

Ab-Initio DFT Modeling of the Oxidation of Methane on Transition Metal Catalysts

by

George Psfogiannakis

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George Psfogiannakis

AUTEUR DE LA THÈSE / AUTHOR OF THESIS

Ph.D. (Chemical Engineering)

GRADE / DEGREE

Department of Chemical Engineering

FACULTÉ, ÉCOLE, DÉPARTEMENT / FACULTY, SCHOOL, DEPARTMENT

Ab-Initio DFT Modeling of the Oxidation of Methane on Transition Metal Catalysts

TITRE DE LA THÈSE / TITLE OF THESIS

Marten Ternan

DIRECTEUR (DIRECTRICE) DE LA THÈSE / THESIS SUPERVISOR

Alain St-Amant

CO-DIRECTEUR (CO-DIRECTRICE) DE LA THÈSE / THESIS CO-SUPERVISOR

EXAMINATEURS (EXAMINATRICES) DE LA THÈSE / THESIS EXAMINERS

Yan Alexander Wang

Javier B. Giorgi

Dr. Marc Dube

Jason Zhang

Gary W. Slater

Le Doyen de la Faculté des études supérieures et postdoctorales / Dean of the Faculty of Graduate and Postdoctoral Studies

STATEMENT OF CONTRIBUTIONS OF COLLABORATORS

I hereby declare that I am the sole author of this thesis. My supervisors, Professor Marten Ternan in the department of Chemical Engineering, and Professor Alain St. Amant in the department of Chemistry at the University of Ottawa, have provided excellent collaboration throughout this research program. Their helpful comments, suggestions and editorial corrections have significantly improved the quality of this thesis.

Signature :

Date: Sept 21, 2007

ABSTRACT

Quantum-mechanical Density Functional Theory (DFT) calculations were performed in order to study catalytic aspects of the oxidation of methane on transition metal catalysts. Metal clusters were used to model the metal surfaces. The work is related to two different systems: the first is the direct electrocatalytic oxidation of methane in fuel cells to produce electrical power. The second is the steam-reforming of methane to produce synthesis gas. Both processes involve the adsorption, dissociation and transformation of methane and water on the surface of a metal catalyst.

The work was divided into three parts. In the first part, the mechanism of electro-oxidation of methane on a Pt(111) surface was studied. The activation energies of surface reactions that correspond to a general reaction network were computed with cluster DFT methods. The network included many reaction pathways from the dissociative chemisorption of methane up to adsorbed CO. The surface reactions included dehydrogenation reactions of adsorbed CH_x species and oxidation of these species by adsorbed OH. It was found that the main reaction pathway is $\text{CH}_4 \rightarrow * \text{CH}_3 \rightarrow * \text{CH}_2 \rightarrow * \text{CH} \rightarrow * \text{CHOH} \rightarrow * \text{CHO} \rightarrow * \text{CO}$, where * denotes an adsorbed species. Frequency analysis and transition-state theory were employed to show that the methane chemisorption elementary step, the first step in the above pathway, is rate-limiting. As a first approximation, electrolyte effects were not included in the model.

In the second part of the work, the dissociative chemisorption of methane on the transition metal catalysts Ru, Rh, Pd, Os, Ir and Pt was studied using cluster DFT methods. The

objective was to explore trends in the reactivity of these metals towards dissociating methane as well as the structure-sensitivity of the reaction. Different clusters were used to simulate close-packed, adatom and step sites. Reaction coordinate calculations were performed. It was found that for terrace sites the energy barrier was lowest for Ru, and was higher for metals with higher d-band occupancy. It was also found that for adatom and step sites, the energy barriers for the 5d metals Os, Ir, Pt were significantly lower than those for the 4d metals Ru, Rh, Pd. A Natural Bond Orbital analysis was performed to identify the reasons for the different reactivity of a Pt and a Ru ad-atom.

In the third part of the work, the dissociation of water on the close-packed surfaces of Ru, Rh, Pd, Os, Ir, Pt and a Pt-Ru alloy, was studied using cluster DFT methods. Reaction coordinate calculations were performed and the results identified trends in the energy barriers and binding energies. The energy barrier for water dissociation was smaller for Ru and Os, and increased for metals with increased d-band occupancy. The binding energy of OH was lowest on Pt among all metals that were used. The weaker binding of OH on Pt suggests that OH is more reactive on Pt and occupies a smaller fraction of surface sites. This explains the experimentally observed higher reactivity of Pt in electrooxidizing methane, compared to other metals. On the other hand, by comparing the model predictions with steam-reforming experimental data, it was found that the trends in the reactivity of transition metals can be either determined by the energy barrier for methane dissociation or the binding energies of the dissociated water species.

RESUME

Afin d'étudier la catalyse de l'oxydation du méthane par les métaux de transition, nous avons fait des calculs quantique dans le cadre de la théorie de la fonctionnelle de la densité (DFT). Des agrégats ont été utilisés pour modéliser la surface métallique. Ce travail se relie à deux systèmes importants. Le premier est l'oxydation électrocatalytique directe du méthane dans des piles à combustibles afin de produire l'électricité. Le deuxième est la production du gaz synthèse à partir de la vapeur d'eau et du méthane. Chaque processus implique l'adsorption, la dissociation, et la transformation du méthane et de l'eau sur la surface d'un catalyseur métallique.

Ce travail est séparé en trois parties. La première partie étudie le mécanisme de l'électro-oxydation du méthane sur une surface Pt(111). Les énergies d'activation des diverses réactions possibles sur cette surface ont été estimées avec l'aide des calculs DFT. Le réseau de réactions ainsi produit a fourni plusieurs trajectoires qui relient la chimisorption dissociative du méthane à l'adsorption du CO. Ces réactions incluent la déshydrogénation des espèces CH_x et l'oxydation de ces mêmes espèces par le OH adsorbé à la surface. Nous avons trouvé que le trajectoire principal est $\text{CH}_4 \rightarrow * \text{CH}_3 \rightarrow * \text{CH}_2 \rightarrow * \text{CH} \rightarrow * \text{CHOH} \rightarrow * \text{CHO} \rightarrow * \text{CO}$. Des analyses vibrationnelles et la théorie de l'état de transition démontrent que la chimisorption du méthane, soit la première étape de la réaction globale, est l'étape limitante du mécanisme.

Dans la deuxième partie, la chimisorption dissociative du méthane sur les surfaces du Ru, Rh, Pd, Ps, Ir, et Pt a été modélisé par nos calculs DFT sur des agrégats de ces métaux. Le but principal est d'explorer les tendances dans la réactivité de ces métaux envers la

dissociation du méthane ainsi que la variation dans les structures des intermédiaires et des états de transition. Des agrégats différents ont été utilisés pour modéliser divers sites sur une surface métalliques. Plusieurs coordonnées de réaction ont été suivies. Pour des sites terrasses, la barrière énergétique est plus petite pour le Ru et est plus haute pour des métaux avec une plus grande population d'électrons d. Pour des sites adatomiques et des sites marches, la barrière énergétique est plus basses pour les métaux 5d tels que Os, Ir, et Pt que pour les métaux 4d tels que Ru, Rh, et Pd. Une analyse des orbitales naturelles nous aide à identifier les raisons pour la réactivité diffère entre Pt et Ru pour un site adatomique.

Dans la troisième partie, la dissociation de l'eau sur les surfaces de Ru, Rh, Pd, Os, Ir, Pt, et un alliage Pt-Ru est étudiée par des calculs DFT sur des agrégats de ces métaux. Notre analyse des réactions nous aide à identifier les tendances dans les barrières énergétiques et les énergies d'adsorption. La barrière énergétique pour la dissociation de l'eau est plus petite pour Ru et Os, et elle augmente avec la population de la bande d. L'énergie d'adsorption de OH est la plus petite pour Pt. Cette petite valeur suggère que le OH est plus réactif sur le Pt et que le OH occupe une plus petite fraction des sites à la surface de Pt. Ceci expliquerait l'observation expérimentale que le Pt est le métal le plus réactif pour l'électro-oxydation du méthane. La comparaison de nos résultats théoriques avec les résultats expérimentaux pour la production du gaz synthèse indique que la réactivité des métaux de transition peut s'expliquer soit par la barrière énergétique pour la dissociation du méthane ou soit par l'énergie d'adsorption de H et de OH (les produits de la dissociation de l'eau).

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TABLE OF ACRONYMS

AFC:	Alkaline Fuel Cell
B3LYP:	Becke, 3 parameter, Lee-Yang-Parr functional
BEP:	Brønsted – Evans – Polanyi
DFT:	Density Functional Theory
DHFC:	Direct Hydrocarbon Fuel Cell
DMFC:	Direct Methanol Fuel Cell
ECP:	Effective Core Potential
FC:	Fuel Cell
HOMO:	Highest Occupied Molecular Orbital
IS:	Initial State
LANL2DZ:	Los Alamos National Laboratory 2-Double-Zeta basis set
LUMO:	Lowest Unoccupied Molecular Orbital
MCFC:	Molten Carbonate Fuel Cell
ML:	Monolayer
NBO:	Natural Bond Orbital
PAFC:	Phosphoric Acid Fuel Cell
PBC:	Periodic Boundary Conditions
PEM:	Polymer Electrolyte Membrane fuel cell
PW91:	Perdue and Wang 1991 functional
QM:	Quantum Mechanics

RHE:	Reversible Hydrogen Electrode
RMS:	Root Mean Square
SM:	Spin Multiplicity
SOFC:	Solid Oxide Fuel Cell
TS:	Transition State
ZPE:	Zero-Point Energy

CHAPTER 1: Introduction

1.1 Research objective / scope

In this research project, quantum-mechanical Density Functional Theory (DFT) calculations were performed to explore catalytic aspects of the oxidation of methane on transition metal catalysts. Metal clusters were used to model the metal surfaces. The work is related to two different systems: the first is the direct electrocatalytic oxidation of methane in fuel cells to produce electrical power. The second is the steam-reforming of methane to produce synthesis gas. Both these processes involve the adsorption, dissociation and subsequent transformation of methane and water on the surface of a metal catalyst. The objective of the project was to use DFT calculations in order to:

- a) explore the reaction mechanism for the electro-oxidation of methane on a platinum catalyst and predict the elementary reactions that determine the overall kinetics
- b) identify trends in the reactivities of various transition metal catalysts towards both the catalytic reforming and electro-oxidation of methane.

This introductory chapter includes a brief overview of fuel cells, in general, and direct hydrocarbon fuel cells, in particular. It also includes a brief overview of steam reforming. The catalytic aspects of these two processes were the general topic of this work. The material presented in the introduction is of general nature, and more extensive literature reviews are given in the introductions of chapters 2, 3, 4. The general overview of fuel cells

in sections 1.2-1.4 summarizes issues discussed in reference 1. The general overview of steam reforming in section 1.6 summarizes issues discussed in references 6 and 7.

1.2 Fuel cells: Principle of operation and structure

A fuel cell^{1a} converts the chemical energy of a fuel directly into electrical energy. The building block of a fuel cell is the unit cell shown in Figure 1:

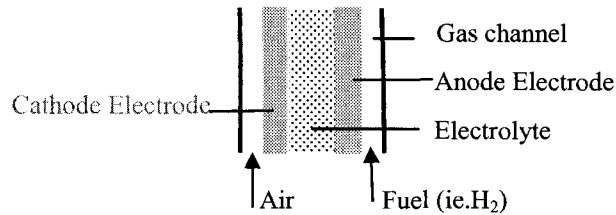


Figure 1: A unit cell

A fuel is supplied to the anode and is electrochemically oxidized. For low-temperature fuel cells, the anodic oxidation reactions, for hydrogen and methane as fuels, are given below:



Air is supplied to the cathode and oxygen is reduced, according to the reaction:



The electrolyte that separates the anode and cathode electrodes serves to transport the ionic current. In a low-temperature fuel cell operating with acid or membrane electrolytes, protons migrate in the electrolyte from the anode to the cathode. As seen from the electrochemical equations above, protons are produced in the anode oxidation reaction and are consumed in the cathode reduction reaction after being transported through the electrolyte. Thus, when the electrodes are connected through an external circuit to an electrical load, an electrical potential difference is set-up between the two electrodes and electric current flows from the anode to the cathode. The circuit is completed with the ionic transport in the electrolyte. As long as fuel and oxidant are continuously supplied to the electrodes, electric current is generated. This is the principle of operation of a fuel cell. The exit gas from the cathode electrode is air (depleted in O_2) and water vapor. The exit gas from a hydrogen anode will be only any unreacted H_2 . If a carbonaceous fuel is used in the fuel cell, such as methane, CO_2 will be produced in the anode.

In practice, a single cell can deliver very little power. For this reason, unit cells are arranged in series with the anode of one cell in electrical contact with the cathode of a neighboring cell, to form a fuel cell stack. Electrons flow from the anode of a cell to the cathode of a neighboring cell, except for the two end plates. ‘Bipolar plates’ are placed between adjacent cells. They are made of graphite or stainless steel, which are good electrical conductors. These plates have channels cut in them on both sides. The reactant gases pass through the channels, the fuel on one side and the oxidant on the other, and flow over the face of a porous electrode. Thus the terminal voltage that is set up across the two end-plates of the fuel cell is the sum of the voltage differences across each cell.

The electrodes that are being used in proton-exchange membrane fuel cells and phosphoric acid fuel cells are called gas-diffusion electrodes. They are porous and contain platinum or a platinum alloy that acts as a catalyst for the electrochemical reactions. Platinum is dispersed inside the pores of a high-surface-area carbon support that is an electronic conductor. Pores inside the electrode are partly filled with the electrolyte and partly filled with the reactant gases during operation. The fuel is transported to the catalyst sites and the protons are conducted through the electrolyte.

A fuel cell stack is the central part of all fuel cell systems. However, for all types of fuel cells, a large amount of auxiliary equipment is required to make a complete system. These can include pumps or blowers, compressors, power conditioning devices, electric motors, fuel storage systems, reformers and fuel processors, controllers, heat exchangers and humidifiers. Depending on the type of fuel cell, not necessarily all of the above are required.

1.3 Types of Fuel Cells

Different types of fuel cells^{1b} are named after the electrolyte being used. However, there are several other critical differences among the different types. The polymer electrolyte, or else, proton exchange membrane fuel cell (PEM) uses a proton-conducting membrane bonded between porous gas-diffusion electrodes and operates at temperatures 60-120°C. A widely-used membrane is “Nafion” and is based on sulphonated polytetrafluoroethylene. The membrane must be kept hydrated to conduct H^+ ions, so that water management is critical. Platinum is the catalyst in both electrodes. The fuel must have extremely low concentration levels of CO, otherwise the catalyst is poisoned. PEM FCs (PEM fuel cells)

have a wide range of possible applications, including stationary power generation, vehicles and electronic devices. PEMFCs are being used for the oxidation of either hydrogen or methanol fuels.

The alkaline fuel cell (AFC) uses NaOH or KOH solutions as the electrolyte. Even though AFCs are of great historical importance, there is little interest in them today. Also, AFCs cannot be used with any carbonaceous fuel, because the CO₂ that is produced reacts with the electrolyte causing precipitation of carbonate salts in the electrode pores.

The phosphoric acid FC (PAFC) uses a concentrated H₃PO₄ solution as the electrolyte and carbon-supported platinum gas-diffusion electrodes. It can operate at temperatures up to 250°C. Low CO-levels in the feed must be maintained but the requirements are less strict than PEM FC's. The PAFC is commercially used for on-site stationary power generation, or more commonly for heat and power cogeneration, in the range 50 – 200 kW. The technology is mature and units have been installed in factories, businesses, military bases, universities, shopping centers etc.

The same electrochemical reactions take place in the PAFC and the PEM fuel cells. When operating on H₂ fuel, the oxidation reaction in the anode is $[H_2 \rightarrow 2H^+ + 2e^-]$. Air is supplied to the cathode, where oxygen is reduced, according to the reaction $[\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O]$. Protons migrate through the acid or membrane electrolyte from the anode to the cathode.

There are two types of high temperature fuel cells: the molten-carbonate FC (MCFC) and the solid-oxide fuel cell (SOFC). The applications of these fuel cells are mainly in the stationary power generation sector. They can be more effectively used for heat – power cogeneration or in a combined cycle fuel cell-gas turbine (or steam turbine) power plant. MCFCs, SOFCs and PAFCs are competitive technologies for fuel -cell based power plants. High-temperature fuel cells can only be considered as the electrochemical engine of a complete power plant that requires a variety of auxiliary equipment and unit operations.

The molten-carbonate FC operates at 600-700°C and uses a molten salt of alkali (Li, Na, K) metal carbonates as the electrolyte. The charge carrier is the carbonate ion (CO_3^-) and is produced in the cathode, which is fed with O_2 and CO_2 , according to the reaction $[\frac{1}{2}\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^-]$. In the anode, H_2 is oxidized: $[\text{H}_2 + \text{CO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-]$ and CO_2 is normally recycled to the cathode. CO can also be oxidized to CO_2 in the anode, which places no restrictions on the composition of the inlet gas. The high temperature allows the use of less expensive catalysts; nickel is used in the anode and nickel oxide in the cathode.

The solid-oxide FC is a complete solid-state device. The electrolyte is a solid that conducts oxide ions (O^{2-}) in the temperature range 800-1100 °C. Oxygen reduction in the cathode takes place on a semiconductor catalyst, according to $[\frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}]$. H_2 is oxidized in the anode usually on a Ni- Y_2O_3 - ZrO_2 catalyst. The anode also oxidizes any CO present in the feed.

High-temperature fuel cells can also utilize natural gas, which can be fed directly into the fuel cell. In this case, CH_4 is reformed to H_2 inside the cell. Part of the steam required for

the reforming is produced in the anode and the rest is added with the fuel. This type of fuel cell is called internal-reforming. In internal-reforming MCFCs, the reforming catalyst is usually placed in the anode gas channels. In SOFCs, the nickel catalyst promotes steam reforming directly inside the anode electrode. Internal and external-reforming MCFCs and SOFCs are competitive technologies.

MCFCs and SOFCs have some disadvantages. The thermodynamic efficiency limit, calculated as $\Delta G/\Delta H$, for the oxidation of H_2 at high temperatures is much smaller than at lower temperatures, because ΔG decreases as the temperature is increased. At high temperatures, the thermodynamic efficiency limit of hydrogen fuel cells becomes comparable to that of heat engines. Thus, one of the main advantages of fuel cells, high maximum thermodynamic efficiency, is lost. This is compensated by the faster kinetics at high temperatures. However, the potential for improvement, as determined by thermodynamics, is greater for low-temperature fuel cells. High temperatures cause mechanical and thermal stability problems and place severe limitations to the materials that can be used. Fabrication processes for fuel cells are more costly. In MCFCs the electrolyte is corrosive. In SOFCs the electrolyte has relatively low conductivity. The application of high –temperature fuel cells is also generally limited to stationary power generation. The three major advantages of high temperature fuel cells, compared to low-temperature fuel cells, are: 1) they don't need a fuel processor and 2) the heat of the exit gases is more useful and 3) the kinetics are better at high temperatures.

1.4 Fuels for fuel cells

Research and development of fuel cells^{1c} is currently centered on two fuels: hydrogen and methanol. Accordingly, it is valuable to summarize how these fuels are produced and utilized in fuel cells. The largest percentage of hydrogen is currently being produced by steam-reforming of natural gas. Steam reforming is discussed more thoroughly in section 1.5 and in the introduction to Chapter 4. The final product from a reforming reactor always contains H_2 , CO , CO_2 and some un-reacted CH_4 . Steam reforming of methane is very endothermic and requires the supply of large quantities of heat. Another fuel that can be reformed into H_2 is methanol. Fuel processors have been developed for fuel -cell powered cars that operate by reforming methanol in the vehicle's reformer-PEM FC system. The high cost of this process is currently prohibitive for wide-spread commercial use.

Fuel cell researchers and developers have envisioned two possible ways of generating and utilizing H_2 for fuel cells. The first is using a reformer adjacent to a fuel cell, in a reformer-fuel cell system. The second is large-scale H_2 -producing plants and subsequent transportation and storage of H_2 adjacent to a fuel cell. Both approaches have disadvantages that are the main reasons why wide-spread use of fuel cells has not yet been realized, despite intense world-wide development efforts. First, it was found to be a very difficult task to produce, transport and store hydrogen effectively, economically and safely. Second, a reformer that is used adjacent to a fuel cell adds substantially to the FC's cost and size and reduces its overall efficiency.

PEMFCs and PAFCs require very low levels of CO in the H_2 feed, because CO poisons the catalyst. The reformat gas from the reformer contains high CO concentrations and cannot be fed directly to a fuel cell. Thus, the reformer is usually followed by a shift-

reactor, which further converts CO to CO₂. PEM fuel cells are too sensitive to CO and require further fuel processing, usually a selective oxidation reactor. The net effect is that the fuel processing system of low-temperature fuel cells with on-site H₂ production is a very costly and complex process.

