has to find the correct way to compare the activities of two nanoparticle shapes (round vs tetrahedral) because they not only have different shapes but also sizes. Moreover, the experimental Pt nanoclusters are of much bigger size than those used in DFT analysis (comparison given in Table 17). In addition, DFT model did not take into account the effect of temperature which is the cause of shape reconstruction in the experiments.
Table 17. Comparison of model (DFT) and experimental clusters (Van Hardeveld and Hartog, 1969)

<table>
<thead>
<tr>
<th></th>
<th>Theoretical clusters</th>
<th>Experimental clusters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hemispherical Pt</td>
<td>Tetrahedral Pt</td>
</tr>
<tr>
<td>Cluster size</td>
<td>1.0 nm</td>
<td>1.0 nm</td>
</tr>
<tr>
<td>Total number of atoms</td>
<td>21</td>
<td>20</td>
</tr>
<tr>
<td>Number of surface atoms</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>Dispersion (N\text{surface}/N\text{total})</td>
<td>0.76</td>
<td>0.95</td>
</tr>
<tr>
<td>Percentage of edge and corner atoms in total atoms</td>
<td>57%</td>
<td>80%</td>
</tr>
<tr>
<td>Percentage of edge and corner atoms in surface atoms</td>
<td>75%</td>
<td>84%</td>
</tr>
</tbody>
</table>

Values in Table 17 are determined based on statistics of surface atoms given in Van Hardeveld and Hartog (1969). The number of surface atoms in this table does not include the atoms on the bottom of the clusters. It is assumed that bottom layers are in contact with the support and are not available for reaction. Accordingly, for the Pt tetrahedron, it is assumed that one face of the tetrahedron lays flat on the support and the rest three faces are available for reaction. Fraction of edge and corner sites in experimental clusters is much smaller than in the model clusters. Round Pt clusters made by polyol method contain the highest percentage of uncoordinated Pt surface sites (of three examined samples, Table 17) which explains their highest initial activity. However, as shown in Figure 64, those nanoclusters are not stable and loose activity fast.
On average, a big experimental tetrahedral Pt cluster has much smaller percentage of these sites than a experimental round Pt nanocluster. Despite smaller fraction of low-coordinate surface atoms, tetrahedral Pt on ceria had similar activity as the round Pt samples (IW). This might indicate that those surface sites on tetrahedrons are more active and that their interaction with the surrounding oxygen vacancies on ceria is stronger than on smaller round Pt clusters. This activity of surface atoms can be presented by normalizing the H₂ evolution rates with respect to the fraction of surface atoms (dispersion) and expressing in terms of turn-over-frequency (TOF) defined as:

\[
\text{TOF} = \frac{\text{Rate} \cdot M_w}{\text{Dispersion}}
\]

(23)

where dispersion is determined as (shown in the above Table 2) the fraction of surface atoms in the total. This assumes that all Pt atoms on the surface are available for reaction (i.e., are not covered by the capping agent). That gives us the lower limit for TOF. Also, we know that only 65% of the Pt nanoparticles are tetrahedral, so that the remainders have irregular shapes. Hence, dispersion for tetrahedral Pt sample can be estimated as a weighted sum of 65% tetrahedral clusters of 7 nm size \(D_{\text{tetra}} = 0.29\) and 35% of round clusters of 7 nm in size \(D_{\text{round}} = 0.15\), just as a rough estimate:

\[
D_T = 0.65 \cdot D_{\text{tetra}} + 0.35 \cdot D_{\text{round}}
\]

(24)

\[
D_T = 0.24
\]

(25)

Results expressed in this way are shown in Figure 65.
Figure 65 indicates that although the catalyst sample with tetrahedral Pt has a smaller fraction of surface atoms, and a much smaller percentage of edge and corner sites, these low coordinated sites are more active than the corresponding sites of the round Pt nanoparticle catalysts. If even smaller tetrahedral Pt clusters could be prepared and more importantly - made stable under reaction conditions, their activity would be even higher.