Hydrogen for fuel cells can also be produced by electrolysis. Electrolysis is the exact opposite process to what happens in a fuel cell. In order to electrolyze water to produce H₂, we must spend at least the same amount of electrical energy (ideally same), as the electrical energy obtainable from oxidizing the produced H₂ in a fuel cell. Thus, the net process could be advantageous only when surplus hydroelectric power is available, or when electrical energy produced by wind or solar technologies is to be stored.

Another type of fuel cell that is being actively researched and developed nowadays is the direct methanol (CH₃OH) fuel cell (DMFC). DMFCs are targeted towards low-power density applications, such as electronic equipment, laptops, mobile phones etc. DMFCs utilize proton-exchange membranes and operate at low temperatures, typically in the range 60-120°C. The feed is a liquid methanol solution, stored adjacent to the cell. DMFCs require no fuel processor, and are very simple, because in the anode CH₃OH is directly oxidized to CO₂. Their performance, however, is not as good as hydrogen fuel cells. Consequently, methanol fuel cells are not being considered a possible choice for applications where high efficiency is important, i.e. for large-scale power generation. Currently, the main competitor of the methanol fuel cell is the rechargeable battery. Methanol is a cheap fuel and is produced mostly from natural gas and other fossil fuels in a process that involves steam reforming of the hydrocarbon and subsequent catalytic combination of CO and H₂.

It is interesting to summarize the importance of natural gas for fuel cells. As mentioned above, natural gas is the primary fuel that is used to produce both H_2 and CH_3OH for fuel cells. Reformers placed close to fuel cells often utilize natural gas. Internal-reforming high-temperature fuel cells also usually utilize natural gas.

1.5 Overview of direct methane oxidation in fuel cells: Justification for research

It would be very advantageous to the fuel cell industry, if natural gas or larger hydrocarbons derived from petroleum could be oxidized directly in the anode of a low-temperature direct hydrocarbon fuel cell. Such a fuel cell would completely eliminate the need for a reformer, bypass the costs and technical difficulties of producing and storing hydrogen and would not be subject to the disadvantages of high-temperature fuel cells.

The maximum thermodynamic efficiency ($\Delta G/\Delta H$) for complete methane oxidation to CO_2 in a CH_4 / O_2 fuel cell at 25°C (producing CO_2 and liquid water) is² 0.92. The same quantity for H_2 oxidation is 0.83 and for liquid methanol it is² 0.97. All these reactions have very high theoretical efficiencies and are good candidates for fuel cells. Thermodynamics assures us that the oxidation of these fuels in a fuel cell with an oxygen (air) cathode is spontaneous and sets the upper limit to the oxidation efficiency. However, the actual performance is determined by the kinetics of the rate processes in the fuel cell.

Previous work³ has demonstrated the possibility and feasibility of direct hydrocarbon fuel cells. During the 1960's several research projects were initiated. Literature work related to

the electro-oxidation of methane will be more comprehensively described in the introduction to Chapter 2. It was generally found that gaseous hydrocarbons such as methane, ethane, propane and higher molecular-weight liquid hydrocarbons are oxidized in a fuel cell completely to CO_2 . However, the current densities (the reaction rates) are orders of magnitude smaller than hydrogen fuel cells on the platinum catalyst, and also considerably smaller than methanol fuel cells. Hydrocarbon fuel cells did not exhibit promising performance and research efforts were soon abandoned. Furthermore, no substitute to the Pt catalyst was ever found to make the reaction proceed faster³. The overwhelming portion of the difference in reactivities among these fuels is caused by the processes in the fuel cell anode. In all fuel cells operating with any fuel, the cathode is very similar. The details may vary, but a fuel cell cathode is invariably an electrode that reduces oxygen. Thus the electrical potential losses associated with the cathode process are similar for any type of fuel cell.

On a microscopic level, the anodic processes are the following³ (1) the diffusion or convection of the reactant to the catalyst sites through gas-filled and liquid-filled electrode pores (2) the adsorption of the reactant on the catalyst and desorption of the product (3) chemical and electrochemical reactions on the surface of the catalyst, (4) back-diffusion and removal of CO_2 product and (5) ionic transport of protons in the electrolyte. Of the above, (1), (4) and (5) are transport processes, whereas (2) and (3) are surface processes. The contribution of transport processes to the total anode electrical potential losses increases as the current density increases and at high current densities they can cause limiting currents. However, in the past decades, much research has gone into optimizing the structure and design of electrodes, in order to minimize losses due to transport phenomena in the fuel cell.

Transport-limitations are usually observed at very high current densities. It is therefore very unlikely that there would be transport-limited currents in a direct hydrocarbon fuel cell when modern electrodes are used, because the current densities are much smaller.

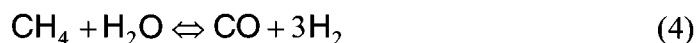
In previous work related to my master thesis^{4,5}, a mathematical model was constructed and solved for the performance of a fuel cell with propane fuel. The model was sufficiently complex to include the majority of the phenomena that take place in a fuel cell, as described by phenomenological equations. The processes that were studied included the diffusion of reactant gases in gas-filled and liquid-filled electrode pores, the ionic conduction in the electrolyte and the oxidation and reduction reactions on the surface of platinum catalyst. The reactions on the catalyst were described by electrochemical reaction-rate expressions (the Tafel equation). Polarization curves were predicted and the contributions of each of the processes in the anode were separated. The solution of the model allowed the separation of the contributions of the various phenomena on the total electrical potential loss (polarization), that is defined as the deviation from the ideal reversible potential of the fuel cell. Two of the conclusions drawn from the solution of the model were: 1) the catalyst surface phenomena account for the overwhelming majority of the electrical potential losses of a direct hydrocarbon fuel cell and 2) the electrical potential loss in the anode is greater than that in the cathode. Thus, the overall process is limited by the kinetics of the electrochemical anode reactions.

The fact that the performance of direct hydrocarbon fuel cells is limited by the slow kinetics of the surface reaction on the anode catalyst, and not by thermodynamics, suggests that there are possibilities for improvements. Hydrogen and methanol fuel cells have been

given great attention in the last decades, but research on hydrocarbon fuel cells does not appear frequently in the literature. Improvements in the performance of DHFCs could only be realized if a better catalyst was found for the anode. In the present work the intention was to study catalytic aspects of the electro-oxidation of methane on transition metal catalysts. In particular, the reaction mechanism, the rate-limiting step and the trends in the reactivities among various transition metal catalysts towards electro-oxidizing methane, were predicted.

1.6 General Overview of steam-reforming of methane: Justification for research

Steam reforming^{6,7} is an industrial process that is used to produce synthesis gas (syngas) from natural gas. Syngas is a mixture of H₂, CO and CO₂ that is used as a feedstock for the manufacture of ammonia, methanol and pure hydrogen for refineries and fuel cells. Steam reforming was also discussed in section 1.4 in relation to the production of H₂ for fuel cells. Apart from these major uses, syngas is also used in a wide variety of industrial applications. Steam reforming was developed at the beginning of the 20th century in Germany, initially to produce H₂ for ammonia synthesis. Many carbon-containing fuels can be used to produce syngas, including oil, coal and biomass. However, natural gas is the dominant feedstock. The reaction that happens on steam – reforming catalysts can be written as:



Simultaneously, at the conditions of steam reforming, the water-gas shift reaction takes place:



The final product is a mixture of H_2 , CO , CO_2 and any remaining unreacted methane. In steam reforming plants, unreacted methane is usually removed in pressure swing adsorption units and recycled. Reaction (4) is very endothermic ($\Delta H = 206$ kJ/mole for methane as the reactant at 298 K). Therefore, high temperatures favor the formation of CO and H_2 . Steam reforming is usually carried out at high temperatures, typically in the range 500-1000°C and moderate pressures (25-35 bar). The temperature and pressure vary according to the required product composition.

The catalysts that are used for steam-reforming usually consist of nickel (Ni) particles dispersed on suitable supports. Typical supports are Al_2O_3 and AlMgO_4 . Many other transition metal catalysts, such as ruthenium, rhodium, iridium, palladium and platinum, can also be used to catalyze the reaction. They are used much less frequently than nickel for economic reasons.

One of the major issues with steam-reforming catalysis is the problem of carbon deposition. Depending on the conditions, carbon can be irreversibly deposited on the catalyst and inactivate it. Carbon deposits frequently consist of long filaments of graphitic carbon, which can severely block the reactor. The 4d and 5d transition metals are less prone to carbon deposition than nickel. The operating conditions for which the formation of carbon deposits is thermodynamically favored have been extensively studied. Low steam-

to-carbon ratios increase the risk of carbon deposition. For this reason, the feed to the reactor is usually enriched in steam, which increases the operating costs of the plant.

Several experimental and theoretical studies have been devoted to the study of the mechanism and kinetics of steam reforming. These will be discussed more extensively in the introduction to Chapter 4. Researchers generally agree that the rate limiting step in the catalytic process is the initial dissociative chemisorption of methane on the metal surface^{6,7}. However, previous published experimental works show that there is no general agreement on the relative reactivities of steam reforming catalysts^{6,8}. For example, among transition metals, one study indicated that Pt is the catalyst with the highest reactivity⁸ for steam reforming, while another study⁶ concluded that Ru and Rh are superior to Pt. As has been pointed out by some researchers, in steam reforming there are many effects^{6,8} that can influence the kinetics, and mask the intrinsic kinetics of the reaction on the metal catalysts. These include the effect of mass transport resistances, the effect of catalyst dispersion and heat effects. Furthermore, the reaction is structure-sensitive and different kinds of sites (terraces, steps, kinks and other defect sites) have a different reactivity towards adsorbing and dissociating methane. For these reasons, the aim in the present work was to explore the trends in the reactivities of different transition metals for steam reforming as well as to study the structure sensitivity of the reaction. Because of the fact that the adsorption and dissociation of methane and water are common features of both a direct methane fuel cell and catalytic steam reforming of natural gas, the calculations performed in the present work were applicable to both processes. This is the reason why conclusions were drawn for both systems.

1.7 The application of Quantum mechanical methodology to heterogeneous catalysis and electrocatalysis

Progress in quantum mechanical methods has contributed to better understanding of the energetics of surface adsorption and reaction processes⁹. Density Functional Theory (DFT) is the most frequently used ab-initio method for calculations involving the solid state. DFT is capable of estimating fairly accurate values for adsorption energies, surface reaction energies and activation energies for molecules adsorbed on a catalyst surface and for surface reactions. DFT is also capable of calculating very precisely the optimum lowest-energy molecular structure of species that are adsorbed on catalyst surfaces. As a result, DFT methods can be used to estimate activation energies for surface reactions, to discriminate among possible reaction mechanisms, to rationalize the catalytic activity of various metals and alloys, or different crystallographic planes of the same metal for many reacting systems and to aid in the design of novel catalysts. A review of the application of quantum mechanics methodology to inorganic reactions has been provided by Ziegler⁹. An overview of the fundamentals of ab-initio methods in general and DFT in particular is given in Appendix 1. The majority of applications of DFT studies for the adsorption of molecules on metals aim to model the solid/gas interface. Recently, however, these methods have been also extensively used to study electrocatalytic reactions. A fairly comprehensive review of the application of ab-initio quantum mechanical methods to electrochemistry has been provided by Koper¹⁰.

Within the framework of quantum mechanical methods, there are three general methods for modeling a metal surface¹⁰: finite atom clusters, embedded clusters and periodic slabs.

Clusters contain a few metal atoms that simulate the reaction site and the neighboring atoms at the surface and/or at the layers below the surface. Embedded clusters methods treat the metal surface as consisting of two distinct regions: a region that contains the reaction site and some metal atoms in its immediate environment (the cluster) and a region that consists of the surrounding metal lattice. Embedded clusters are discussed more comprehensively in Chapter 5. Periodic slab calculations are based on choosing a repeating unit of metal atoms of a few atomic layers thickness and imposing the restriction that this unit and the wavefunction corresponding to it are periodically repeated in two dimensions. The periodic slab calculations result in more accurate energetics but require much greater computation times. For the present work it was required to perform a large amount of calculations for many adsorbed species and it was also necessary to obtain transition states, which is a more computationally demanding task than estimating adsorption energies. Consequently, calculations with metal clusters were performed.

Some examples of metal cluster calculations in the literature, relevant to fuel cell reactions may be noted. The adsorption of hydronium ions on a cluster modeling the Ag(111) surface has been studied¹¹. The binding energies of H, O and OH on several metals using clusters consisting of 13 atoms have been calculated¹². The authors found that the calculated binding energies for these adsorbates are in good agreement with both experimental data and slab calculations. In another work¹³, a Pt₁₀ cluster was used to obtain activation energies for the reaction of CO oxidation [CO(ads) + OH(ads) → COOH(ads)], which is relevant to fuel cell electrocatalysis. The energetics of adsorption of the formyl (HCO) species and the CO molecule on platinum have been studied^{14,15} using Pt₁₀ clusters.

The successes and future potential in the application of ab-initio methodology to heterogeneous catalysis can not be disputed. The application of these methods to the electrochemical interface faces additional challenges¹⁰. Accurate ab-initio and DFT methods are mainly limited by the fact that they require large computing times for systems that contain more than a few atoms. The computation times are proportional to the 3rd or 4th (or higher) power of the size of the system that is being studied. The metal-electrolyte interface (the double layer) at the surface of an electrode requires the following species to be included in the calculations: many metal atoms that can represent the metal fairly, water molecules, ions, and electrolyte species that can have a significant role on the surface phenomena, the reactant, intermediates and products of the electrochemical process, in the adsorbed state and in solution. Furthermore, an additional complication is the electrical potential field of the interfacial region that has a profound role in the kinetics of surface reactions. Because of these complications, the representation of electrochemical phenomena based solely on quantum mechanical methods is still inaccurate. Nazmutdinov et al¹⁶ note that it remains an unsolved problem to generate polarization curves on the basis of quantum mechanical modeling alone.

For electrochemical studies, ab-initio methodology is often coupled with phenomenological equations and several simplifications are often necessary. Quantum mechanical models can be more effectively used to obtain the *relative* rates of an electrochemical reaction on different catalysts, or of different reactions on the same catalyst. For example, Norskov et al¹⁷ used DFT calculations to predict correctly the relative activities of many metals for the oxygen reduction reaction. Liu et al¹⁸ used DFT calculations to predict correctly the effect of alloying Pt with Ru and Sn, as an anode

catalyst for the oxidation of H_2 / CO mixtures. The present work was also aimed at studying trends. In all cases the focus was either on the relative rates of several surface reactions on a particular metal catalyst or the relative rates of a particular surface reaction on a variety of metal catalysts.

1.8 Benchmark calculations

In this work, transition metal surfaces were represented by finite clusters that contain 10-30 metal atoms. The calculation setup is detailed in chapters 2-4. In summary, two different functionals were used in the calculations: B3LYP and PW91. Furthermore, the chosen basis sets were LANL2DZ for the transition metal atoms, with the corresponding effective core potential, and 6-31G** for C,H,O. A preliminary assessment of the quality of the combination of the functionals and the basis sets was done by comparing the calculated bond lengths and binding energies for 3 diatomic species: a H_2 molecule, a PtH dimer and a Pt_2 dimer.

The results are shown in Table 1. The comparison between the experimental and calculated bond lengths indicates that the agreement is excellent for all 3 dimers and for both the B3LYP and PW91 functionals. The maximum deviations from the experimental results were 0.01 Å. The calculated binding energy of the H_2 molecule were in very good agreement with experiment (within 2% of the experimental value, for both functionals). The binding energy of the PtH species, calculated with B3LYP (3.46 eV), was in excellent agreement with the experimental value (3.44 eV). The PW91 functional overestimated the experimental value by 5% (3.62 eV), which is satisfactory agreement. However, the calculated binding energies of the Pt_2 dimer deviated from the experimental value by 14 % for the PW91 functional and 18% for the B3LYP functional. This deviation may be a result

of either the functional or the basis set for Pt, that makes use of effective core potentials for the core electrons. Because the calculations in this work model involved adsorbed species, it is more important that the binding energy of the PtH species agrees well with experiment, rather than the Pt₂ species. In summary, the results of these calculations show that the quality of the calculational setup is satisfactory. However, based on the results for Pt₂, the accuracy of the calculations can not be expected to be excellent. For this reason, the emphasis in the present work is given in the study of trends, rather than in obtaining accurate absolute values for the quantities of interest.

Table 1: Experimental and calculated bond lengths and binding energies for H ₂ , PtH and Pt ₂			
	H ₂	PtH	Pt ₂
Experimental ^a Bond length (Å)	0.74	1.53	2.37
B3LYP Bond length (Å)	0.74	1.52	2.38
PW91 Bond length (Å)	0.75	1.52	2.37
Experimental ^b Binding Energy (eV)	4.75	3.44	3.14
B3LYP Binding Energy (eV)	4.84	3.46	2.59
PW91 Binding Energy (eV)	4.65	3.62	3.58

^a From references 19,20 ^b From references 19,21

1.9 Overview and organization of the thesis

This thesis consists of chapters that have been submitted for publication to research journals. Chapter 2 (article 1, J. Phys. Chem. B 2006, 110, 24593) describes a DFT study that was done in order to elucidate the reaction mechanism of methane electro-oxidation on Pt (111) and the rate-limiting step(s) in the overall reaction. This paper has been peer-reviewed and published in a scientific journal²².

Chapter 3 (article 2, submitted to the J. Phys. Chem. B in July, 2007) describes a cluster DFT study of the dissociative chemisorption of methane on the transition metals ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). The metal clusters used in this work aimed to model three different kinds of sites in order to explore the structure sensitivity of the reaction. Terrace sites, step sites and adatom sites were examined. Trends in the activation energy barriers for the reaction were obtained. The results were discussed in relation to steam reforming. A natural bond orbital (NBO) calculation was also performed in order to investigate the difference in the reactivity of Pt and Ru in dissociating methane in terms of molecular orbital theory.

Chapter 4 (article 3, submitted to the journal Surf. Sci. in July, 2007) describes a cluster DFT study of the dissociative chemisorption of water on the transition metals Ru, Rh, Pd, Os, Ir, Pt and on a Pt-Ru alloy. Calculations were performed for the close-packed terrace sites of these metals and trends in the activation energy barriers for the reactions were obtained. The relation of the energy barriers to the binding energies of the reactants and products was also explored. The combination of the results for the dissociation of water and

the dissociation of methane were discussed in relation to both steam-reforming and the electrochemical oxidation of methane.

Chapter 5 summarizes the contributions to scientific knowledge, the conclusions from the entire work and proposes some recommendations for further research. Appendix A summarizes the fundamentals of quantum mechanical methodology.

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CHAPTER 2: Methane oxidation mechanism on Pt (111): a cluster model DFT study**

George Psofogiannakis*^{†L}, Alain St-Amant[‡] and Marten Ternan^{†§L}

Department of Chemical Engineering and Department of Chemistry, University of Ottawa,
Ottawa, Ont., K1N 6N5, Canada, Centre for Catalysis Research and Innovation, University
of Ottawa, Ont., K1N 6N5, Canada and EnPross Inc., 147 Banning Road, Ottawa, Ont.,
K2L 1C5, Canada

*Corresponding author. E-mail: psofogi@hotmail.com. Phone: (+1) 613 562 5800 ext. 6120

[†] Department of Chemical Engineering, University of Ottawa

[‡] Department of Chemistry, University of Ottawa

^L Centre for Catalysis Research and Innovation

[§] EnPross Inc.

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Abstract

The electronic energy barriers of surface reactions pertaining to the mechanism of the electro-oxidation of methane on Pt (111) were estimated with density functional theory calculations on a 10-atom Pt cluster, using both the B3LYP and PW91 functionals. Optimizations of initial and transition states were performed for elementary steps that involve the conversion of CH₄ to adsorbed CO at the Pt/vacuum interface. As a first approximation we do not include electrolyte effects in our model. The reactions include the dissociative chemisorption of CH₄ on Pt, dehydrogenation reactions of adsorbed intermediates ($*CH_x \rightarrow *CH_{x-1} + *H$ and $*CH_xO \rightarrow *CH_{x-1}O + *H$) and oxygenation reactions of adsorbed CH_x species ($*CH_x + *OH \rightarrow *CH_xOH$). Many pathways were investigated and it was found that the main reaction pathway is $CH_4 \rightarrow *CH_3 \rightarrow *CH_2 \rightarrow *CH \rightarrow *CHOH \rightarrow *CHO \rightarrow *CO$. Frequency analysis and transition-state theory were employed to show that the methane chemisorption elementary step is rate-limiting in the above mechanism. This conclusion is in agreement with published experimental electrochemical studies of methane oxidation on platinum catalysts that have shown the absence of an organic adlayer at electrode potentials that allow the oxidation of adsorbed CO. The mechanism of the electrooxidation of methane on Pt is discussed.

Keywords: methane, fuel cell, chemisorption, platinum cluster, density functional theory, direct hydrocarbon

2.1 Introduction

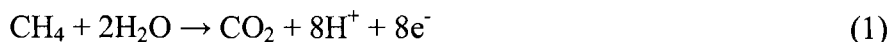
The electro-oxidation of methane in low-temperature fuel cells is a slow process that has received little attention by the scientific community in recent years. Nevertheless, the direct oxidation of methane at low temperatures (60-150 °C) has been experimentally demonstrated by several workers on various types of platinum anode electrodes using acid electrolytes, such as phosphoric acid¹, hydrofluoric acid², sulphuric acid^{3,4,5,6}, perchloric acid^{7,8} as well as polymer electrolyte membranes^{9,10}. The thermodynamic efficiency limit for complete methane oxidation to CO₂ in a CH₄ / O₂ fuel cell at 25°C is¹¹ 92%. However, the process is of limited technical interest because of very slow anode kinetics. Among gaseous saturated hydrocarbons, methane has the smallest rate of electro-oxidation¹². In all experiments that the CO₂ yield has been measured^{1-3,6}, it was found that it is very close to ~100% and no other products have been reported.

The rate of adsorption of methane from HClO₄ electrolyte on Teflon-bonded Pt electrodes has been previously investigated⁷ using potentiodynamic electrochemical methods. In these experiments, methane was allowed to adsorb on the electrocatalyst for several different periods of time at electrode potentials in the range 0.2-0.6 volts vs. RHE (Reversible Hydrogen Electrode). The adlayer was then oxidized with an anodic potential sweep and the charge that passed through the interface, which indicates the amount of adsorbed material, was measured. It was found that the maximum rate of adsorption occurs at adsorption potentials around 0.3 volts and that for adsorption potentials greater than about 0.45 volts, the surface coverage after long adsorption times is very small. The authors noted that at these intermediate potentials, the rate of oxidation of the adlayer is increased, and the

adsorption process becomes rate-limiting. In another study⁵, similar electrochemical methods were used to arrive at the conclusion that methane chemisorption on Pt in H₂SO₄ becomes rate-limiting at potentials around ~0.3 volts. At higher potentials the reaction proceeds on a surface that is free of any adsorbed carbon-containing species.

For adsorption at potentials in the hydrogen region (0-0.35 volts), CO and other adsorbates can be present on the surface. The presence of a carbon-containing adsorbate in an oxidized state was first inferred indirectly from electrochemical experiments¹³. In-situ infrared spectroscopy was later used¹⁴ to investigate the mechanism of CH₄ electrooxidation at 25°C in HClO₄ on noble metal electrodes. After adsorption at 0.26 volts on Pt, the presence of *CO and *CHO (or *COOH) on the Pt surface was detected (* refers to an adsorbed species). The presence of *CO is not surprising. It is the major surface species in the oxidation of all carbon-containing molecules that have been investigated, including methanol, formic acid, formaldehyde and H₂/CO mixtures. It acts as either a surface blocking species or a reactive intermediate or both. Adsorbed CO at the metal-solution interface is oxidized at intermediate electrode potentials presumably by surface hydroxyl (OH) groups^{15,16}.

The overall anode reaction that takes place during methane electro-oxidation can be written as:



Bagotzky et al¹⁷ have proposed a generalized reaction network of the possible elementary steps involved in the mechanism of electrooxidation of methane and other organic molecules that have a single carbon atom. For methane this network is shown in Figure 1, in

which we have excluded the formation of other stable molecules (CH_3OH , H_2CO and HCOOH) based on the experimental observation of 100% CO_2 yield on platinum. The various suggestions for the rate-limiting step have included methane adsorption⁷ as noted above, dehydrogenation of adsorbed unspecified hydrocarbon intermediates⁵, and dehydrogenation of adsorbed CH_3 intermediates⁶ following methane adsorption.

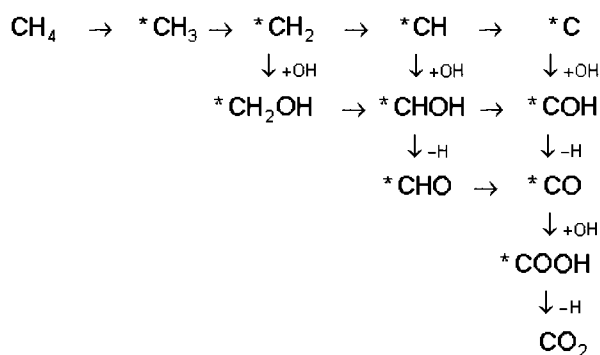


Figure 1. The Bagotzky mechanism for the electro-oxidation of methane.

Unlike at the electrochemical interface, the chemisorption of methane at the metal-gas interface has been the focus of several studies because of its relevance to industrially important catalytic reactions, particularly steam reforming¹⁸. Single-crystal surfaces of platinum and various other metals have been studied. In steam reforming of methane the C-H bond cleavage of the very stable methane molecule is the rate limiting step¹⁸⁻²⁰. Most of the experimental studies are molecular beam studies²¹⁻²⁸ that independently assess the effects of translational and vibrational energies of the beam, the surface temperature and the angle of incidence. Theoretical models have also been proposed^{20,29,30}. The mechanism of the chemisorption process of methane has not been unequivocally verified^{20,22,26,27,31}. Direct

dissociation^{23,28,30,31}, steering-assisted direct dissociation²¹, precursor-mediated dissociation^{26,29} and quantum mechanical tunnelling²⁰ are some of the mechanisms that have been proposed to explain experimental trends of the sticking probability data from methane molecular beams. Other complications arise because the translational energies used in molecular beams are much higher than catalytic reactors and because it is usually not possible to predict the outcome of thermal activation experiments from the results of molecular beam results^{18,22}. Perhaps more relevant to fuel cell conditions is a low-temperature thermal ‘bulb’ experimental study³¹, in which methane dissociation on Pt (110) was interpreted by a direct dissociation mechanism. The evidence for direct dissociation is stronger than precursor-mediated dissociation^{18,21,23} because it can explain the observed large increase in CH₄ sticking probability with increasing kinetic energy of the beam. Dynamic steering³² in a direct dissociation mechanism has been used²¹ to explain the observed minimum in the CH₄ sticking probability at low translational energies.

Our objective in this study is to use quantum-mechanical methodology to predict the mechanism and rate determining step of the anodic methane oxidation reaction on a Pt (111) surface. This may result in understanding the requirements and attributes of a possible improved catalyst for methane electro-oxidation. Several DFT studies have been directed towards mechanistic understanding of various electrochemical and fuel cell reactions³³. No computational or theoretical studies directed towards understanding of the electro-oxidation of methane have been previously reported in the literature. Also, we do not know of any study that has reported any information on the structure-sensitivity of the methane electro-oxidation reaction. Thus, as a first step we have chosen to limit our scope to the Pt (111) surface. This surface was chosen because it is the most abundant surface of the Pt metal.

Furthermore, it is possible that the (111) surface determines the reactivity of the surface as lower-coordination sites, that are generally more reactive, may be blocked under reaction conditions. The (111) surface is also easier to model using clusters.

Despite considerable advances in computational methodologies, the currently available ‘ab-initio’ computational tools do not allow the quantitative estimation of electrochemical reaction rates, particularly for complex reactions such as the one shown in Equation 1. In comparison to the metal-gas interface, the electrochemical interface presents several complexities including the electrical potential field, the double-layer, the existence of a liquid phase adjacent to the metal, and the occurrence of electron-transfer reactions. These complexities are coupled with the fact that predictions of reactions rates are very sensitive to the accuracy of estimating energy barriers for surface reactions. However, DFT can be more effectively used for mechanistic studies, as well as for qualitative trends of reaction rates, such as comparing the activities of different catalysts for the same reacting system, or comparing the rates of different reactions on the same catalyst.

In order to predict the reaction mechanism, we estimated with DFT calculations the electronic energy barriers for the reactions shown in Figure 1, excluding the CO oxidation reaction. This general reaction network corresponds to methane oxidation reactions at the electrochemical interface but the calculation setup is the metal-vacuum interface. The absence of electrolyte in our model is an approximation that allows us to focus on metal – adsorbate interactions. The oxidant of the adsorbed CH_x radicals in the mechanism of Figure 1 was taken to be adsorbed hydroxyl radicals (OH) in analogy with the predominant view that OH is also the species that oxidizes adsorbed CO, either when CO is contained in the

feed¹⁵ or when it forms on the surface during the oxidation of organics, such as methanol¹⁶. The nature of the oxidizing agent in acid fuel cells has been the topic of long-standing debate. In situ x-ray scattering results¹⁵ were interpreted in favor of reversible OH formation on Pt (111). Thus, our calculations pertain to electrode potentials greater than ~ 0.4 volts vs. RHE in the double layer region, for which hydroxyl groups form on the Pt surface by the deprotonation of water molecules. In this range of potentials the reverse of the dehydrogenation reactions shown in Fig. 1 need not be considered because the coverage of the surface with hydrogen atoms is negligible. We refrain from describing the reaction of the electro-oxidation of adsorbed CO because of the known³⁴ failure of DFT cluster and slab calculations in predicting the most stable surface site of CO adsorption on platinum, whereas DFT is considered to be successful for other adsorbates. In order to predict the rate-limiting step, we employed transition-state theory to estimate the rate constants for some of the elementary steps, as will be described later. Based on previous work discussed above, we used direct dissociative chemisorption of methane in order to estimate the pre-exponential factor for this elementary step.

2.2 Computational and Theoretical methods

We used a planar 10-atom Pt cluster to simulate the surface. The cluster is shown in the figures of the results section. The locations of the atoms correspond to the Pt (111) surface. This is the minimum size required to keep the optimized structures of the initial and final states of the reactions inside the boundary defined by the edge atoms of the cluster, without imposing any geometric constraints. Our objective requires the correct prediction of the relative magnitudes of the energy barriers of the elementary steps rather than chemical

accuracy in their actual values. This justifies the small cluster size. However, we also support our conclusions by presenting comparisons of our results with periodic boundary conditions (PBC) calculations for those elementary steps for which PBC predictions have been found in the literature. Furthermore, in order to investigate cluster-size effects, one calculation for a single elementary reaction was also performed on a 3-layer 25-atom platinum cluster, as described in the results section.

Density functional theory (DFT) calculations were carried out using the GAUSSIAN 03 program³⁵. We used two different exchange-correlation functionals: B3LYP³⁶ and PW91³⁷. We present results for both functionals. For the Pt atoms, we used the Los Alamos National Laboratory³⁸ basis set of double-zeta quality (LANL2DZ) and the corresponding scalar relativistic effective core potential that replaces the inner-shell electrons. 18 electrons in the outer shells $5s^2 5p^6 5d^9 6s^1$ were treated explicitly. The 6-31G** basis set was used for carbon, hydrogen and oxygen atoms. No significant spin contamination was found. For geometry optimizations, the convergence criteria corresponded to a maximum step size of 0.01 au and an RMS force of 0.0017 au. The Pt-Pt inter-atomic distance was kept fixed in the optimizations at the experimental bulk value³⁹ for solid platinum, 2.775 Å. No further constraints were imposed in geometry optimizations. For each adsorbate, the most stable adsorption site was found by optimizations of different starting structures, at on-top, bridged and 3-fold hollow adsorption sites of the cluster. For most reactions the transition state (TS) was located by analytical methods as implemented in the default Gaussian 03 method. Vibrational frequency calculations were performed on all transition states at the DFT-optimized geometries using the default Gaussian03 algorithm that calculates force constants analytically. It was verified that the TS geometry possesses only one negative imaginary

frequency. Animation of the TS negative frequencies allowed us to verify that the TSs corresponded to the reactions that were studied. Reaction coordinate scans were performed for all reactions by selecting an internal coordinate (a bond distance) and performing constrained energy minimizations for various fixed values of this coordinate. For the PW91 calculations the TS energy was estimated as the maximum energy of the reaction scan.

Furthermore, we investigated the effect of the spin state of the cluster-adsorbate systems. In each case, the ground state of the reactants was found by performing calculations for several different spin multiplicities ($SM=1+\text{number of unpaired electrons}$). Reaction paths were followed for the ground-state spin of the initial state for each reaction. The product state of the reaction has, in most cases, a different spin state than the reactant. We performed calculations on the reaction pathways with two and more different spin multiplicities. We observed that in every case the spin multiplicity of minimum energy did not change from the initial reactant state to the transition state. Because we are interested only in the part of the pathway up to the transition state, we present here only calculations with the minimum-energy reactant spin states. The effect of the spin-state on the electronic energy of small Pt clusters has been previously examined⁴⁰, and the preferred high-spin states were explained by a model that predicts the bonding orbitals within the cluster.

The binding energy of each of the intermediate species involved in the reaction mechanism of Figure 1, was calculated as⁴¹:

$$E_{\text{binding}} = E_{\text{cluster+adsorbate}} - E_{\text{cluster}} - E_{\text{adsorbate}} \quad (2)$$

where $E_{\text{cluster} + \text{adsorbate}}$, E_{cluster} and $E_{\text{adsorbate}}$ are the total electronic energies of the optimized structures of the adsorbed configuration, the isolated bare cluster and the isolated radical, respectively. The electronic energy barrier (non-ZPE corrected) for each reaction was calculated as the difference between the electronic energies of the transition state (TS) and initial state (IS) of the reaction:

$$\Delta E_{\text{elec}}^{\ddagger} = E_{\text{elec}}^{\text{TS}} - E_{\text{elec}}^{\text{IS}} \quad (3)$$

Within the framework of transition state theory, rate constants for adsorption and surface reaction elementary steps at the metal-vacuum interface can be estimated provided that estimates of the electronic energy barriers and the vibrational frequencies of the initial states and the transition states exist. We describe the methodology here because it was used to identify the rate-limiting step as described in the next section. The rate constant of a chemical reaction is given by^{42a}:

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{k_B}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{k_B T}\right) \quad (4)$$

where k_B is Boltzmann's constant, h is Planck's constant and $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ are the standard-state entropy and enthalpy of activation for the reaction.

A non-linear molecule such as CH_4 has three translational, three rotational and $3N-6$ vibrational degrees of freedom in the gas-phase, where N is the number of atoms in the molecule. In the adsorbed state, all translational and rotational degrees of freedom are replaced by vibrational modes corresponding to frustrated rotation and translation on the surface. An adsorbed molecule has $3N$ vibrational degrees of freedom. At the transition state, the mode that corresponds to the reaction coordinate gives rise to an imaginary

negative frequency, and is excluded from the calculation of the partition function of the TS⁴³. As a result, the calculation of the entropy of the transition state is based on 3N-1 vibrational modes.

For the calculation of the rate constants for these reactions we make use of Equation 4. The analysis is based on statistical thermodynamics^{42b}. The following equations include translational and rotational energies and entropies, which were used for gaseous methane but were not used for adsorbed intermediates. The standard enthalpy of activation for a surface reaction is approximately equal to the standard internal energy of activation and is given by:

$$\Delta H^{\circ\ddagger} \approx \Delta U^{\circ\ddagger} = \Delta U_{\text{trans}}^{\circ\ddagger} + \Delta U_{\text{rot}}^{\circ\ddagger} + \Delta U_{\text{vib}}^{\circ\ddagger} + \Delta(\text{ZPE}) + \Delta E_{\text{el}}^{\ddagger} \quad (5)$$

where the terms on the right-hand side denote the differences in translational energy, rotational energy, vibrational thermal energy, zero-point energy and electronic energy, between the TS and the IS, respectively. E_{el} is the electronic energy predicted by the DFT calculation. The standard-state energies are evaluated for T=298K and are given by^{42b}:

$$U_{\text{trans}} = \frac{3}{2} k_B T \quad (6)$$

$$U_{\text{rot}} = \frac{3}{2} k_B T \quad (7)$$

$$U_{\text{vib}} = \sum_i \frac{h\nu_i}{(e^{h\nu_i/k_B T} - 1)} \quad (8)$$

$$\text{ZPE} = \sum_i \frac{h\nu_i}{2} \quad (9)$$

where ν_i are the vibrational frequencies (Hz) and all quantities are evaluated on a molecular basis (J/molecule). The standard entropy of activation is given by:

$$\Delta S^{\circ\dagger} = \Delta S_{\text{trans}}^{\circ\dagger} + \Delta S_{\text{rot}}^{\circ\dagger} + \Delta S_{\text{vib}}^{\circ\dagger} \quad (10)$$

where the terms on the right-hand side denote the standard-state differences in translational, rotational, and vibrational entropies between the TS and the IS, respectively. The standard-state entropies are given by^{42b}:

$$S_{\text{trans}} = k_B \left\{ \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P} \right] + \frac{5}{2} \right\} \quad (11)$$

$$S_{\text{rot}} = k_B \left\{ \ln \left[\frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \right] + \frac{3}{2} \right\} \quad (12)$$

$$S_{\text{vib}} = k_B \sum_i \left(\frac{h\nu_i}{k_B T (e^{h\nu_i/k_B T} - 1)} - \ln(1 - e^{-h\nu_i/k_B T}) \right) \quad (13)$$

where m is the molecular mass of the adsorbed species, I_A , I_B , I_C are the principal moments of inertia of the molecule and σ is the symmetry number. The standard-state pressure $P=1$ atm was used in the calculation of the standard-state translational entropy of a gas-phase species (CH_4) and all standard state quantities were evaluated for $T=298\text{K}$.

The rate constant in equation 4 can also be written in a form that separates the pre-exponential factor and activation energy terms⁴¹:

$$k = A_o \exp \left(- \frac{E_{\text{act}}}{k_B T} \right) \quad (14)$$

In this definition, the pre-exponential (frequency) factor A_o is also temperature dependent, but the temperature dependence of the exponential term dominates. Equating the corresponding terms of equations 4 and 14, we have:

$$A_o = \frac{k_B T}{h} \exp \left(\frac{\Delta S^{\circ\dagger}}{k_B} \right) \quad (15)$$

$$E_{\text{act}} = \Delta H^{\circ\dagger} \quad (16)$$

2.3 Results and Discussion

The binding energies of all adsorbed intermediates on the Pt₁₀ cluster, calculated using both the B3LYP and PW91 functionals, are shown in Table 1. Even though binding energies were not necessary for the prediction of the energy barriers of the reactions, they served to make comparisons of our predictions with other literature results⁴⁴⁻⁴⁸. The optimized geometries of the adsorbed species are the initial states of all dehydrogenation reactions and are shown in the uppermost structures of Figures 3 – 14. In Table 1, the binding energies are compared to previously published Pt₈ and Pt₃₅ cluster/B3LYP and PBC/PW91 calculations corresponding to 1/4 and 1/9 monolayer (ML) coverage. For clusters, the results correspond to limitingly low coverage because there are no interactions between adsorbates in the calculations. When comparing cluster results with PBC calculations, the unit cell used in the PBC calculations should be large enough to minimize the adsorbate coverage. For example, 3 × 3 unit cells are preferred to 2 × 2 unit cells in making this comparison.