5.4. Conclusions

The objective of these experiments was to investigate the effect of Pt nanocluster shape on methane activation. Earlier work by Cheng et al. (2012) indicated that tetrahedral Pt nanoparticles containing higher fractions of edge and corner sites may enhance methane adsorption, and that the structure of the support also plays a very important role. To validate their model, colloidal tetrahedral Pt
nanoparticles were successfully synthesized following the protocol of Lee et al. (2008). However, experimental Pt clusters were much bigger (7nm) than the model clusters (1 nm); thus they contained a smaller fraction of low coordinated active sites. These colloidal nanoparticles were then successfully deposited onto silica powder and ceria powder. TEM analysis on ceria supported samples was difficult because dark CeO$_2$ contrast obscured the profile of precious metal particle. Samples containing round Pt nanoparticles were synthesized by modified polyol method and used for comparison with tetrahedral ones. Round Pt/ceria prepared by incipient wetness method was also compared. The activity of the catalysts was tested in a laboratory scale packed bed reactor in the temperature range 200$^\circ$C - 450$^\circ$C. Catalyst performance was compared based on the rates of H$_2$ evolution during 10 min exposure to methane flow.

Experimental tetrahedral clusters, 7 nm in size, had similar activity as the round Pt nanoclusters, 2.6 nm in diameter (made by incipient wetness). Their activity was compared only for reaction at 350$^\circ$C because below that temperature H$_2$ evolution was hardly detected on round Pt nanoclusters. This may indicate that tetrahedral clusters might be more active at temperatures below 350$^\circ$C. However, under the reaction conditions tetrahedrons were not stable- they lost their shape and became round. New preparation methods that will prevent surface reconstruction would have to be developed.

For all tested samples, increase in temperature increased H$_2$ evolution rate and therefore CH$_4$ activation. Also, for all sample, H$_2$ evolution dropped within first 2 minutes of catalyst exposure to the CH$_4$ flow. This result is in accordance with the previous observations on round Pt and Pd catalysts (Belgued et al., 1996; Ding et al., 2007) Amounts of evolved H$_2$ were very low but are comparable to the values reported in literature (Belguet et al. 1996; Ding et al. 2007).
Strong effect of the support on the activity of tetrahedral Pt nanoclusters has been observed. Ceria supported catalyst was more than 2 times more active than silica based catalyst. This is in accordance with the results presented in Chapter 5 and the findings of Cheng et al. (2012) which all indicate the presence of strong metal support interaction between Pt and ceria which lowers the activation barrier for CH₄ activation. Future modeling efforts should include the effect of temperature, as well as the effect of nanocluster size.

Acquiring the tools for enhancing catalyst activity and selectivity by controlling Pt nanoparticle size and shape with the help of first principle analysis is of great importance and its potential needs further investigations. Taking into account the price of noble metals, a viable option for commercial use, the amount of Pt used on the catalyst support should be used as effectively as possible meaning achieving highest possible catalyst efficiency. Results presented here suggest that smaller Pt clusters that contain higher fraction of low coordinated sites can enhance CH₄ activation at temperatures lower than 350°C. However, new synthesis methods would need to be developed that would enhance Pt clusters stability and prevent reconstruction of their shape. Important question to also be addressed in the future is how these, shaped, Pt nanoparticles affect the distribution of CHₓ species on the catalyst surface, their reactivity with CO₂ and consequently selectivity towards desired products. Protocol described in the Chapter 4 for studying the state of adsorbed carbon film, could not be applied here because of the instability of these shaped particles.
6. Conclusions and recommendations

The presented work contributes to the development of an integrated approach in catalyst design involving both experimental and theoretical aspects of the studied heterogeneous catalytic reaction. An integrated method involving both experimental and modeling efforts enables more rational design of new materials with improved activity and selectivity and could potentially cut the costs and duration of extensive “trial-and-error” approach commonly practiced in industry. The possibility of tailoring catalyst activities and selectivities through shape and size control could lead to the more efficient catalyst utilization.

The objective of the work was to develop a bifunctional heterogeneous catalyst for a low temperature (200°C - 450°C) direct conversion of methane and carbon dioxide. It is considered that in this reaction, there are two limiting steps: methane activation, which is the focus of this research effort, and insertion of CO₂ molecule. Optimization of the structure of two components of the catalyst, metal active center and the support, could enhance catalyst activity and selectivity towards desired commodity chemicals and help identify the critical reaction mechanisms on the catalyst surface that still remain largely unknown.