Table 1. Binding energies and binding sites for species in the network of Figure 1 predicted with B3LYP and PW91 functionals.

	binding	E _{binding} (eV)	E _{binding} (eV)	E _{binding} (eV)	E _{binding} (eV)
species	site	Pt ₁₀ / B3LYP	Pt ₁₀ / PW91	Pt _x / B3LYP	PBC/ PW91
		(this work)	(this work)	(previous work)	(previous work)

H	top	-3.02	-2.86	-2.92 ^a	-2.71 ^b
OH	bridge	-1.81	-2.06	-1.77 ^a	-2.12 ^b
CH ₃	top	-2.17	-2.40	-2.33 ^c , -2.16 ^d	-1.93 ^b , 2.04 ^e
CH ₂	bridge	-4.21	-4.56	-4.52 ^c , -4.13 ^d	-3.95 ^e
CH	hollow	-7.03	-7.55	-7.22 ^c , -6.36 ^d	-6.43 ^e
C	hollow	-6.33	-6.99	-6.59 ^c , -6.41 ^d	-6.75 ^e
CH ₂ OH	top	-2.42	-2.79	-2.85 ^a	-1.98 ^b
CHOH	bridge	-3.68	-4.20	-3.68 ^a	-3.24 ^b
COH	hollow	-5.20	-5.64	-5.25 ^a	-4.45 ^b
CHO	top	-2.55	-2.80	-2.72 ^a	-2.36 ^b
CO	hollow	-1.88	-2.34	-1.82 ^a	-1.82 ^b

^a Pt₈ cluster, B3LYP, from ref 44. ^b PBC, PW91, 1/9 ML, from ref 45. ^c Pt₈ cluster, B3LYP, from ref 46. ^d Pt₃₅ cluster, B3LYP, from ref 47. ^e PBC, PW91, 1/4 ML, from ref 48

As shown in Table 1, this work predicts that methyl (CH₃), hydroxymethyl (CH₂OH) and formyl (CHO) bind on top sites of the cluster, hydroxyl (OH), methylene (CH₂) and hydroxymethylene (CHOH) bind on bridge sites, and methyldiyne (CH), carbon (C), hydroxymethyldiyne (COH) and carbon monoxide (CO) bind on hollow sites. The cluster surface model can not differentiate between the two different kinds of hollow sites, fcc and hcp, of the Pt (111) surface. The H atom is predicted to bind on-top but all sites are nearly degenerate. Atomic hydrogen has a nearly flat potential energy profile on the Pt(111) surface. Thus, for H the accepted accuracy limits of DFT methods do not allow a

trustworthy comparison with experiment. A minor energetic preference for the on-top site was also found with periodic calculations⁴⁴. The conclusions for the other species also agree with the preferred adsorption sites predicted by periodic boundary conditions (PBC) calculations for Pt (111) and other cluster calculations cited in Table 1. The third and fourth columns of Table 1 show that the PW91 functional predicts stronger binding on the Pt₁₀ cluster than the B3LYP functional for all adsorbates except H. Literature results with Pt clusters (B3LYP) and periodic boundary conditions (PBC) using the PW91 functional are shown in the last two columns. As representative figures of comparison, we note that the average deviation of our Pt₁₀ / B3LYP results from the PBC / PW91 results shown in the table is 11%. Our Pt₁₀ / PW91 results agree less with the PBC / PW91 results, the average deviation being 19%. As expected, our Pt₁₀ / B3LYP results are in much better agreement with Pt₈ / B3LYP results, the average deviation being 5%. However, some cluster-size dependence is evident for small clusters, as predicted by comparing the Pt₈ and Pt₃₅ results cited in column 5 of the table. For the carbon-containing adsorbates that were studied, our results show that the adsorption energy on Pt (111) decreases in the order $E(\text{CH}) > E(\text{C}) > E(\text{COH}) > E(\text{CH}_2) > E(\text{CHOH}) > E(\text{CHO}) > E(\text{CH}_2\text{OH}) > E(\text{CH}_3) > E(\text{CO})$. PBC results predict the same order with the only exception $E(\text{C}) > E(\text{CH})$.

Experimental data⁵² obtained by laser-induced fluorescence for OH desorption from Pt indicate a binding energy 2.04 eV. This value compares very well with the value we obtained using the PW91 functional (2.06 eV), while the B3LYP result (1.81 eV) underestimates the experimental value by 11%. The heat of adsorption of H₂ on Pt(111) has been measured experimentally by thermal desorption spectroscopy⁵³⁻⁵⁶. The experimental results indicated that the binding energy of a H atom was in the range 2.67-2.74 eV. Our

calculated values (3.02 eV with B3LYP and 2.86 eV for PW91) overestimate the mean experimental value by 12% and 6% respectively. These comparisons indicate that the accuracy afforded by the cluster methods is sufficient for the study of trends.

The good agreement of the binding energies of the adsorbates on the Pt₁₀ cluster with those on slabs, obtained using periodic calculations, manifests that the Pt₁₀ cluster is sufficient for studying trends in activation energies of surface reactions that involve the species discussed above. Jacob et al⁴⁹ have shown that a Pt₁₂ cluster, which is very similar to the Pt₁₀ cluster of our work, does very well in describing top, fcc-hollow and bridge sites and only fails for hcp-hollow sites. In recent work⁴⁷ with Pt₃₅ clusters, it was found that none of the CH_x fragments preferred to bind to an hcp site. Of all other adsorbates involved in the mechanism in our work, periodic calculations⁴⁵ have shown that none of them prefers the hcp site. Those that bind on 3-fold sites, such as *COH and *CO are more stable on fcc sites. Furthermore, keeping the cluster fixed does not adversely affect the accuracy because the Pt(111) surface has nearly no relaxation⁴⁷. Jacob and Goddard⁴⁷ performed cluster calculations with a 35 atom Pt(111) cluster. The positions of the non-fixed Pt surface atoms changed by less than 3% indicating negligible relaxation.

The initial states and transition states for all reactions that were studied are shown in Figures 2-14 for optimizations with the B3LYP functional. The top picture in each figure is the optimized geometry of the initial state. The second is the optimized geometry of the transition state, followed by the energy profile for the reaction path for B3LYP (■) and PW91 (▲) calculations. The zero of energy corresponds to the initial state for each reaction for both functionals. Open squares (□) refer to TS calculations in which the TS structure

was obtained in a separate calculation with direct optimization to the saddle point structure. In every case, there is good agreement between the TS energy and the energy maximum of the reaction coordinate scan. For these cases that a TS calculation did not properly converge or was not attempted, the maximum energy of the reaction coordinate scan provided a good estimate of the TS structure and energy. TS optimizations were not performed for the PW91 functional. For most dehydrogenation reactions, the reaction paths were followed from the initial state to a state just after the TS for hydrogen cleavage, so that the geometry of the final state was not found.

Figure 2 shows the initial state, transition state and energy profile for the methane dissociative chemisorption reaction $\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$. The initial state consists of the CH_4 molecule and the Pt_{10} cluster at infinite separation. The initial state energy was calculated as the sum of the energies of two separate calculations, in which CH_4 and Pt_{10} are each at their optimum spin state ($\text{SM} = 1$ for CH_4 and $\text{SM} = 9$ for Pt_{10}). The calculated reaction path corresponds to $\text{SM} = 9$. At the TS, the C atom is located 2.33 Å on top of a Pt atom and the H atom 1.38 Å from the C atom and is bridge-bonded to the underlying Pt atoms. The electronic energy barrier predicted by B3LYP is 1.15 eV and that predicted by PW91 is 0.91 eV. The calculation corresponds to the direct dissociation mechanism, in which CH_4 does not first adsorb in a physisorbed state. As mentioned in the introduction, most experimental molecular beam studies support the direct dissociation mechanism for methane on transition metals. In a fuel cell that operates with a liquid electrolyte, the adsorbed H atoms would subsequently combine with water molecules to produce protons and migrate through the electrolyte towards the cathode electrode.

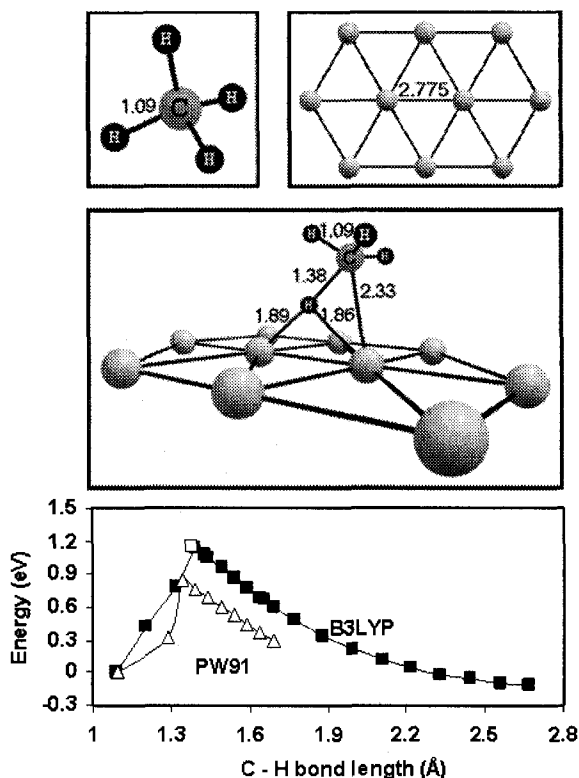


Figure 2. Initial state (top) and transition state (middle) for the reaction $\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$ for the B3LYP functional calculations on a Pt₁₀ cluster. Electronic energy profile as a function of C-H bond length (bottom). ■ = B3LYP, ▲ = PW91, □ = Transition state (TS) energy for the B3LYP calculation. The zero of energy corresponds to the initial state.

In Figure 2, the energy profile was plotted against the C-H bond length and seems to present a cusp at the TS. This is a consequence of the fact that the actual reaction coordinate is not well represented by the C-H bond length. If the actual reaction coordinate was used instead, the energy profile would be smooth and parabolic around the TS. However, when the TS involves both bond-making and bond-breaking, scanning only one internal coordinate can result in a sudden change in geometry near the TS. This makes the profiles non-parabolic. For example, in Fig. 2, the C-H bond length was being decreased at each step

to obtain the profile. At the TS, the geometry changed substantially with very small C-H bond-length changes, by breaking the Pt-C bond. However, the primary purpose of the energy profiles was to obtain an initial structure for an accurate TS calculation. Thus, the energy profiles presented in these figures use as the independent variable our initial choice of internal variable. After the analytic TS calculation, it was verified by frequency analysis that the TS indeed possessed one imaginary frequency. Similar considerations apply to some of the other reactions in the network.

Figure 3 shows that the preferred adsorption site of methyl (CH_3) is on-top. At the TS geometry for the reaction $\text{*CH}_3 \rightarrow \text{*CH}_2 + \text{*H}$, the C atom has been displaced about 20 degrees from the on-top position towards the bridge-bonded position. The C-H bond length at the TS is 1.70 Å and the dissociating H atom is close to the on-top site of the adjacent Pt atom. The energy barrier predicted by B3LYP for this reaction is 1.61 eV, while PW91 predicts 1.42 eV. The calculated reaction path corresponds to SM=8.

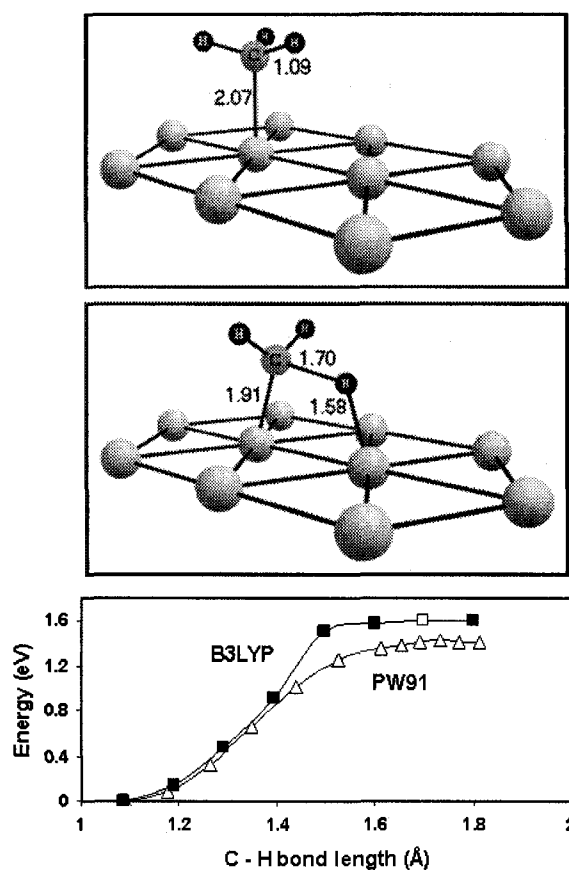


Figure 3. B3LYP initial and transition states for the reaction $*\text{CH}_3 \rightarrow *\text{CH}_2 + *\text{H}$. Energy profile as a function of C-H bond length. $\square$ = B3LYP TS.

Figure 4 shows that methylene (CH_2) binds at the bridge site. At the TS geometry for the reaction $*\text{CH}_2 \rightarrow *\text{CH} + *\text{H}$, the C atom has been displaced towards the hollow site, the dissociating H atom is located 1.38 Å away from the C atom and is close to the on-top site of the adjacent Pt atom. The other H atom has rotated away from the surface. The energy barrier predicted by B3LYP for this reaction is 0.63 eV, while PW91 predicts 0.48 eV. The reaction path was calculated for SM=7.

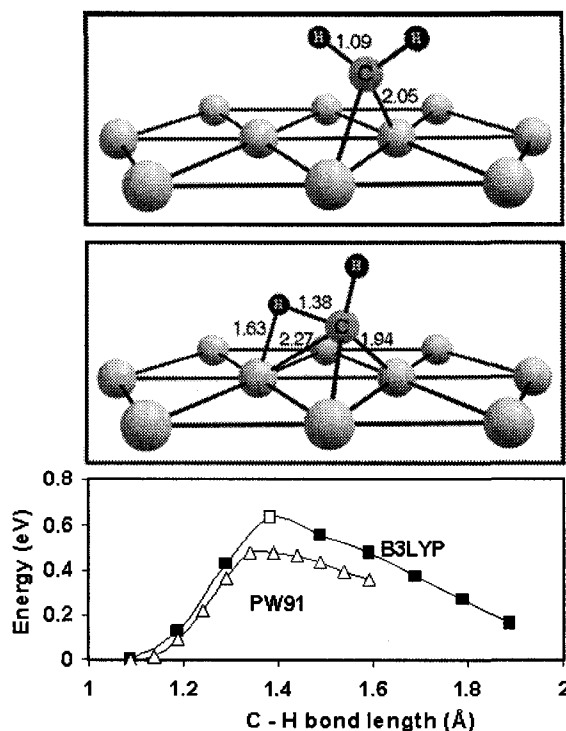


Figure 4. B3LYP initial and transition states for the reaction $*CH_2 \rightarrow *CH + *H$. Energy profile as a function of C-H bond length. $\square$ = B3LYP TS.

Figure 5 shows that methylidyne (CH) binds at the hollow site. At the TS geometry for the reaction $*CH \rightarrow *C + *H$, the C atom remains at the hollow site, which is the preferred adsorption site for the final adsorbed C atom. The H atom has rotated towards one of the Pt binding atoms and is located 1.78 Å away from the C atom. The energy barrier predicted by B3LYP for this C-H cleavage reaction is 2.51 eV, while PW91 predicts 2.18 eV. The reaction path was calculated for SM=8.

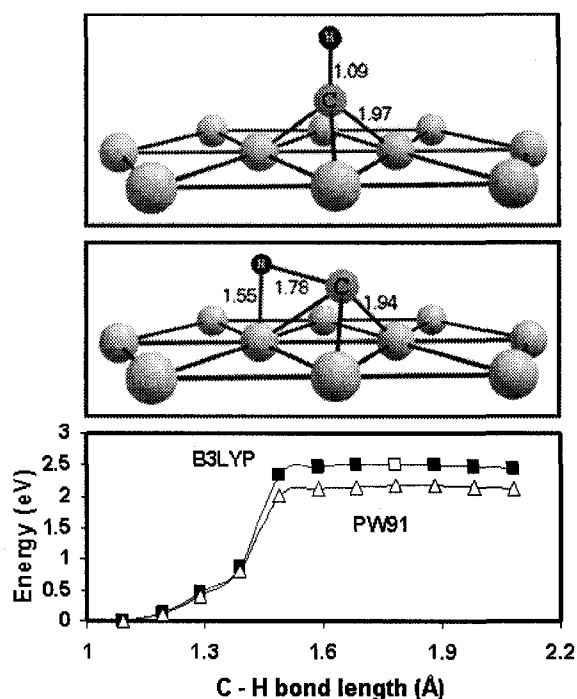


Figure 5. B3LYP initial and transition states for the reaction $*CH \rightarrow *C + *H$. Energy profile as a function of C-H bond length. $\square$ = B3LYP TS.

Figure 6 shows the initial and transition states for the reaction $*CH_2 + *OH \rightarrow *CH_2OH$. A Pt_{13} cluster was used for this reaction because on the Pt_{10} cluster $*OH$ shifts to the edge of the cluster upon optimization of the initial state. The on-top adsorbed $*OH$ shown in the top picture of Figure 6 is a local minimum, because B3LYP predicts a small preference (0.15 eV) for the bridge site. Thus a small energy barrier would have to be overcome for $*OH$ to move from a bridge site to the top site that corresponds to the initial state of the reaction. Thus, if the initial state had OH on a bridge site, the stronger binding energy of the reactant would suggest a larger energy barrier for the reaction. At the TS, $*OH$ is located close to on-top of one of the Pt atoms that bind $*CH_2$, while $*CH_2$ has moved closer to the other Pt atom. This Pt atom binds the carbon atom of the product of this reaction, $*CH_2OH$. The

energy barrier predicted by B3LYP for this oxygenation reaction is 1.03 eV, whereas PW91 predicts 0.87 eV. The reaction path was calculated for SM=10 on the 13-atom Pt cluster.

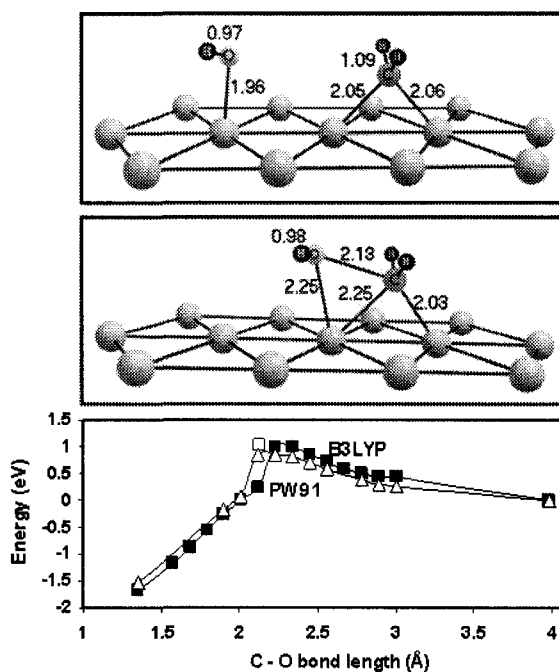


Figure 6. B3LYP initial and transition states for the reaction $*CH_2 + *OH \rightarrow *CH_2OH$ on a Pt_{13} cluster. Energy profile as a function of C-O bond length. $\square$ = B3LYP TS.

Figure 7 shows the initial and transition states for the reaction $*CH + *OH \rightarrow *CHOH$. The initial state consists of $*CH$ bound at the hollow site and $*OH$ bound at the on-top site. At the TS geometry, the C atom has shifted to the bridge position, and the C-O distance is 1.88 Å. The final state is bridge-bonded $*CHOH$. The energy barrier predicted by B3LYP for this reaction is 1.17 eV, whereas PW91 predicts 0.95 eV. The reaction path was calculated for SM=7.

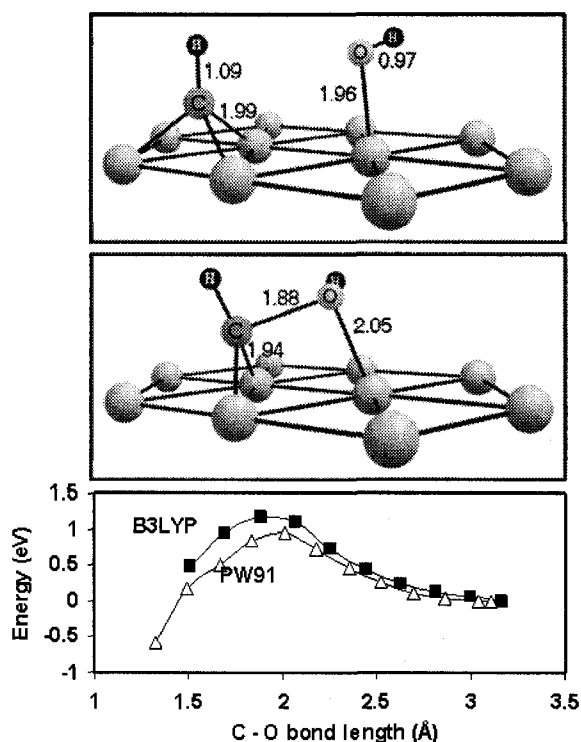


Figure 7. B3LYP initial and transition states for the reaction $*CH + *OH \rightarrow *CHOH$. Energy profile as a function of C-O bond length.

Figure 8 shows the initial and transition states for the reaction $*C + *OH \rightarrow *COH$. The initial state consists of $*C$ bound at the hollow site and $*OH$ bound at the top site. At the TS geometry, the C atom remains at the hollow site, while $*OH$ has moved towards it. The C-O distance is 2.13 Å at the TS. The final state is $*COH$ bonded through C at the hollow site. The energy barrier predicted using B3LYP for this reaction is 0.93 eV, while PW91 predicted 0.61 eV. The reaction path was calculated for SM=8.

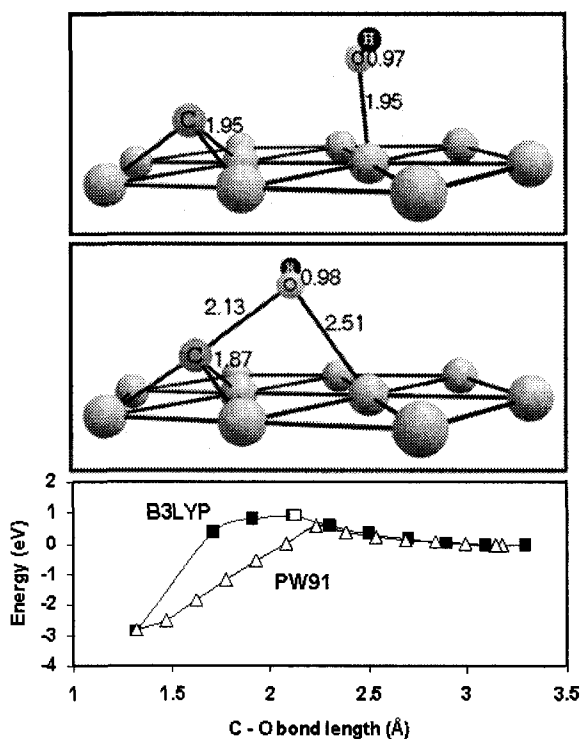


Figure 8. B3LYP initial and transition states for the reaction $*C + *OH \rightarrow *COH$. Energy profile as a function of C-O bond length. $\square$ = B3LYP TS.

Figure 9 shows that hydroxymethyl (CH_2OH) binds through C at the top site. At the TS structure for the reaction $*CH_2OH \rightarrow *CHOH + *H$, the C atom has been displaced about 16 degrees from the on-top position towards the bridge-bonded position. The C-H bond is 1.58 Å and the dissociating H atom has moved towards the on top site of the adjacent Pt atom. The energy barrier predicted using B3LYP for this reaction is 1.07 eV, while PW91 predicted 0.77 eV. The reaction path was calculated for SM=8.

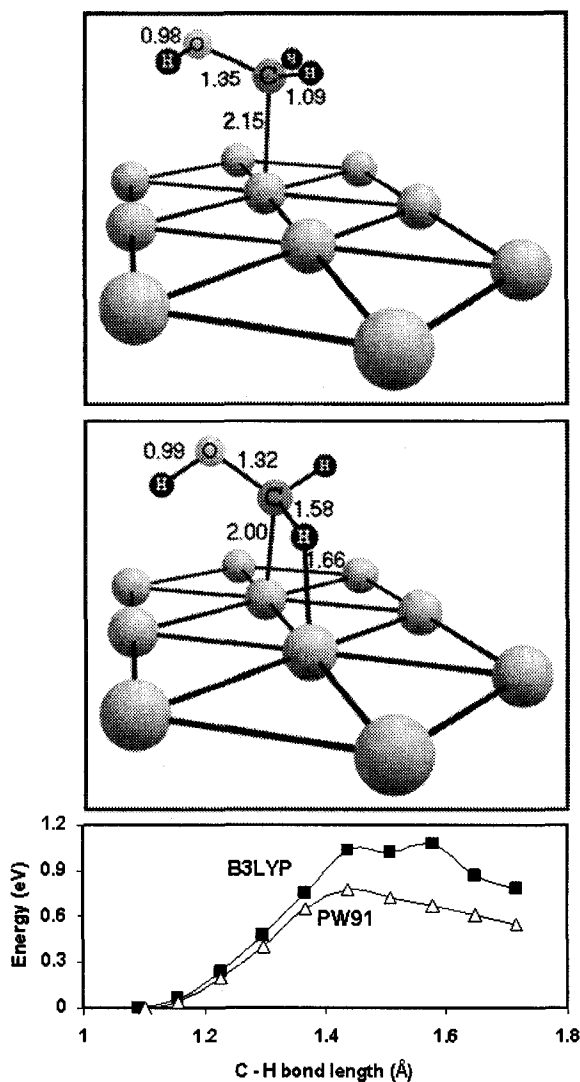


Figure 9. B3LYP initial and transition states for the reaction $*\text{CH}_2\text{OH} \rightarrow *\text{CHOH} + *\text{H}$. Energy profile as a function of C-H bond length.

Figure 10 shows the initial and transition states for the reaction $*\text{CHOH} \rightarrow *\text{COH} + *\text{H}$. The hydroxymethylene (CHOH) group is initially bound at the bridge site. At the TS predicted by B3LYP, the dissociating H atom is 1.76 Å away from the C atom. The C atom is still at the bridge site and slightly shifted towards the hollow site, which is its final location. The OH group has rotated away from the surface. The energy barrier predicted

using B3LYP for this reaction is 1.33 eV, while PW91 predicted 1.14 eV. The reaction path was calculated for SM=8.

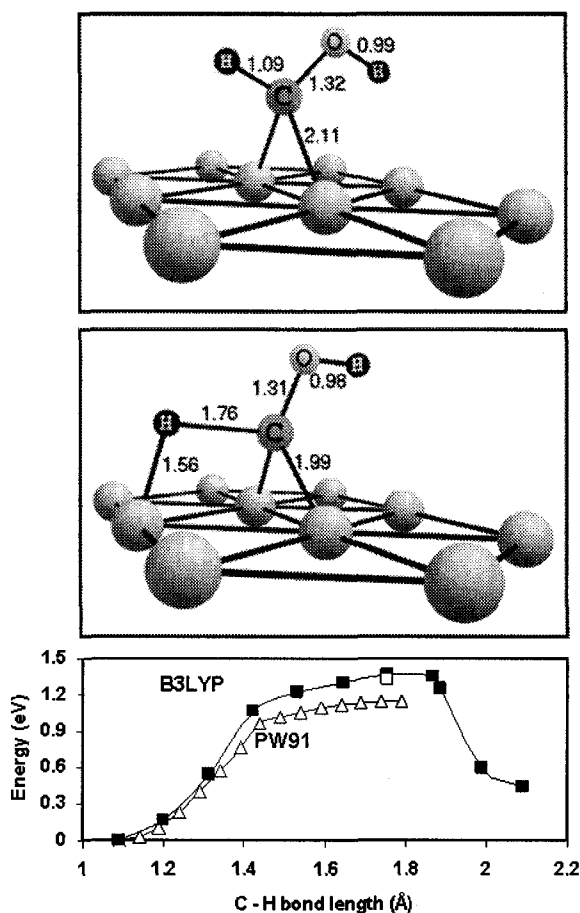


Figure 10. B3LYP initial and transition states for the reaction $*\text{CHOH} \rightarrow * \text{COH} + * \text{H}$. Energy profile as a function of C-H bond length. $\square$ = B3LYP TS.

Figure 11 shows the initial and transition states for the reaction $*\text{CHOH} \rightarrow * \text{CHO} + * \text{H}$. For this reaction there is a qualitative difference between the reaction pathways predicted by B3LYP and PW91. The final state for the reaction is predicted by B3LYP to have $* \text{CHO}$ bonded on top of one of the Pt atoms that initially bind $* \text{CHOH}$, as shown in the initial state of Figure 13. On the other hand, PW91 predicted a stable state in which $* \text{CHO}$ is still bridge bonded, as shown in the first structure of Figure 12. This structure is a local minimum and

dissociates to the state $^*CO + ^*H + ^*H$ with a very small activation energy barrier. For the reaction $^*CHOH \rightarrow ^*CHO + ^*H$, B3LYP predicts a TS in which the C atom is still bridge-bonded and the O-H bond length is 1.50 Å. The energy barrier predicted by B3LYP for this reaction is 0.50 eV, while PW91 predicts 0.35 eV. The reaction path was calculated for SM=9.

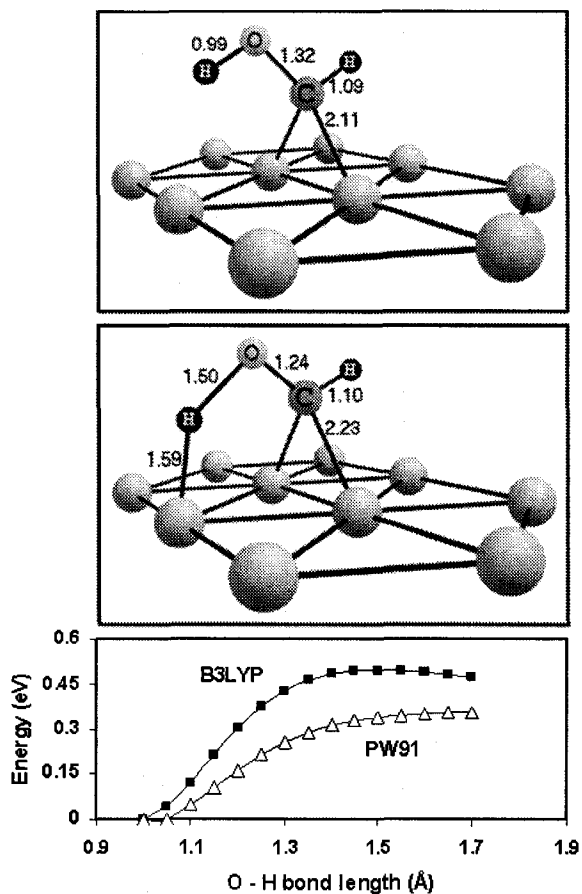


Figure 11. B3LYP initial and transition states for the reaction $^*CHOH \rightarrow ^*CHO + ^*H$. Energy profile as a function of O-H bond length.

Figure 12 shows the dissociation of the intermediate state of the reaction $^*\text{CHOH} \rightarrow ^*\text{CO} + ^*\text{H} + ^*\text{H}$ for the PW91 calculation. The initial state is the final state of the reaction $^*\text{CHOH} \rightarrow ^*\text{CHO} + ^*\text{H}$, as discussed above. Both hydrogen atoms dissociate from this

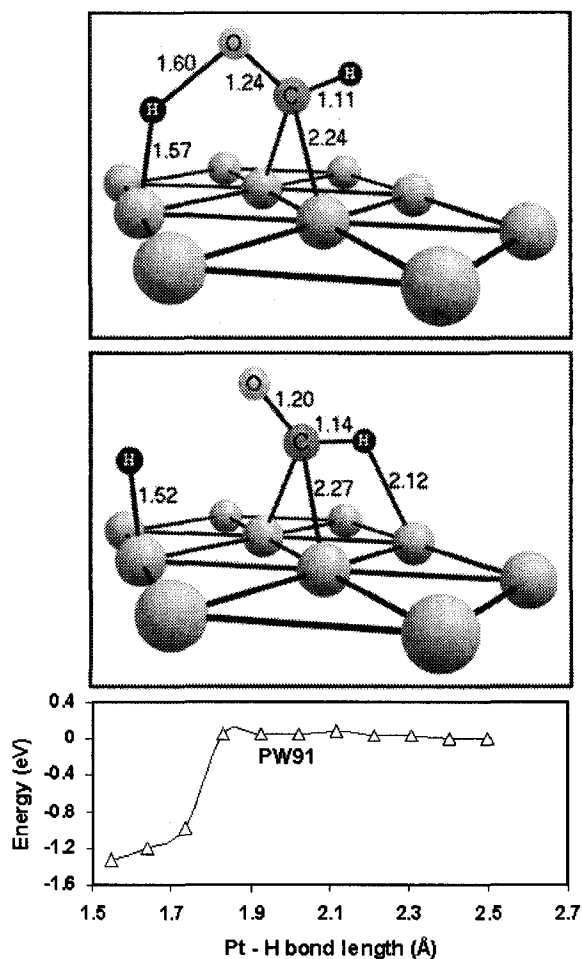


Figure 12. B3LYP initial and transition states for the reaction $^*\text{CHO} \rightarrow ^*\text{CO} + ^*\text{H}$ where the initial state is the final state of reaction $^*\text{CHOH} \rightarrow ^*\text{CHO} + ^*\text{H}$. Energy profile as a function of Pt-H bond length.

state. At the TS, the Pt-H distance is shown in Figure 12 to be 2.12 Å. This bond length was used as the reaction coordinate for the reaction pathway energy profile. The energy barrier was found to be only 0.08 eV. The reaction path was followed for SM=9. A previously reported PBC/PW91 study⁴⁵ has found that *CHOH dissociates directly to the state *CO + *H + *H with a single transition state, after which the dissociation of both hydrogen atoms is spontaneous. Our cluster calculations predict an intermediate local minimum, but the energy barrier of the second step is very small. In effect, the two results are in good agreement.

Figure 13 shows the initial and transition states for the reaction $*CHO \rightarrow *CO + *H$, where the initial state is taken to be formyl (CHO) bonded on-top. At the TS for the

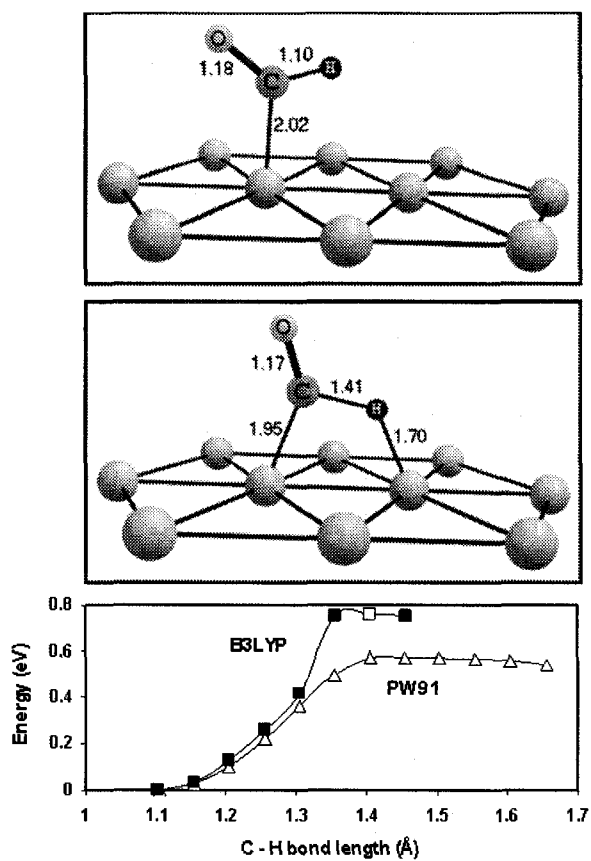


Figure 13. B3LYP initial and transition states for the reaction $*\text{CHO} \rightarrow *\text{CO} + *\text{H}$ where the initial state is CHO bonded on-top. Energy profile as a function of C-H bond length. □ = B3LYP TS.

reaction, the C atom has moved towards the bridge site, the O atom has partly rotated away from the surface and the C-H bond length is 1.41 Å. The energy barrier predicted by B3LYP for this reaction is 0.76 eV, while PW91 predicts 0.57 eV. However, the reaction pathway described in Figure 12 with the bridge-bonded initial state for $*\text{CHO}$ is favorable for the case of the PW91 predictions. The reaction path was calculated for SM=10.

Figure 14 shows that hydroxymethyldyne (COH) binds at the hollow site with the C-O bond normal to the surface. At the TS structure for the reaction $*\text{COH} \rightarrow *\text{CO} + *\text{H}$, the C atom is bridge bonded, the C-O bond rotates towards the surface and the O-H bond length is 1.32 Å. After dissociation takes place, CO returns to the more stable hollow site. The energy barrier predicted by B3LYP for this reaction is 1.49 eV, while PW91 predicts 1.18 eV. The reaction path was calculated for SM=8.

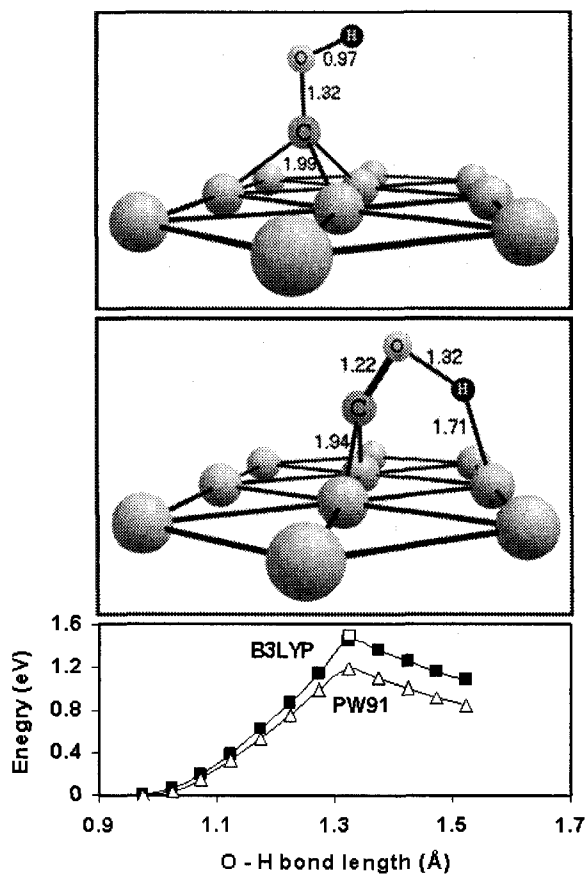


Figure 14. B3LYP initial and transition states for the reaction $*\text{COH} \rightarrow * \text{CO} + * \text{H}$. Energy profile as a function of O-H bond length. $\square$ = B3LYP TS.

Table 2 summarizes the results of the electronic energy calculations for the activation energy barriers (not corrected for ZPE) predicted by B3LYP and PW91 on the Pt_{10} clusters for the reaction pathways of Figure 1. In all cases the energy barriers found with B3LYP were consistently larger than the PW91 ones by 0.15-0.3 eV. The table also shows a characteristic bond length of the TS structure and compares the energy barriers of this work with PBC/PW91 results for those elementary steps that have been previously studied. In one study⁵⁰ the activation energies for the reactions $*\text{CH}_x \rightarrow * \text{CH}_{x-1} + * \text{H}$ were predicted on Pt (111). The electronic energy barriers predicted by our Pt_{10} /PW91 model are higher than

Table 2. DFT-predicted electronic energy barriers ($\Delta E_{\text{elec}}^{\ddagger}$) and characteristic bond length at the transition state for the reactions of Figure 1.

Reaction	$\Delta E_{\text{elec}}^{\ddagger}$ (eV) Pt ₁₀ /B3LYP (this work)	$\Delta E_{\text{elec}}^{\ddagger}$ (eV) Pt ₁₀ /PW91 (this work)	$\Delta E_{\text{elec}}^{\ddagger}$ (eV) PBC / PW91 (previous work)	TS bond length (Å) (B3LYP) (this work)
CH ₄ → *CH ₃ + *H	1.15	0.91	0.63 ^a	C-H: 1.38
*CH ₃ → *CH ₂ + *H	1.61	1.42	0.88 ^a	C-H: 1.70
*CH ₂ → *CH + *H	0.63	0.48	0.21 ^a	C-H: 1.38
*CH → *C + *H	2.51	2.18	1.54 ^a	C-H: 1.78
*CH ₂ + *OH → *CH ₂ OH	1.03	0.87		C-O: 2.13
*CH + *OH → *CHOH	1.17	0.95		C-O: 1.88
*C + *OH → *COH	0.93	0.61		C-O: 2.13
*CH ₂ OH → *CHOH + *H	1.07	0.77	0.63 ^b	C-H: 1.58
*CHOH → *COH + *H	1.33	1.14	0.80 ^b	C-H: 1.76
*CHOH → *CHO + *H	0.50	0.35	0.43 ^b	O-H: 1.50
*COH → *CO + *H	1.49	1.18	0.97 ^b	O-H: 1.32
*CHO → *CO + *H	0.76	0.57 ^c		C-H: 1.41

^a from ref 50 ^b from ref 45 ^c Initial state is CHO bonded on top

those predicted by PBC/PW91. However, both methods predict the same order in the magnitudes of the energy barriers for this series of reactions. Another PBC/PW91 study⁴⁵ predicted the activation energies on Pt (111) for the sub-network of Figure 1 that involves dehydrogenation reactions of the oxygenated adsorbed radicals. Our Pt₁₀ / PW91 energy barriers are higher in most cases but again the same order is predicted in their magnitudes. We cannot directly compare the trends for the entire set of the eight reactions, as the two

cited works do not use the same methods for the slab calculations. We are not aware of any work that predicted the activation energies of reactions of the type $*CH_x + *OH \rightarrow CH_xOH$ on Pt (111).

Figure 15 shows schematically the reaction network of Figure 1 and the electronic energy barriers of each reaction for the calculations with the B3LYP functional. In addition to activation energies, pre-exponential factors are also required to estimate and compare all rate constants using transition-state theory according to equation 14. We performed frequency calculations for the initial and transition states of the reaction network of Figure 1 and estimated pre-exponential factors using equations 10-13 and 15 (using $T=298K$). For all elementary surface reactions, except the methane chemisorption step ($CH_4 \rightarrow *CH_3 + *H$) all reactants and products were taken to be immobile and therefore only the vibrational entropy enters into equation 15. Frustrated translation and rotation modes were taken into account⁴¹ in the estimation of the vibrational entropy. We found that pre-exponential factors for the surface reactions of Figure 1 in which both the initial and final states are adsorbed species, vary from $5 \cdot 10^{11}$ to $5 \cdot 10^{13} \text{ s}^{-1}$. This range is in good agreement with PBC literature results⁴¹ for similar reactions on Pt (111). The only exception is the methane chemisorption step which involves translational and rotational entropy losses and has a much smaller pre-exponential factor, as discussed below. Using Equation 14, we calculate that, for $T=298K$, the difference in activation energies that is required to counterbalance a two orders-of-magnitude difference in pre-exponential factors, is $RT \ln(100) \approx 11.4 \text{ kJ / mole} \approx 0.12 \text{ eV}$. Figure 15 shows that the differences between the electronic energy barriers of elementary reactions that have the same initial state (parallel reactions) are much larger than 0.12 eV.