Structure and composition of the metal cluster and the catalyst support were selected based on molecular modeling and DFT analysis (Cheng et al., 2012, 2013). DFT findings (Cheng et al., 2013) showed that ceria is a promising catalyst for the reduction of carbon dioxide in part because of its high oxygen storage capacity. On the other hand, they found that tetrahedral Pt nanocluster, containing higher fraction of low coordinated surface Pt atoms, adsorbs CH₄ more strongly than the corresponding
hemispherical Pt cluster. In addition, adding ceria as a support to their model cluster, further lowered the energy barrier for CH₄ activation.

To validate this model, colloidal tetrahedral Pt nanoparticles in solution first had to be prepared and then deposited onto the support. Colloidal tetrahedral Pt nanoclusters were successfully synthesized by carefully adjusting the concentration ratio between the Pt precursor salt and the capping polymer. Resulting experimental Pt clusters were much bigger (7 nm) than the model clusters (1 nm); thus they contained a smaller fraction of low coordinated active sites. Furthermore, 65 ± 8% of colloidal Pt nanoparticles in the solution had tetrahedral shape. The remaining particles were either truncated tetrahedral, “near spherical”, or completely irregular in shapes. Synthesis of ceria nanorods exposing targeted, more easily reducible, (110) and (100) facets, was performed by hydrothermal method in the autoclave, as described in Zhou et al. (2005). Nanorods’ dimensions were around 93 ± 30 nm in length and 12 ± 3 nm width.

Deposition of colloidal tetrahedral nanoparticles onto three different supports: silica powder, ceria powder and ceria nanorods was performed by simple mixing. Silica was used as a baseline for the comparison. Tetrahedral Pt nanoparticles were successfully deposited onto silica and ceria powder. However, only silica supported sample could be imaged with TEM because the dark CeO₂ contrast obscured the profile of the Pt nanoparticles. Deposition onto ceria nanorods was not successful and the difficulty might be attributed to the nanorods not being long enough to “hold” Pt tetrahedrons. To achieve nanorod structures that could possibly provide increased stability for big Pt tetrahedrons, further optimization of the operating parameters in the autoclave reactor is needed.
Consequently, only tetrahedral Pt supported on silica and ceria powders were used in this work. For comparison, conventional round shape Pt catalysts were prepared by standard incipient wetness method and modified polyol method. Our results for catalyst preparation confirmed the intrinsic complexity of the shape- and size- controlled synthesis strategies. Applied preparation methods are strongly affected by numerous operating conditions (reagent concentrations, concentration ratios, pH, temperature etc.) and further trial-and-error investigations should be done to find the right set of conditions that would results in desired structures. Conditions that would enable preparation of smaller tetrahedral nanoclusters that would be stable in the solution and would not aggregate need to be determined. Also, a higher purity and uniformity of the colloidal nanoparticles that have desired shape has to be achieved.

Conventional round shaped Pt, prepared by incipient wetness, were first tested in a small packed bad reactor to study the effect of the support on the methane activation and after that, the effect of Pt cluster shape was investigated. Methane activation is the first limiting step in its reaction with carbon dioxide. One way to overcome the thermodynamic barrier in this process is the periodic operation during which a catalyst is first exposed to CH₄ flow after what CO₂ is introduced to react with adsorbed carbonaceous species (Ding et al., 2007). Structure of the adsorbed carbonaceous CHₓ (x = 0, 1, 2, 3) species, formed upon the methane chemisorption on the catalyst surface, strongly affects their reactivity with CO₂ and selectivity towards desired oxygenates (i.e., acetic acid).

It is concluded that all investigated factors: support, temperature, CH₄ partial pressure and Pt loading, have strong effect on the amount of chemisorbed methane. Results for both ceria and silica samples, have shown that the increase in the reaction temperature increases the amounts of chemisorbed methane. H₂ evolution, which occurs as a result of CH₄ chemisorption, also increases with the increase of
temperature. Increase in CH₄ partial pressure in the inlet flow also causes an increase in the total amount of chemisorbed methane, for both ceria and silica based samples. Results also confirmed that smaller Pt nanoparticles (in the sample with smaller Pt content) are more active for CH₄ conversion which is explained by the presence of the low coordinated Pt surface atoms with increased electron density that favors CH₄ activation.

Results have shown that, within the operating range, neither reaction temperature, CH₄ partial pressure nor Pt loading, have significant effect on the structure of the adsorbed CH₄ species formed during 1 minute of exposure to the CH₄ flow. It was found that, upon the exposure to the CH₄ flow, only hydrogen deprived carbon species remained on the catalyst.