This means that the main reaction pathway can be determined by comparing only the electronic energy barriers of the reactions.

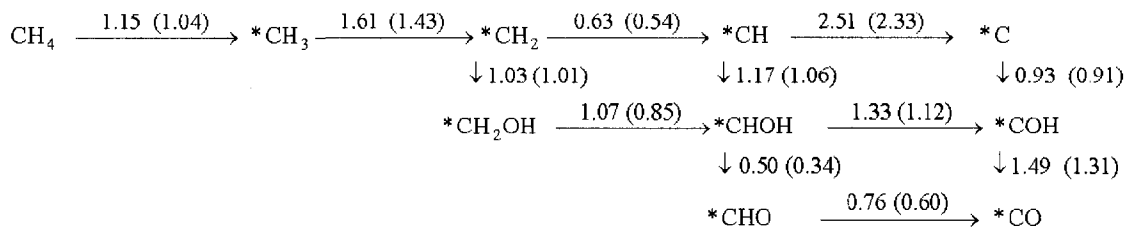


Figure 15. Electronic energy barriers for the reaction network of Figure 1 based on DFT-B3LYP calculations on a Pt₁₀ cluster. The values in parentheses were corrected for ZPE.

From Figure 15 we conclude that the reaction pathway is $\text{CH}_4 \rightarrow * \text{CH}_3 \rightarrow * \text{CH}_2 \rightarrow * \text{CH} \rightarrow * \text{CHOH} \rightarrow * \text{CHO} \rightarrow \text{CO}$. The PW91 calculations predict the same pathway. Furthermore, the rate-limiting step in this pathway can be identified by comparing the rate constant for the methane chemisorption step ($\text{CH}_4 \rightarrow * \text{CH}_3 + * \text{H}$) with the slowest of the subsequent steps of the reaction pathway. The latter is the one with the highest electronic energy barrier in the reaction pathway, which is the reaction $* \text{CH}_3 \rightarrow * \text{CH}_2 + * \text{H}$. Therefore, we need only perform a quantitative comparison between the rate constants of these two reactions on the Pt₁₀ cluster.

The vibrational frequencies corresponding to the initial state and transition states for the two elementary steps $\text{CH}_4 \rightarrow * \text{CH}_3 + * \text{H}$ and $* \text{CH}_3 \rightarrow * \text{CH}_2 + * \text{H}$ are shown in Table 3. They were obtained for the 10-atom Pt cluster by a frequency calculation at the geometry of the corresponding minima and saddle points at the B3LYP/LANL2DZ/6-31G** level. The frequencies include frustrated translation and rotation modes and the negative real part of

the imaginary frequency of the TS. Based on the discussion in the previous section, for the direct dissociative chemisorption of methane, the reactant has 9 vibrational modes, 3 translational and 3 rotational modes whereas the TS has 14 real positive vibrational modes. For the surface reaction $^*\text{CH}_3 \rightarrow ^*\text{CH}_2 + ^*\text{H}$, the reactant has 12 vibrational modes and the TS has 11 real vibrational modes.

Table 3. Vibrational frequencies of the initial and transition states (IS, TS) of the reactions $\text{CH}_4 \rightarrow ^*\text{CH}_3 + ^*\text{H}$ and $^*\text{CH}_3 \rightarrow ^*\text{CH}_2 + ^*\text{H}$ on a 10-atom Pt cluster at the B3LYP / LANL2DZ / 6-31G** level.

Reaction	IS Frequencies (cm-1)	TS Frequencies (cm-1)
$\text{CH}_4 \rightarrow ^*\text{CH}_3 + ^*\text{H}$	3164, 3164, 3164, 3048, 1579, 1579, 1356, 1356, 1356	3264, 3192, 3070, 1524, 1434, 1337, 1096, 1010, 709, 525, 450, 165, 151, 71, -1186
$^*\text{CH}_3 \rightarrow ^*\text{CH}_2 + ^*\text{H}$	3221, 3212, 3086, 1451, 1447, 1254, 849, 846, 529, 170, 159, 60	3264, 3130, 1945, 1370, 957, 826, 708, 619, 324, 170, 120, -832

The values shown in parentheses in Figure 15 were obtained by applying zero-point energy (ZPE) corrections to the electronic energy barriers. ZPE corrections were obtained using equation 9 by frequency analysis of the initial and transition states of the reactions.

For all dehydrogenation reactions, ZPE corrections act in the direction of decreasing the activation energy barrier by ~ 0.1 - 0.2 eV, because C-H and O-H bonds vibrate at higher frequencies than Pt-H bonds. The $\text{CH}_x + \text{OH}$ reactions are only mildly affected by ZPE. From Fig. 15 we can observe that the inclusion of ZPE in the energy barriers does not affect the conclusions on the mechanistic pathway.

Using equations 5-16 and the results of the electronic energy and frequency calculations, we calculated the pre-exponential factors, activation energies and rate constants for the two reactions of interest. The results appear in Table 4. For the direct dissociative chemisorption of methane ($\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$), in which the reactant is in the gas phase and the TS was considered immobile, the translational partition function of the reactant was evaluated in units of atm^{-1} , in which case the rate constant has units of $\text{s}^{-1}\text{atm}^{-1}\text{site}^{-1}$, where ‘site’ means free platinum site available for adsorption. For the surface reaction $\text{*CH}_3 \rightarrow \text{*CH}_2 + \text{*H}$, both the reactant and the TS were considered immobile and have no translational degrees of freedom so that the rate constant has units of $\text{s}^{-1}\text{site}^{-1}$, where ‘site’ denotes a site covered with a *CH_3 species. Molar units have been used for the activation energies in Table 4. The first set of rate constants in the third row of Table 4 was calculated using the electronic energy barriers calculated with the 10-atom Pt cluster using the B3LYP functional. The results with the B3LYP functional were used in the calculations because transition state optimizations and frequency calculations were done with B3LYP. The second set of rate constants, in the last row of Table 4 was calculated with the same procedure, using the electronic energy barriers of previous PBC calculations⁵⁰, shown in Table 2, for Pt (111), and using the same pre-exponential that we obtained on the 10-atom Pt cluster, since frequency analysis was not performed in the cited work.

Table 4. Estimates of pre-exponential factors, activation energies and rate constants for the reactions $\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$ and $\text{*CH}_3 \rightarrow \text{*CH}_2 + \text{*H}$ on Pt (111)

Based on		
current Pt₁₀ results	$\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$	$\text{*CH}_3 \rightarrow \text{*CH}_2 + \text{*H}$
Pre-exponential factor (298K)	$8.2 * 10^4 \text{ s}^{-1} \text{ site}^{-1} \text{ atm}^{-1}$	$1.7 * 10^{12} \text{ s}^{-1} \text{ site}^{-1}$
Activation energy	99.5 kJ / mol	137.2 kJ / mol
Rate constant (298 K)	$3 * 10^{-13} \text{ s}^{-1} \text{ site}^{-1} \text{ atm}^{-1}$	$1.5 * 10^{-12} \text{ s}^{-1} \text{ site}^{-1}$
Based on		
Literature PBC results	$\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$	$\text{*CH}_3 \rightarrow \text{*CH}_2 + \text{*H}$
Activation energy ^a	49.8 kJ / mol	66.9 kJ / mol
Rate constant (298 K)	$1.5 * 10^{-4} \text{ s}^{-1} \text{ site}^{-1} \text{ atm}^{-1}$	$3.1 \text{ s}^{-1} \text{ site}^{-1}$
^a from ref 50		

The activation energies of the PBC / PW91 calculations are much smaller than the Pt10 / B3LYP ones, resulting in rate constants that are many orders of magnitude greater. However, both calculations agree in that the rate constant for CH_4 adsorption is smaller than the rate constant for CH_3 dehydrogenation. Pt10 / B3LYP results predict one order of magnitude difference between the rate constants, whereas PBC results predict 4 orders of

magnitude. Despite the uncertainty in the magnitudes of the rate constants, we can safely conclude that methane chemisorption is the slowest step of the reaction mechanism. This result is a consequence of the combination of both a high electronic energy barrier for dissociative chemisorption caused by Pauli repulsion and the loss of the translational and rotational degrees of freedom upon adsorption of the methane molecule on the surface of the catalyst. The large entropy loss makes the pre-exponential factor for methane adsorption many orders of magnitude smaller than a surface reaction step. Even though the dissociation of the methyl radical that forms upon adsorption has higher activation energy than CH₄ chemisorption, the entropy effect predominates.

The calculations in Table 4 refer to T=298K. At higher temperatures, the ratio of the rate constant for methane dissociation (the first step) divided by the rate constant for the dissociation of the methyl radical (the second step), will be even smaller and the conclusion will be strengthened. If k_1 , E_{act1} denote the rate constant and activation energy for the first step, and k_2 , E_{act2} denote the same quantities for the second step, we obtain from Eq. 14:

$$\frac{k_1}{k_2} = \exp\left(\frac{E_{act2} - E_{act1}}{k_B T}\right) \quad (17)$$

In Eq. 17, it has been taken into consideration that the ratio of pre-exponential factors does not change with temperature (Eq. 15). Thus, from equation 17, we conclude that at higher temperatures, such as those encountered in fuel cells, k_1/k_2 decreases, so that the conclusion that the first step is rate-limiting would be strengthened.

Evident in Table 4 is the sensitivity of the estimates of the rate constants on the DFT estimates of activation energies. This dictates that the nature of the conclusions should be

kept strictly qualitative and only used for mechanistic analysis. In a recent experimental kinetic study¹⁹ of methane decomposition on supported platinum catalysts, the activation energy for methane chemisorption was found to be 78 kJ/ mole. Our results, using a Pt₁₀ cluster were 99.5 kJ/mole (B3LYP functional) and 77 kJ/mole (PW91 functional). The experimental pre-exponential factor at T= 873K for the same reaction was $2.9 \times 10^6 \text{ s}^{-1} \text{ atm}^{-1}$. We calculated, using the B3LYP functional, the pre-exponential factor to be 2.4×10^5 at the same temperature using equation 14 for T = 873K and taking into account the temperature dependence of the pre-exponential factor. Thus, considering the approximations used in our model and the uncertainties in experimental values, the agreement is satisfactory. The relatively good agreement between the experimental and calculated pre-exponential factors is evidence that the direct dissociation hypothesis is reasonable. Considering the complexity of the real catalyst, the structure sensitivity of the methane chemisorption process and simplifications in our approach, this quantitative comparison is somewhat arbitrary. The PBC calculations cited in Table 4 also seem to under-predict the activation energy of methane dissociation. In fact, our results are in better agreement with this experiment than the PBC results. Nevertheless, we limit the implications of our results to strictly qualitative conclusions.

Because the elementary reaction $\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$ was identified as the rate limiting step in the reaction network of Figure 15, we performed an additional calculation on a 25-atom, 3-layer Pt(111) cluster in order to investigate the cluster-size effect on the electronic energy barrier. The reaction scan and the geometry that corresponds to the maximum of the scan, and thus approximates the TS structure, are shown in Figure 16. The calculation was performed using the B3LYP functional. The cluster consists of 14 Pt atoms in the first layer,

8 atoms in the second and 3 atoms in the third layer and all Pt atoms were kept fixed in the optimizations. The reaction scan was calculated for SM=17. The initial state was taken as the methane molecule and the bare cluster at infinite separation. The approximate TS structure on the Pt₂₅ cluster resembles the structure of the TS on the Pt₁₀ cluster (Figure 2) with small differences in bond lengths. The electronic energy barrier for the dissociative chemisorption of methane on the Pt₂₅ cluster was calculated to be 1.28 eV. This value is not very different from the energy barrier that was obtained on the Pt₁₀ cluster, 1.15 eV. The comparison suggests only minor cluster-size effects but is not conclusive for this argument. Nevertheless, it helps to establish further confidence for our conclusions on the mechanism of the reaction.

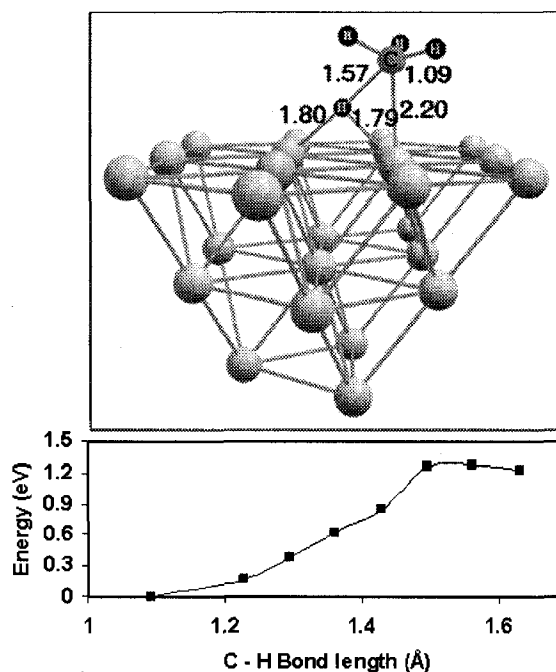


Figure 16. Transition state for the reaction $\text{CH}_4 \rightarrow \text{*CH}_3 + \text{*H}$ on a Pt₂₅ cluster (top) and electronic energy profile as a function of C-H bond length (bottom) calculated using the B3LYP functional .

The calculations and kinetic analysis in this work assume that the reactions happen at the Pt / vacuum interface. The following qualitative arguments can be used to justify that methane chemisorption would be expected to be the rate determining step at the electrochemical interface as well. Water molecules, OH species and electrolyte anions are adsorbed at the Pt / electrolyte interface of an acid electrolyte. The strength of the interaction of the catalyst with any of these species is a function of the electrode potential. For a methane molecule to adsorb on the electrode, it has to compete with all molecular species at the double layer. Because methane adsorption requires activation to break the C-H bond, the competition of water and methane for adsorption sites favors water adsorption. Thus, only a fraction of the surface sites would be available for methane to adsorb. Furthermore, the surface charge would tend to increase the binding energy of the more polar water molecules compared to an uncharged surface. Microscopically, a methane molecule can adsorb on a vacant site that is created by the continuous exchange of water molecules between the surface and the solution. Steric hindrance effects and electronic effects caused by electrolyte anions at the interface can also be significant. In a comparative study²⁷ of methane adsorption on clean and oxygen-precovered Pt (111), it was found that the dissociation probability is smaller on the oxygen-covered surface by one to two orders of magnitude. An analogous trend can be expected for the electrochemical interface compared to the clean surface. Another factor that would diminish the rate of adsorption from solution is the very low solubility of methane in the electrolyte because the CH₄ dissociation rate increases with increasing the pressure or concentration of CH₄ above the surface¹⁹. At 25 °C and 1 atm pressure the solubility of methane in water is⁴ 24.4 g CH₄/10⁶ g H₂O. These considerations suggest that the chemisorption of CH₄ from a liquid electrolyte should be

much slower than its chemisorption from the gas phase. This allows us to extend the conclusion that methane chemisorption is rate-limiting in the reaction network of Figure 1 to the electrochemical interface.

The effect of the electrolyte on the decomposition-oxidation pathway may be more complex than its effect on the rate limiting step. As a first approximation, the electrolyte was not included in our model. In the work of Cao et al⁵¹ on the mechanism of methanol decomposition, the water phase was found to affect reaction energies. In contrast to our work, Cao et al did not calculate activation barriers. We note however that, despite the fact that including the water phase in the calculations is a considerable improvement in the description of the interface, the agreement of the results of his work with experiment was not good. This can be partly because the electrolyte is not sufficiently represented only with water molecules. It includes protons and electrolyte species as well. Furthermore, static calculations that represent the water phase as a fixed ice-like structure may be insufficient because they can not describe the dynamics of the water phase interactions. In this work we have focused on the interactions between the metal and the adsorbed species of the reaction network. The effects of the electrolyte on the mechanism can not be included realistically in our cluster model.

The effect of the electrode potential was not included in the present calculations. Strictly, the calculations on an uncharged cluster correspond more accurately to the potential of zero charge. Cao et al⁵¹ performed periodic calculations on the mechanisms of methanol decomposition on Pt and calculated potential-dependent reaction energies. For a wide range of potentials up to 1V vs. NHE, it was found that the magnitude of the electrical potential

did not affect the calculated main reaction pathway because the potential had a very similar effect on all reaction energies. This can be expected because the electrical potential has only a minor effect on the binding energies of uncharged adsorbed species. Many of these dehydrogenation reactions are common in our work. Based on this we don't expect any changes on the rate determining step and mechanism with varying the potential. It is typical of electrodic reactions that the rate determining step extends in a wide potential range and this is manifested in single-slope Tafel plots. However, we note that a more realistic model that would be able to make quantitative predictions on the kinetics of methane oxidation would need to account for the effects of both the electrolyte phase and the electrical potential variable.

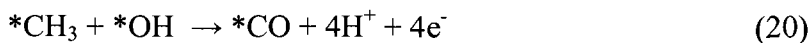
Based on the combination of these results with widely accepted mechanistic aspects of the electrooxidation of CO that forms from organics (i.e. methanol) on platinum¹⁶ we postulate the following complete reaction mechanism for methane electro-oxidation at anodic potentials greater than ~0.4 volts. In acid solution, hydroxyl groups form on the surface by deprotonation of water molecules according to the reaction¹⁶ :



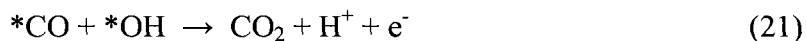
Methane adsorbs dissociatively and the resulting adsorbed H quickly passes into solution at double layer potentials:



The adsorbed methyl radical forms CO through the pathway $\text{*CH}_3 \rightarrow \text{*CH}_2 \rightarrow \text{*CH} \rightarrow \text{*CHOH} \rightarrow \text{*CHO} \rightarrow \text{*CO}$, in which all steps are faster than (19). Written concisely:



Adsorbed CO is oxidized by adsorbed OH through the reaction¹⁶:



Reaction (18) to (21) sum up to the complete methane electro-oxidation reaction (1). As discussed in the introduction the experimental results indicate that reactions (18) and (21) proceed faster than (19) at potentials in the double layer region. This means that reaction (19) is the rate-limiting step, which is consistent with the rate limiting step found in these calculations for Pt(111). Another implication of this result is that catalysts that remove adsorbed CO more effectively than pure platinum but impede the rate of chemisorption of methane would not increase the rate of methane electro-oxidation. This is most probably the case of Pt-Ru alloys that have been found to be less active towards methane electro-oxidation compared to pure platinum^{5,10,12,14}. For electrode potentials in the hydrogen region (0 – 0.35 volts) no definitive conclusions can be made for the rate-limiting step, which can be either methane adsorption or $*\text{CO}$ oxidation. The above considerations apply to anode potentials greater than ~ 0.35 volts.

2.4 Conclusions / Recommendations

The present computational work has resulted in the following conclusions:

- 1) The electro-oxidation of methane on Pt proceeds according to the mechanism: $\text{CH}_4 \rightarrow *\text{CH}_3 \rightarrow *\text{CH}_2 \rightarrow *\text{CH} \rightarrow *\text{CHOH} \rightarrow *\text{CHO} \rightarrow *\text{CO} \rightarrow \text{CO}_2$, where $*$ denotes an adsorbed species.
- 2) The rate determining step for the pathway from CH_4 to $*\text{CO}$ is the dissociative chemisorption of CH_4 . The rate of this elementary step is slow because it has a relatively large electronic energy barrier and it is accompanied by a large entropic loss. Although not studied here, two further reasons that pertain to liquid electrolytes are the low solubility of

methane in water-based electrolytes and the fact that adsorbing methane molecules must compete with water molecules from the solid/ liquid interface.

3) As a result of (2), the only two possible rate-determining steps for the overall reaction of methane electro-oxidation are the methane chemisorption step and the *CO oxidation step. This conclusion is in agreement with the experimental observation of no adsorbed organic adlayer at electrode potentials above about 0.4 V at which the *CO oxidation reaction takes place on the Pt surface.

4) As a result of (2) and (3), an anode catalyst that could possibly result in higher current densities than platinum for the direct oxidation of CH₄ is one for which the rate of adsorption is faster. On the other hand, an improved catalyst should not impede the rates of dehydrogenation and oxidation reactions at the catalyst surface. A catalyst that is able to oxidize adsorbed CO at lower anode potentials would not necessarily enhance the rates of the electro-oxidation of methane if it decreases the rate of chemisorption of methane.