Comparison between ceria and silica supported samples revealed that the strong metal-support interaction and the presence of high concentration of oxygen vacancies at the interfacial areas around Pt, a characteristic for ceria supported samples, had a pronounced impact not only on the total amount of chemisorbed CH₄, but also on the structure of the adsorbed carbon film. This effect was more pronounced at higher temperatures (400°C, 450°C), at which Pt/ceria had more than 5 times higher activity than the Pt/silica. At those temperatures, the adsorbed hydrogen-deprived carbon species were more loosely bound to ceria than to silica supported catalysts. On the other hand, at lower reaction temperatures (200°C, 300°C), the total amounts of CH₄ converted were similar and the adsorbed carbonaceous species were more loosely bound to the Pt/silica surface and hence more reactive than on Pt/ceria. While all adsorbed carbon species desorbed from ceria samples at fairly uniform temperatures, multiple desorption peaks were observed on silica sample, indicating different bond strengths between carbon and Pt/silica surface or the existence of different kinds of carbon. Another indication of different nature of the adsorbed carbonaceous species between two samples is that, although in very small
amounts, some hydrogen rich CH₄ species have been detected on Pt/silica while on ceria, there is none detected, under all operating conditions that were used in this work.

Further studies need to be done to investigate the reactivity of adsorbed carbonaceous species with CO₂ in a periodic catalyst operation. Duration of the cycle has been determined based on the maximum H₂ evolution rate during the exposure of the catalyst to the CH₄ flow. Catalyst would cycle between CH₄ and CO₂ flow for 1 minute each, and distribution of different oxygenates would be determined. Based on our findings, if operating at temperatures up to 300°C, silica would be a better choice of a support for the Pt catalysts prepared by incipient wetness method, because at these lower temperatures, adsorbed carbonaceous species are more loosely bonded to the catalyst surface and hence, more reactive. Furthermore, higher concentration of hydrogen rich species, detected in very small amounts on Pt/silica, may enhance the selectivity towards the desired oxygenates. At temperatures above 300°C, ceria would be the better choice, because under those conditions, Pt/ceria is much more active and the adsorbed carbon species are less loosely bound than on Pt/silica. However, further experiments involving CO₂ are required to make a definite decision on which catalyst would achieve higher selectivity towards desired product.

The effect of Pt nanocluster shape was studied by comparing the performance of tetrahedral and round Pt nanoparticles supported on ceria and silica powders, by tracking H₂ evolution rates during the 10 minute exposure to the CH₄ flow in a small packed bed reactor. Activity of the tetrahedral Pt/ceria at 350°C was very similar to the activity of round Pt/ceria made by incipient wetness although experimental tetrahedral clusters were much bigger (7 nm) than the round Pt clusters (2.6 nm) and therefore contained less low-coordinated surface sites. In addition, for tetrahedral Pt/ceria H₂ evolution
was detected already at 200°C, while on round H₂ there was no consistent H₂ observation below 350°C indicating higher activity of supported tetrahedral Pt nanoclusters than conventional round Pt catalysts. TEM images of tetrahedral Pt/silica samples taken after the reaction, have shown that Pt nanoclusters lost their tetrahedral shape and became round. TEM imaging of ceria supported samples was difficult, as mentioned earlier, so the loss of shape could not be verified. However, there was no observed deactivation which might also mean that the particles might have lost their shape very soon upon reaching higher temperatures (350°C and above).

Further experiments are necessary to examine the effect of Pt shape on the distribution of CHₓ species during the exposure to the CH₄ flow. Protocol used for determining the structure of carbonaceous film on conventional round samples, could not be applied on tetrahedral nanoclusters due to their temperature sensitivity. This information is crucial in determining the desired CHₓ intermediates (CH₃, CH₂, CH, or C) that react with CO₂ to produce certain oxygenates and hence advance the knowledge about the reaction mechanism. Accordingly, H₂ evolution rates might not be the right criteria for the catalyst selection. Additional experiments should involve introduction of CO₂, in a periodic fashion, as explained earlier, to investigate the reactivity of adsorbed carbon species with CO₂ and the product distribution.

For both tetrahedral and round supported Pt samples, the increase in temperature resulted in the increase of H₂ evolution rates, and consequently CH₄ conversion rates. Ceria supported tetrahedral Pt catalyst was more than 2 times more active than silica based catalyst at 300°C and 350°C, further confirming the promoting effect of ceria shown in previous experiments with round Pt.
In order for the shaped nanoparticles to reach any practical application, new preparation methods that will prevent surface reconstruction would have to be developed. There have been some recent attempts to protect the surface atoms, by, for example, encapsulating Pt atoms into mesoporous silica shell which enable high temperature CO oxidation studies or by the coating of silver nanoprisms edges with thin layer of gold film in order to protect them against etching by chloride (Aherne et al., 2009). Perhaps, instead of so-called “bottom-up” approach, “top down” preparation method could give some promising results in the future. For example, the electrochemical synthesis of tetrahedral Pt nanoparticles, stable up to 800°C, from Pt nanospheres by applying square-wave potential, has been reported (Tian et al., 2007). Although their specific activity (per surface mass) is high, the mass activity of resulting clusters is small due to their size (200 nm). Due to high cost of noble metals, both size and shape of Pt clusters should be optimized.

In addition to the developments of new preparation techniques, one other way of trying to extend the stability of catalysts structure is to run the reaction at lower temperatures while still achieving the acceptable levels of activities and selectivities (Linic and Christopher, 2010). Although, all the materials tested in this work, exhibit activities comparable to those reported in the literature (Belgued et al., 1996; Ding et al., 2007; Martins et al., 2007), these values are still far from any practical application. For all tested samples, H₂ evolution rates reach their maximum in the first minute of the exposure to the CH₄ flow, which would be an optimum time to introduce CO₂ into the system to react with the adsorbed surface species. Future studies should investigate the reactivity of the adsorbed surface species with the CO₂ and the selectivities towards desired oxygenates. Due to time constraints, these studies were not done in this work.
The application of a more sophisticated measurement in situ/spectroscopic technique could provide better insights into the state of the catalytic material and the structure of the intermediate species. On the other hand, modeling efforts should be dedicated towards understanding the effect of cluster size, as well as the temperature, to bring the findings closer to the “real” conditions and bridge the gap between idealistic models and real catalytic systems. Of course, this depends on the available computational powers. Despite these limitations, molecular modeling analysis, advance preparation and characterization methods together provide a powerful tool in the development of new, more selective heterogeneous catalysts.
Appendix A. Chemisorption results

A.1. Chemisorption results for 1.7% Pt/CeO₂

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Data Reduction Parameters

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<thead>
<tr>
<th>Gas Parameters</th>
<th>Metal Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name: Hydrogen</td>
<td>Name: Platinum</td>
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<tr>
<td>Mol. Weight: 2.165 g/mol</td>
<td>Mol. Weight: 195.08 g/mol</td>
</tr>
<tr>
<td>Cross Section: 10.41 Å/mol</td>
<td>Surf.Area: 8 Å Atom</td>
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<tr>
<td>Crit. Density: 1 gcc</td>
<td>Density: 21.45 g/cc</td>
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<td>Crit. Temperature: 5.2 K</td>
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<tr>
<td>Metal Loading: 1.71 %</td>
<td>Stoichiometry: 2</td>
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</table>

Extrapolation summary

- Active Metal Surface Area (per gram of sample) = 2.883 m²/g
- Active Metal Surface Area (per gram of metal) = 165.055 m²/g
- Percent Metal Dispersion = 67.557 %
- Average Crystallite Size = 15.76 Å
- Slope = 0.00091
- Y_intercept = 0.86366
- Correlation coefficient = 0.99978
- Monolayer Uptake (Nm) = 29.606 µmol/g
Extrapolation on Strong/Difference

Data Reduction Parameters

Gas Parameters

Name: Hydrogen
Mol.Weight: 2.016 gmol
Cross Section: 10.41 Å²/mmol
Crt. Density: 1 g/cm³
Crt. Temperature: 52 K
Metal Loading: 1.71 %

Metal parameters

Name: Platinum
Mol.Weight: 195.08 gmol
Surf.Area: 8 A²/atom
Density: 21.45 g/cm³
Shape Factor: 8
Stoichiometry: 2

Extrapolation summary

Active Metal Surface Area (per gram of sample) = 187.1 m²/g
Active Metal Surface Area (per gram of metal) = 189.416 m²/g
Percent Metal Dispersion = 44.301 %
Average Crystallite Size = 25.565 Å
Slope = 0.00016
Y - intercept = 0.4326
Correlation coefficient = 0.9988
Monolayer Uptake (N㎡) = 15.414 µmol/g
A.2. Chemisorption results for 0.3% Pt/CeO₂