5) The B3LYP exchange-correlation functional predicts significantly higher (by 0.15-0.3 eV) electronic energy barriers than the PW91 functional for the set of reactions that was studied. However, the same trends in the magnitudes of the barriers for different reactions were found. A comparison of the cluster calculations of the present work with PBC calculations available in the literature, revealed good agreement in trends but very different results in the magnitudes of electronic energies.

Some recommendations for future work can be identified. Based on the above conclusions, quantum mechanical DFT studies of methane adsorption on catalytic surfaces could be used as a screening tool for possible improved catalysts for the electro-oxidation process. The results of experimental investigations of methane adsorption at the gas-solid

interface of metal catalysts could also prove useful, provided that the catalysts are also stable at the electrochemical environment. Alloys of platinum might offer possibilities for improvement. Furthermore, to our knowledge, the activities of single-crystal surfaces towards the electro-oxidation of methane have not been experimentally investigated. Considering the fact that many fuel cell reactions are structure sensitive, as well as the variability of alloy catalysts, the possibility remains open that an effective catalyst for the direct oxidation of methane and other hydrocarbon fuels still eludes our knowledge. Ab-initio DFT studies at the metal-water interface combined with modeling of electrode potential effects would be expected to provide an improved understanding of the methane electro-oxidation process.

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CHAPTER 3: Cluster DFT study of the dissociative chemisorption of methane on Ru, Rh, Pd, Os, Ir and Pt.**

George Psofogiannakis^{†L}, Alain St-Amant[‡] and Marten Ternan^{*†§L}

Department of Chemical Engineering, Department of Chemistry, and Centre for Catalysis
Research and Innovation, University of Ottawa, University of Ottawa, Ont., K1N 6N5,
Canada, and EnPross Inc., 147 Banning Road, Ottawa, Ont., K2L 1C5, Canada

*Corresponding author. E-mail:ternan@sympatico.ca Phone: (+1) 613-831 8080

[†] Department of Chemical Engineering, University of Ottawa

[‡] Department of Chemistry, University of Ottawa

^L Centre for Catalysis Research and Innovation

[§] EnPross Inc.

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Abstract

Ab-initio Density Functional Theory (DFT) cluster calculations were performed for the dissociative chemisorption of methane ($\text{CH}_4 \rightarrow \text{CH}_{3(\text{ads})} + \text{H}_{(\text{ads})}$) on the transition metal catalysts Ru, Rh, Pd, Os, Ir and Pt. Various clusters of 14-26 metal atoms were used to model the close-packed terrace site, an ad-atom site and a step site for the metals. Reaction coordinate calculations were performed and the results identified trends in the calculated energy barriers for CH_4 dissociation among the metals and reaction sites. It was found that for terrace sites the energy barrier was lowest for Ru, and was higher for metals with higher d-band occupancy. It was also found that for adatom and step sites, the energy barriers of the 5d metals Os, Ir, Pt were significantly lower than those of the 4d metals Ru, Rh, Pd. Natural Bond Orbital analysis was performed to identify the reasons for the different reactivity of a Pt and a Ru ad-atom.

Keywords: methane, chemisorption, transition metals, density functional theory, clusters

3.1 Introduction

The dissociative chemisorption of methane on metal catalysts is the first step in the catalytic industrial process of steam-reforming of natural gas¹⁻³. In steam-reforming, methane and steam are converted to a mixture of hydrogen, carbon monoxide and carbon dioxide, otherwise known as synthesis gas (syngas). Syngas has extensive industrial use in the manufacture of methanol, higher alcohols, ammonia and synthetic fuels, as well as in the production of hydrogen for refineries and fuel cells. The significance of the large-scale industrial process of steam reforming of natural gas has stirred intense experimental and theoretical research in the field. Much experimental work has also been done on CO₂ – reforming, where steam is replaced by CO₂. Many details of the reforming of methane have been summarized in fairly comprehensive reviews¹⁻⁵. Our group is also interested in the direct oxidation of methane and other saturated hydrocarbons in low-temperature direct hydrocarbon fuel cells⁶. The adsorption and dissociation of methane on transition metal electrodes would also be the first step in the sequence of elementary reaction steps in the anode of a fuel cell operating with methane. Thus dissociative chemisorption of methane is an important reaction for both steam reforming and direct methane fuel cells.

Catalysis is of central importance in steam reforming of methane. Supported nickel catalysts and 4d and 5d transition metal catalysts (platinum, palladium, ruthenium, rhodium and iridium) are capable of catalyzing the reaction¹. Nickel is usually preferred for economic reasons despite being less reactive than the 4d and 5d transition metal catalysts^{1,7}. Apart from the activation of the very stable C-H bonds of methane (bond energy¹ 439

kJ/mol), a good catalyst should also not be susceptible to carbon poisoning, sintering and large diffusion losses¹.

It is generally believed that the initial dissociative chemisorption of methane controls the rate^{3,7}. It was found⁸ by isotope tracer and kinetic studies that the C-H bond activation is rate-limiting in reforming over noble metals, and that reforming rates increase with better dispersion, which in turn is influenced by the nature of the support. An ab-initio DFT computation⁹ of activation energies of the complete reaction network suggested that the electronic energy barrier of the initial dissociation step, despite being quite large (~100 kJ/mol), was not the largest in the mechanism. However, the large entropic loss associated with the initial dissociative chemisorption of methane makes the pre-exponential factor many orders of magnitude smaller than the surface reaction steps and renders the initial step rate-controlling⁷. The same conclusion was drawn from cluster calculations⁶ on Pt(111).

There is controversy regarding the relative reactivity of reforming catalysts. An experimental study⁸ of methane reforming suggested that, among transition metals at equal dispersion, platinum is the most reactive, followed by iridium, rhodium and ruthenium, in order of decreasing reactivity. However, another set of experiments^{1,10} indicated that ruthenium and rhodium are more reactive than platinum and palladium. A few more comparative studies have been noted⁴ and no definite conclusions can be made.

Experimental and ab-initio DFT studies suggest that the presence of low-coordination sites generally reduces activation energies for the dissociation of methane. For example, a molecular beam experiment¹¹ of methane dissociation on a Pt(533) crystal showed that the

energetic barrier to dissociation was lower on the (100) steps compared to the (111) terrace sites by about 0.3 eV. An ab-initio DFT study⁹ of the methane decomposition reaction network on the close-packed Ni(111) and the stepped Ni(211) surfaces, found a lower energy barrier on Ni(211) for the initial dissociation of CH₄, as well as for most of the surface elementary steps. In another DFT study¹², a substantially lower dissociation barrier was reported for Rh steps (0.32 eV) compared to Rh(111) sites (0.67 eV). Also, based on DFT work¹³, a reduced energy barrier was reported for methane dissociation on Rh adatoms over a Rh(111) surface, compared to that of a terrace site, by ~0.32 eV.

An industrial catalyst contains both flat terrace sites and various step and defect sites. However, it is still unclear if step and defect sites participate in the reactions. Being highly reactive, they can be more easily poisoned by carbon^{1,7}. Computations¹³ suggest that those catalysts that break the first C-H bond more efficiently, are also likely to break the C-H bonds of the adsorbed species and result in coking. The catalytic activity of steam reforming catalysts would be determined not only by the intrinsic activity of the various kinds of sites (steps, kinks, terrace sites, defects), but also by their relative contributions under reaction conditions.

Several periodic plane-wave DFT calculations have been performed for the dissociative chemisorption of methane on transition metal single-crystal surfaces. The majority of them model the close-packed terraces. For 2×2 unit cells the energy barrier for the initial CH₄ dissociation was estimated to be 77 kJ/mol on Ru(0001)¹⁴, 67 kJ/mol on Rh(111)¹², 66 kJ/mol on Pd(111)¹⁵, 30 kJ/mol on Ir(111)¹⁶ and 75 kJ/mol on Pt(111)¹⁵. In the study¹⁶ of

Ir(111), a large surface relaxation was observed. At the transition state, the Ir atom that binds to the carbon atom was displaced outwards from the surface by 0.41 Å.

Modern theories¹⁷ of chemisorption and dissociation of adsorbates on metal surfaces stress the role of the interaction between metal electronic energy bands and the molecular orbitals of the adsorbate. Dissociative chemisorption involves¹⁸ the donation of electron density from the highest occupied molecular orbital (HOMO) of the adsorbate to empty energy states on the metal, as well as back-donation of electron density from the metal to the lowest unoccupied molecular orbital (LUMO) of the adsorbate. Both effects lead to the weakening and ultimate dissociation of the adsorbate bond. The mechanism of dissociation of the C-H methane bond was previously examined through extended Huckel calculations¹⁹. It was found to involve both donation and back-donation and was similar on transition metal surfaces and on transition metal complexes.

In the present DFT work, we examined the initial step in the steam reforming process, the dissociative adsorption of methane, $\text{CH}_4 \rightarrow \text{CH}_{3(\text{ads})} + \text{H}_{(\text{ads})}$, on the transition metal catalysts Ru, Rh, Pd, Os, Ir, and Pt. These are the Group VIII metals of the second (4d) and third (5d) transition series that exhibit catalytic activity for the dissociation of methane. The objective was to identify trends in the activation energies among those metals for close-packed terraces, ad-atoms and step sites. We calculated the electronic energy profiles as a function of the C-H bond length of the breaking bond and the corresponding activation energies. Our calculations employed small clusters that were chosen to mimic terrace and defect sites on the surface. We also performed a Natural Bond Orbital analysis to examine the differences in orbital interactions for the dissociation of methane on two different metal

clusters. Because natural bond orbitals are centered on either one or two atoms, this approach permits a more localized view of the orbital interactions between the adsorption site and the adsorbate.

The small sizes of the clusters (14-19 atoms) introduced some inaccuracy as they are a simplification of the extended surface and do not provide an accurate description of the metal band structure. However, we used the same cluster sizes, geometries and computational methods for all different metals. Thus, we attach greater significance to the established trends. Using the same computational setup also makes a comparison of trends more appropriate than comparing literature values that have been obtained with a variety of methods.

3.2 Computational methods

Several different cluster structures were used in the calculations. These are shown in the figures of the results section. A 14-atom symmetric planar cluster was used to model the close-packed surfaces Ru(0001), Rh(111), Pd(111), Os(0001), Ir(111), and Pt(111). The structure of the (111) surface of the fcc metals Rh, Pd, Ir, Pt is equivalent to the (0001) surface of the hcp metals Os, Ru. Two sets of calculations were performed for the 14-atom clusters for all six metals. In the first set, the structure was kept fixed throughout the reaction energy scan. In the second set, the metal atom that was involved in the formation of the metal-carbon bond, was allowed to freely optimize its position for each computed point in the reaction coordinate. The incentive for this set of calculations was provided by the large surface relaxation that was previously observed¹⁶ in the periodic slab DFT model of

the dissociative adsorption of methane on Ir(111). In particular, it was observed from the slab calculations that only one metal atom was significantly displaced during the reaction. The second set of calculations allowed us to assess the extent and significance of surface relaxation effects. For the 14-atom cluster, the dissociated methane fragments, the methyl group and the hydrogen atom, are bonded to internal sites of the cluster without imposing any geometric constraints. One energy scan was also performed for platinum for a 3-layer, 26-atom (111) cluster to assess the extent of cluster-size effects.

Other clusters were used to model ad-atom and step sites. A 15-atom cluster was employed to model the reaction on an ad-atom site of the type M/M(111): the adatom and surface were the same metal. The calculations were done for all six metals. The structure consisted of a 14-atom base layer and a single atom in a second layer, that was 3-fold coordinated to internal metal atoms of the base layer. The close-packed base layer was kept rigid while the adatom was allowed to freely optimize. A 19-atom cluster was employed to model the reaction on monatomic step sites. The 2-layer cluster consisted of a 14-atom base layer and 5 atoms on a second layer, such that a distinct step was formed. The Pt atom that formed the Pt-C bond was freely allowed to optimize its coordinates for each point in the energy scan. The step-site calculations were done for Rh, Ir and Pt.

Density functional theory (DFT) calculations were performed using GAUSSIAN 03 software²⁰. We employed the generalized gradient approximation functional of Perdew and Wang²¹ (PW91) to describe exchange and correlation effects. In a previous DFT cluster study⁶ of methane chemisorption on Pt we found significant differences (~ 0.25 eV) between the activation energies obtained with the PW91 and B3LYP functionals. Our

present results allow better comparison with periodic plane-wave DFT calculations that usually employ the PW91 functional. For the transition metal atoms, we used the Los Alamos National Laboratory²² basis set of double-zeta quality (LANL2DZ) and the corresponding scalar relativistic effective core potential that replaces the inner-shell electrons. The outer-shell s,p and d electrons (18 for Pt and Pd, 17 for Rh and Ir and 16 for Ru and Os) were treated explicitly. The 6-31G** basis set was used for carbon, hydrogen and oxygen atoms. No significant spin contamination was found. For geometry optimizations, the convergence criteria corresponded to a maximum step size of 0.01 au and an RMS force of 0.0017 au.

Except for the metal atom that was allowed to optimize freely, the interatomic distance in the metal clusters was kept fixed in the optimizations at the experimental bulk values²³, 2.775 Å for Pt, 2.714 Å for Ir, 2.734 Å for Os, 2.750 Å for Pd, 2.689 Å for Rh and 2.706 Å for Ru. No further constraints were imposed in geometry optimizations. To assess the effect of fixing the cluster, one energy scan for the Ru₁₄ planar cluster was performed by first optimizing the geometry and spin state of the cluster. The optimized interatomic distance was 2.526 Å, compared to the experimental 2.706, but the ground-state spin multiplicity also changed significantly from 29 (for 2.706 Å) to 19, for the optimized structure. Then the reaction coordinate calculation was performed with the atoms fixed at the geometry of the optimized cluster. We found a very small change in the activation energy (0.03 eV), compared to the calculation with the atoms fixed at the experimental bulk structure. Optimizing the spin state seems to compensate for the differences in the interatomic distances between the two calculations. Another alternative would be to let the interatomic distance optimize at each point in the reaction coordinate. However, that seems an

unacceptable model, as the many low-coordination edge sites would have more freedom to move during the dissociation process compared to the real catalyst.

For each reaction, the initial state was taken to be the minimum energy molecularly adsorbed state of CH₄ that was found to exist at large distances from the surface and was optimized in a separate calculation. Reaction coordinate scans were done for all reactions by selecting the C-H bond length as the internal coordinate to scan through the potential energy surface. We performed constrained energy minimizations for various fixed values of this coordinate. We found that it was computationally more efficient to perform the scans in the reverse (associative) direction, reducing the C-H bond length in the process. The transition state (TS) energy was estimated as the maximum energy of the reaction scan. In our previous work⁶, we obtained the exact TS saddle point of many reactions on Pt(111), including the dissociative adsorption reaction, using analytical frequency methods. We observed that, as long as enough points were included in the reaction energy scans, the energy of the maximum point in the scan was in all cases very close to the exact TS energy. The inaccuracy introduced by not performing TS optimizations is very small compared to the inaccuracy introduced by using small cluster sizes. We also found that analytical TS optimizations for systems of this size often have convergence difficulties. Thus, the electronic activation energy was taken to be the energy difference between the maximum point in the scans and the molecularly-adsorbed initial state. Zero-point energy (ZPE) corrections to the activation energies could not be calculated without vibrational frequencies. In a previous cluster study with a similar calculation set-up⁶, the inclusion of ZPE resulted in a 0.11 eV reduction of the activation energy for the reaction on Pt(111).

The effect of the spin state of the cluster-methane systems was included in the calculations. In each case, the spin multiplicity (SM) that minimizes the total energy (the ground state) was found by performing calculations for several different spin multiplicities ($SM=1+\text{number of unpaired electrons}$). Reaction paths were followed for the ground-state spin of the initial state for each reaction. We performed calculations on some reaction pathways with two and more different spin multiplicities and found that there is no change in the spin state from the initial state to the TS. The final state has a lower spin than the reactants but this has no consequence on the activation energies. In general, we found that the ground states of the clusters are high-spin and vary significantly between metals. The effect of the spin-state on the electronic energy of Pt clusters has been previously examined²⁴ and the preferred high-spin states were explained by a model that predicts the bonding orbitals within the cluster.

Natural bond orbital (NBO) analysis^{25,26} was used to explain the differences between the dissociation of methane on two particular clusters, Pt₁₅ and Ru₁₅, as detailed in the results section. The set of NBOs is an orthogonal set of molecular orbitals and consists of occupied orbitals localized on either one (core and valence lone pair orbitals) or two atoms (bond orbitals), together with unoccupied orbitals (antibonding orbitals, non-Lewis lone pair orbitals and extra-valence Rydberg orbitals). The NBOs are linear combinations of natural hybrid orbitals that are in turn obtained as linear combinations of natural atomic orbitals. The result is an interpretation of the electron density that is closer to familiar orbital theories, because the orbitals are localized. The set of occupied orbitals provides the Lewis structure of the molecule or, more generally, collection of atoms. The non-Lewis, delocalization effects are taken into account by the fact that neither the occupied orbitals are

completely filled, nor the unoccupied orbitals are completely empty. The stabilization energy that is caused by the interaction between a filled (Lewis, donor) orbital i and unfilled (non-Lewis, acceptor) orbital j is calculated by second order perturbation analysis²⁵:

$$E^{(2)} = \frac{q_i F_{i,j}^2}{\epsilon_i - \epsilon_j} \quad (1)$$

where $E^{(2)}$ denotes the 2nd order stabilization energy, q_i is the occupancy of the donor orbital, $F_{i,j}$ is the off-diagonal NBO Fock matrix element (the overlap element) and ϵ_i , ϵ_j are the energies of the donor and acceptor orbitals. Thus, the NBO orbital treatment identifies donor – acceptor interactions, which lead to loss of occupancy from the donor to the acceptor orbital, and therefore charge transfer. In the present case, the NBO analysis was performed to the open-shell wavefunction, because we did open shell calculations to obtain the electronic energies. Thus the NBO orbitals consist of two sets of orbitals (alpha and beta) that have maximum possible occupation of one electron.

The NBO approach conveniently identifies donation and back-donation effects²⁵ because the occupancy of NBO bonding and antibonding orbitals of the C-H bond are given in the output of the analysis. In the cluster approach, the molecular orbitals energies are discrete and we can identify specific donor and acceptor orbitals. Within the NBO framework, orbitals of the metal that are localized on the adsorption sites are interacting more strongly with the adsorbate. These are the HOMO that acts as a donor and the LUMO that acts as an acceptor. However, many more orbitals have smaller contributions to the bonding and dissociation mechanism. Also, within the NBO framework, in a dissociative chemisorption reaction, the orbitals of the molecule that are more involved in donation and back-donation interactions are the bonding and antibonding orbitals of the dissociating bond. As a result,

using NBO analysis, we are able to identify the NBOs that are involved in charge transfer, their energies, their electron occupancies and the stabilization energies caused by donor – acceptor interactions.

3.3 Results and Discussion

A. Structures

Because of the large amount of calculations that were performed on different clusters and metals, we show here only some representative initial and transition state structures for methane dissociation on platinum clusters. The results of the structures for other metals were qualitatively similar to those for Pt. However, there were considerable differences in the C-H bond length of the transition states among the various metals. There were also some differences in the C-H bond length of the initial molecularly adsorbed states of methane on the ad-atom and step sites, as will be discussed in more detail.

Figure 1 shows the initial optimized structure of molecularly adsorbed methane on the 14-atom planar cluster. The carbon atom was found to be 3.97 Å away from the surface and one of the hydrogen atoms was coordinated towards an on-top surface site. The energy of this state was 0.08 eV lower than the energy of the two fragments, an isolated methane molecule and a Pt cluster, at infinite separation. We also found that another structure with 3 hydrogen atoms pointing towards the surface had essentially the same energy. When the metal atom that interacts with the H atom was allowed to relax, we found that there was essentially no surface relaxation at the initial state.

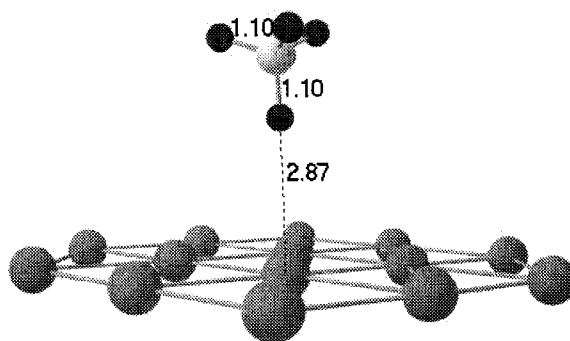


Figure 1. Initial state of CH₄ adsorbed on a Pt₁₄ cluster. Grey = Pt, black = H and white = C.