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Extrapolation on Combined

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<td>Mol.Weight :</td>
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<tr>
<td>Cross Section</td>
<td>Surf.Area :</td>
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<tr>
<td>Crit.Density</td>
<td>Density :</td>
</tr>
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<td>Metal Loading</td>
<td>Stoichiometry :</td>
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Extrapolation summary

Active Metal Surface Area (per gram of sample) = 8.801 m²/g
Active Metal Surface Area (per gram of metal) = 235.441 m²/g
Percent Metal Dispersion = 95.329 %
Average Crystallite Size = 11.881 Å
Slope = 0.00035
Y - intercept = 0.19820
Correlation coefficient = 0.99691
Monolayer Uptake (Nm) = 8.306 μmol/g
Extrapolation on Strong/Difference

Extrapolation summary:
- Active Metal Surface Area (per gram of sample) = 0.458 m²/g
- Active Metal Surface Area (per gram of metal) = 146.440 m²/g
- Percent Metal Dispersion = 59.292%
- Average Crystallite Size = 19.101 Å
- Slope = 0.00007
- Y-intercept = 0.11581
- Correlation coefficient = 0.99563
- Monolayer Uptake (nm) = 5.166 μmol/g
A.3. Chemisorption results for bare ceria

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<td>Comment:</td>
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<td>Sample Weight:</td>
<td>Analysis Metod:</td>
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<td>Analysis Gas:</td>
<td>Instrument:</td>
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<td>0.9400 g</td>
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<td>Hydrogen</td>
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![Graph showing chemisorption results](image-url)
Combined Data

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Treatment Macro
1. Change Gas to #3: Hydrogen
2. Ramp Temp To 400.00 deg @ 10.0 deg/min
3. Flow until SetPoint
4. Flow Gas for 120 min
5. Evacuate for 120 min
6. Force Cool Furnace to 40 deg (Evacuate, Stabilize)
7. End Macro

Weak Data

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A.4. Chemisorption results for 1.7% Pt/SiO₂

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Acquisition and Reduction
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version 3.0

Analysis
Operator/Lab: 1.7% Pt/SiO₂
Sample ID: From Pt(NH₃)₄(NO₃)₂
Sample Weight: 0.4736 g
Analysis Time: 100.1 min
Analysis Gas: Hydrogen

Report
Operator: Universität von Washington, 1.7 pct Pt/SiO₂, Lab #998
Date: 2013/05/06
Comment: University of Washington St. Louis, Lab #998
Date: 2013/05/07

Extrapolation on Combined

Data Reduction Parameters

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<td>Mol. Weight: 2.015 g/mol</td>
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<td>Cross Section: 10.41 Å nmol</td>
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<td>Stoichiometry: 2</td>
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Extrapolation summary

- Active Metal Surface Area (per gram of sample) = 2.660 m²/g
- Active Metal Surface Area (per gram of metal) = 196.487 m²/g
- Percent Metal Dispersion = 63.350 %
- Average Crystallite Size = 17.875 Å
- Slope = 0.00026
- Y-Intercept = 0.61978
- Correlation coefficient = 0.99773
- Monolayer Uptake (Nm) = 27.604 μmol/g
Extrapolation on Strong/Difference

### Data Reduction Parameters

**Gas Parameters**
- **Name:** Hydrogen
- **Mol. Weight:** 2.016 g/mol
- **Cross Section:** 10.41 Å²/mol
- **Crit. Density:** 1 g/cc
- **Crit. Temperature:** 5.2 K
- **Metal Loading:** 1.70 %

**Metal parameters**
- **Name:** Platinum
- **Mol Weight:** 195.08 g/mol
- **Surf. Area:** 8 A²/atom
- **Density:** 21.45 g/cc
- **Shape Factor:** 6
- **Stoichiometry:** 2

---

**Extrapolation summary**
- Active Metal Surface Area (per gram of sample) = 1.705 m²/g
- Active Metal Surface Area (per gram of metal) = 105.696 m²/g
- Percent Metal Dispersion = 42.759 %
- Average Crystallite Size = 26.497 Å
- Slope = 0.00002
- Y - intercept = 0.41759
- Correlation coefficient = 0.96039
- Monolayer Uptake (Nm) = 18.629 μmol/g
Appendix B. Statistics of surface atoms on metal crystals

Figure 66. Model representation of a f.c.c. cubo-octahedron for m=4 (on the left) and f.c.c. tetrahedron for m=9 (on the right, Van Hardeveld and Hartog, 1969)

Table 18. Formulae for the numbers of different surface atoms for f.c.c. cubo-octahedron (Van Hardeveld and Hartog, 1969)

<table>
<thead>
<tr>
<th>m</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tbody>
<tr>
<td>N_{T}</td>
<td>225</td>
<td>688</td>
<td>1529</td>
<td>2844</td>
<td>16m^{3} - 3m^{2} - 108m + 144</td>
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<tr>
<td>N_{B}</td>
<td>87</td>
<td>370</td>
<td>965</td>
<td>1974</td>
<td>16m^{3} - 33m^{2} - 84m + 120</td>
</tr>
<tr>
<td>N_{S}</td>
<td>138</td>
<td>318</td>
<td>564</td>
<td>870</td>
<td>30m^{3} - 24m - 66</td>
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<tr>
<td>N(C_{4}^{9,10})</td>
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<td>0</td>
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<tr>
<td>N(C_{5}^{5})</td>
<td>24</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N(C_{6}^{6})</td>
<td>24</td>
<td>72</td>
<td>96</td>
<td>96</td>
<td>96</td>
</tr>
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<td>N(C_{7}^{7})</td>
<td>24</td>
<td>72</td>
<td>120</td>
<td>192</td>
<td>24(3m-10)</td>
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<td>N(C_{8}^{8})</td>
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<tr>
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<td>0</td>
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<td>6(m-5)^{2}</td>
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<td>N(C_{9}^{4})</td>
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<td>24(m-3)^{2}</td>
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<td>N(C_{10})</td>
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<td>N(C_{11})</td>
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<td>48</td>
<td>72</td>
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Table 19. Formulae for the numbers of different surface atoms for f.c.c. tetrahedron (Van Hardeveld and Hartog, 1969)

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<tr>
<td>$N_B$</td>
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<td>0</td>
<td>0</td>
<td>1</td>
<td>$\frac{1}{6}(m-4)(m-3)(m-2)$</td>
</tr>
<tr>
<td>$N_s$</td>
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<td>10</td>
<td>20</td>
<td>34</td>
<td>$2m^2-4m+4$</td>
</tr>
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<td>$N(C_6^{10})$</td>
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<td>12</td>
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<td>2(m-2)(m-3)</td>
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</table>

$N_T$ is total number of atoms, $N_B$ is number of bulk atoms, $N_s$ is number of surface atoms and $j$ in $C_j$ is the number of nearest neighbors.
References


II. Hydrogenation of the adspecies resulting from the chemisorption of methane. *Journal of Catalysis, 159*, 441-448


44. IEA statistics, CO₂ emissions from fuel combustion, 2009 edition.


Vita

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Degrees
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Professional Societies
American Institute of Chemical Engineers
American Chemical Society

Presentations
Havran, V., Duduković, M., Lo, C. Catalyst development for direct conversion of methane and carbon dioxide to higher value products, Oral presentation at the 2012 ACS Annual Meeting, San Diego, CA (2012)

Havran, V., Duduković, M., Lo, C. Catalytic conversion of methane and carbon dioxide to higher value products, Oral presentation at the 2011 AIChE Annual Meeting, Minneapolis, MN (2011)

Havran, V., Duduković, M., Lo, C. Catalyst development for direct conversion of CH4 and CO2 to higher value products, Poster presentation at the 22nd North American Catalysis Society Meeting, Detroit, MI (2011)

Havran, V., Duduković, M., Lo, C. Catalyst development for direct conversion of CH4 and CO2 to higher value products, Poster presentation at the Catalysis Club of Chicago Symposium, Naperville, IL (2011)

Havran, V., Duduković, M., Gleaves, J., Lo, C. Multiscale Analysis of CH4 and CO2 Conversion, Poster presentation at the 14th Graduate Student Research Symposium, St. Louis, MO (2011)

Havran, V., Duduković, M., Gleaves, J., Lo, C. Multiscale Analysis of CH4 and CO2 Conversion, Poster presentation at the 3rd International Symposium on Energy and Environment, St. Louis, MO (2010)
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