Figure 2 shows the maximum-energy structure of the scan for the methane dissociation reaction on a Pt₁₄ cluster in which relaxation of the bonding Pt atom was allowed. This is the approximate geometry of the transition state (TS) of the reaction. At the TS, a single Pt atom interacts with both the methyl and hydrogen fragments of CH₄. The H atom was in an approximately bridged site and dissociated to an internal Pt on-top site, so that edge effects were avoided. The C-H bond length was elongated from 1.10 at the initial state to 1.35 Å at the transition state. The large surface relaxation is evident in the figure. The underlying Pt atom was displaced vertically outward from the surface by 0.36 Å. However for geometries of adsorbed methane before the TS on the reaction coordinate, the Pt atom remained on the surface. We found a similar outward displacement for the TS for the other metals: 0.38 Å for Ru, 0.41 Å for Rh, 0.52 Å for Pd, 0.36 Å for Os and 0.40 Å for Ir. In a periodic slab DFT calculation¹⁶ of methane chemisorption on Ir (111) it was found that the Ir atom was displaced outward by 0.41 Å, in excellent agreement with these results.

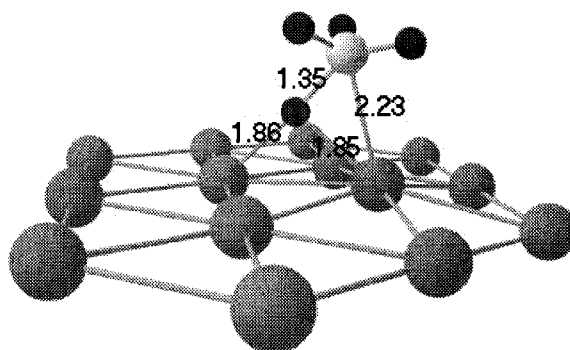


Figure 2. Transition state of methane dissociation on a Pt_{14} cluster, with surface relaxation.

Figure 3 shows the approximate TS structure for the three-layer Pt_{26} cluster. The cluster consisted of 14 atoms in the first plane, 8 atoms in the second and 4 atoms in the third. The second and third layers contained the atoms that are coordinated to three metal atoms of the layer above for the Pt(111) metal. Some geometric differences between the Pt_{26} TS structure and the TS structure of the planar Pt_{14} cluster can be observed. The C-H bond length for the 3-layer cluster is somewhat longer at the TS compared to the 1-layer cluster (1.47 vs. 1.35 Å). The bonding of the underlying Pt atom with both the C and H is evident in the picture. The Pt atom was displaced outward by 0.34 Å, in good agreement with the 1-layer cluster. This suggests that relaxation on the planar cluster was not a consequence of missing nearest-neighbor atoms. Based on the optimized structures of this study and on the previously reported DFT study¹⁶ for Ir(111), we conclude that the outward displacement of the underlying metal atom at the TS is a significant effect. The weakened Pt-Pt bonds of the dissociation site help to strengthen the bonding to the metal. It has been argued²⁷ that surface relaxation results in an upward shift of the d-electron band that aids in chemisorption.

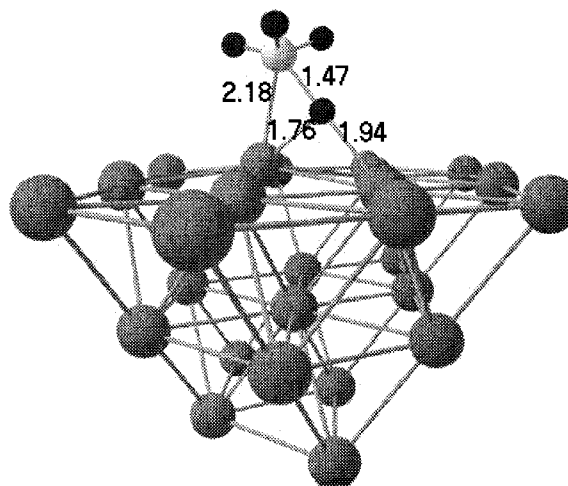


Figure 3. Transition state structure for methane dissociation on a Pt_{26} cluster.

Figure 4 shows the initial state for methane dissociation on a Pt_{15} cluster that models an ad-atom Pt site on Pt(111) (Pt/Pt(111)). The adatom was allowed to relax during the reaction while the coordinates of the base layer Pt atoms were fixed. An energy minimum was found in which methane was molecularly chemisorbed on the adatom. The Pt-C bond distance was 2.51 Å, much closer than the corresponding distance for Pt(111) (3.97 Å). The energy of this state was 0.33 eV lower than the energy of the cluster and CH_4 at infinite separation. The binding energy was much larger than that of the Pt (111) cluster (0.08 eV). Also, one C-H bond was elongated to 1.14 Å at the adsorbed state. This shows that there are significant donation and/or backdonation orbital interactions between the CH_4 molecule and the surface. A molecularly chemisorbed state had been previously found by slab DFT calculations on Ir(111) ad-atom and step sites¹⁶. It was reported that the Ir-C distance was 2.5 Å and the binding energy was 0.22 eV. In the present work, this molecularly chemisorbed state with a relatively short metal-carbon distance was found for all metals on

the ad-atom sites. However, the elongation of the C-H bond at the chemisorbed state was only found on the 5d metals, Os, Ir and Pt.

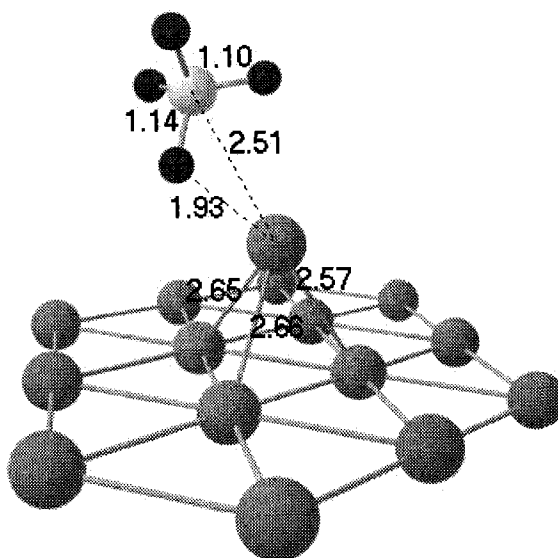


Figure 4. Initial state for methane molecularly chemisorbed on Pt/Pt(111) ad-atom

Figure 5 shows the TS for methane dissociation on the Pt/Pt(111) ad-atom site. Compared to the TS on the Pt(111) site (Fig.2), the C-H bond in Figure 5 was more elongated (1.6 Å), while the Pt-H bond was shorter (1.58 Å). We also noticed that the Pt bonds between the ad-atom and the surface plane (Fig. 5) were elongated compared to the initial state (Fig. 4). This effect is similar to surface relaxation at the TS of the planar clusters. In fact, for most metals (Ru, Os, Rh and Pd) the adatom moved to a bridge position at the TS.

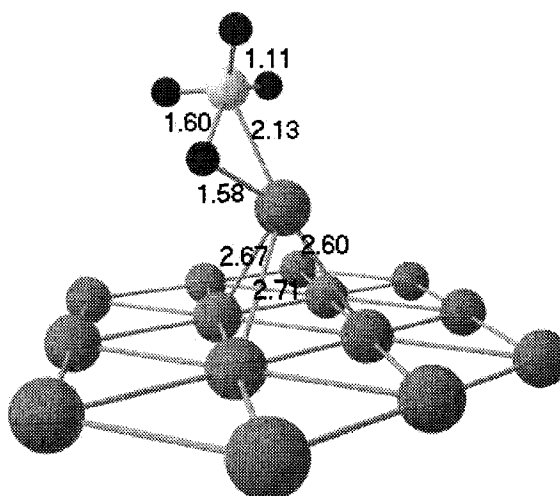


Figure 5. Transition state for methane dissociation on Pt/Pt(111) adatom.

Figure 6 shows the initial state found for methane dissociation on a stepped Pt surface. The 19-atom cluster consists of 14 atoms in the base layer and 5 atoms in the top layer, thus forming a distinct monatomic step. Methane was dissociated at the central atom of the step. This atom was allowed to relax during the reaction scan. A minimum was found where methane was molecularly chemisorbed, just as for the adatom site, but with a longer Pt-C interatomic distance (2.99 Å). One C-H bond was elongated to 1.13 Å at the initial state. The binding energy of the CH₄ molecule was 0.17 eV, which is larger than on the “111” cluster (0.08 eV) but smaller than the adatom cluster (0.33 eV). The Pt atom that interacts with CH₄ was displaced from its original location, forming 2.86 Å bonds with the underlying atoms.

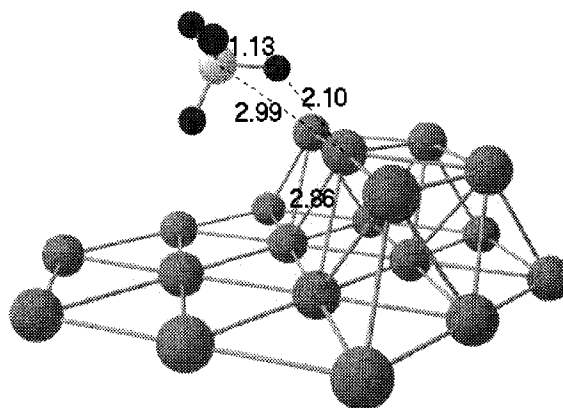


Figure 6. Initial state for methane molecularly chemisorbed on a step site of a Pt_{19} cluster.

Figure 7 shows the TS for the dissociation on the step site. The H atom bonded on top of the step site and the methyl group was directed at an angle to the step. There was considerable surface relaxation as the Pt atom moved further outward ($2.93 \text{ \AA}$ from the underlying plane atoms). We followed the reaction coordinate far from the TS after dissociation to identify the final state of this reaction. A minimum was found in which both the methyl group and the H atom were bonded to the same metal step site. The structure is shown in Figure 8. In this structure, the H atom is bonded close to the on-top position ($\sim 10^\circ$ angle to the surface normal) while the methyl group is directed at an angle of 81° from the Pt-H bond. One of the H atoms points down towards the base layer, $2.81 \text{ \AA}$ away from the nearest atom. The base layer atom could possibly be the site of the subsequent dehydrogenation of the methyl group.

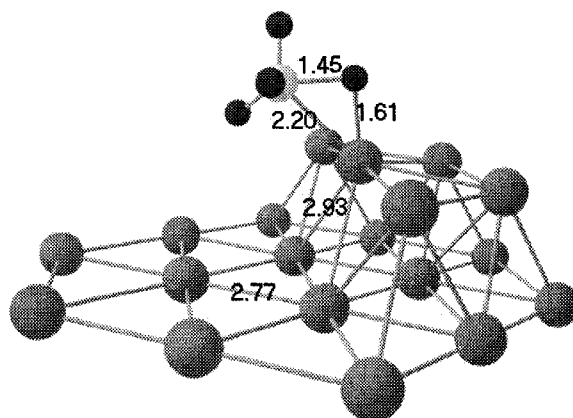


Figure 7. Transition state for methane dissociation on a step site of a Pt₁₉ cluster.

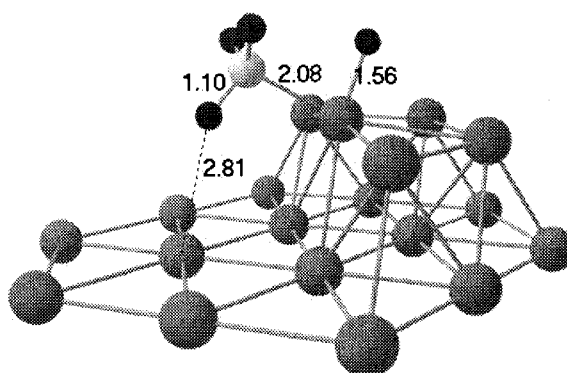
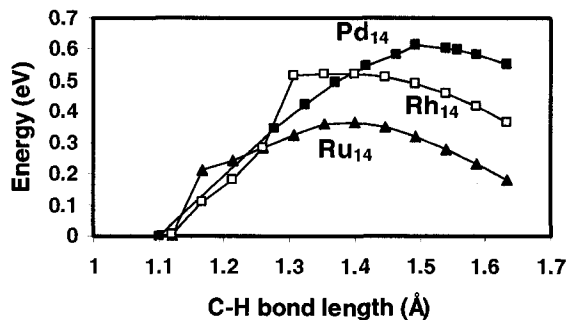


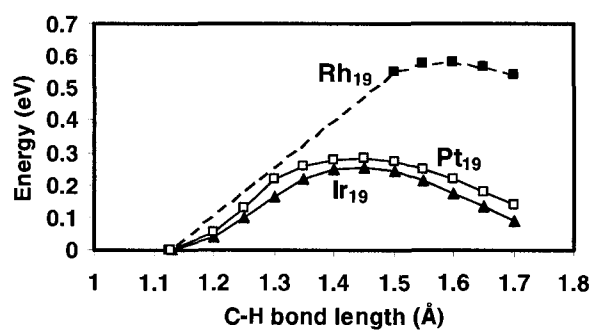
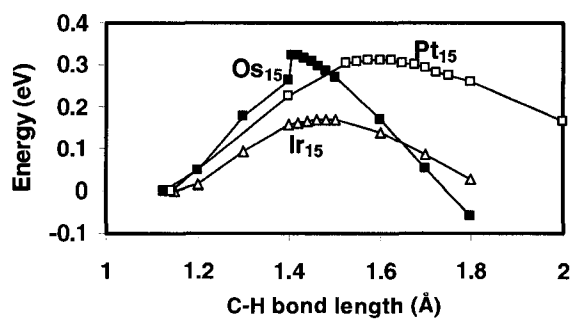
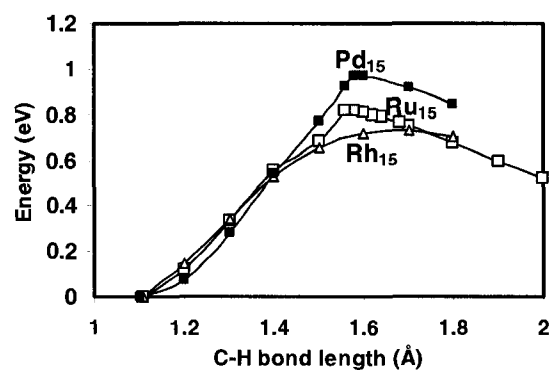
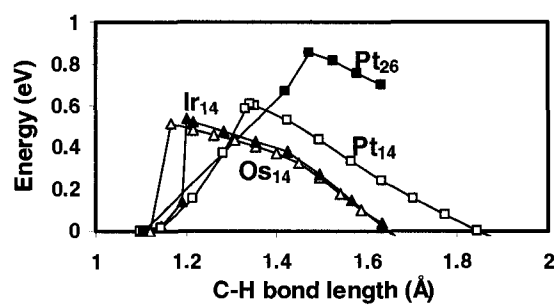
Figure 8. Final state for the dissociation reaction on a step site of a Pt₁₉ cluster.

B. Energetics

Figures 9-13 show the reaction coordinate-energy graphs that were prepared by choosing the C-H bond distance to represent the reaction coordinate. Figures 9 and 10, for the 14 - atom clusters correspond to the set for which surface relaxation was allowed. In all cases, constrained optimizations were performed, by fixing the C-H bond length to several values.

For all data points in these graphs convergence was successful. Separate initial point optimizations were performed. The graphs presented are those for the spin multiplicity of minimum energy. For the 14-atom 1-layer clusters the spin multiplicity was 29 for Ru, 19 for Rh, 7 for Pd, 25 for Os, 19 for Ir and 11 for Pt. The TS energy was approximated by the maximum of the curve. In some cases there was a sudden change in geometry after the maximum for a small step-change in the C-H bond length, which produced a sharp change in energy. This is a consequence of the C-H bond length not being the real reaction coordinate. Since all internal coordinates are changing as the reaction proceeds, the real reaction coordinate would be a composite of all internal coordinates. The maximum of the energy versus C-H bond length curve should still correspond to the TS. More closely-spaced points close to the TS, or a harmonic curve at the TS, provided better accuracy for the estimate of the TS energy. The only case where there is considerable uncertainty in the estimate is that for the 26-atom cluster, where a minimum estimate for the energy barrier is 0.86 eV and an upper estimate ~ 0.92 eV. These bounds were based on extrapolating to the left and right of the maximum in the graph.





Figures 9-13. Electronic energy versus C-H bond length for the various cluster. The cluster size is shown in the inset of the graphs.

Table 1 summarizes the results of the calculations for the energy barriers for the dissociation reaction of methane on the various metal clusters. The position of the metals in each entry of Table 1 corresponds to their respective locations in the periodic table. The first line contains the 4d- series metals and the second line contains the 5d-series metals.

Table 1. Electronic barriers (eV) for the dissociation of methane on $M_{14}(\text{planar})$, $M_{14}(\text{planar})+\text{Relaxation}$, $Pt_{26}(111)$, $M_{15}(M/M_{14}\text{-adatom})$ and $M_{19}(\text{step})$ clusters $M = \text{Ru, Rh, Pd, Os, Ir, Pt}$

A. M_{14} (planar) – fixed cluster		
Ru 0.58	Rh 0.67	Pd 0.72
Os 0.67	Ir 0.71	Pt 0.71
B. M_{14} (planar) with relaxation		
Ru 0.37	Rh 0.52	Pd 0.61
Os 0.51	Ir 0.53	Pt 0.61
C. Pt_{26} (111) with relaxation		
	Pt 0.86	
D. M_{15} (M/ M_{14}) adatom with relaxation		
Ru 0.82	Rh 0.72	Pd 0.98
Os 0.32	Ir 0.17	Pt 0.31
E. M_{19} (step) – with relaxation		
	Rh 0.58	
	Ir 0.26	Pt 0.28

Entry A of Table 1 shows the results for the 14-atom clusters, in which the planar cluster was kept frozen during the scans. The results indicate that the close-packed Ru surface has the lowest energy barrier. We attach more significance to the results of entry B of the table that were obtained by allowing the metal atom of the forming M-C bond to relax for each point of the energy scan. When these are compared to the corresponding results of entry A, we notice a reduction in the energy barriers that is caused by surface relaxation. This reduction is in the range 0.10-0.20 eV, for all the metals, with the largest difference observed for Ru. The results of entry B suggest that the activation energy barrier for dissociation of methane on Ru(0001) was 0.37 eV and was significantly smaller than the rest of the transition metals' close-packed terrace sites. The trend that emerges from the results shown in entry B is that the energy barrier for dissociation on terrace sites increased as the d-band occupancy of the valence shell of the metal increased (Ru < Rh < Pd and Os < Ir < Pt). When metals of the same column are compared, there were no differences in the energy barriers between Pt and Pd and between Rh and Ir, whereas CH₄ dissociation on Ru had a lower barrier than on Os.

Entry C of Table 1 shows that the activation energy for CH₄ dissociation on the larger Pt₂₆ cluster was 0.86 eV, which is 0.25 eV greater than that obtained on the planar Pt₁₄ cluster (with relaxation) and 0.14 eV greater than for the frozen Pt₁₄ cluster. The results on the Pt₂₆ cluster were obtained by allowing a single metal atom to relax during the scan. The higher barrier for the larger cluster is a result of the effects of the additional atoms on the reaction site, of which the nearest-neighbor atoms should have the strongest effect. Since we compare various metals that have the same cluster size, the trends obtained on the smaller clusters should be valid, even if there are some errors in the absolute value of their energies.

Entry D of Table 1 shows the energy barriers for CH₄ dissociation on the Pt₁₅ clusters in which the C-H bond dissociates on an ad-atom site. The results indicated that the metals of the 5d series have much smaller energy barriers than those of the 4d series. For example, the energy barrier for the Pt adatom site was 0.31 eV whereas that of the Pd adatom site was 0.98 eV. Among the 5d metals the smallest energy barrier was found for Ir/Ir(111) (0.17 eV). Among the 4d metals the smallest energy barrier was found for Rh/Rh(111) (0.72 eV). Thus, there is an optimal d-band occupancy that minimizes the energy barrier. Furthermore, if we compare the activation energies on the 5d metal (Os, Ir, Pt) adatoms (0.17-0.32 eV) with those on the close-packed terrace sites (0.51 – 0.61 eV), we observe much smaller energy barriers for the adatoms. This conforms to the idea that metal sites that have low-coordination number are more reactive in dissociating methane. However, for the 4d metals (Ru, Rh, Pd) the barriers were found to be smaller on the terrace sites. For the 4d metals this comparison may not be generally valid, because of the complication of cluster-size effects. In particular, the 14-atom cluster does not contain the second-layer nearest neighbors of the metal site that bonds to methane, whereas the adatom site has all its nearest neighbors included in the cluster. However, for Ru the calculated barrier is 0.37 eV on the planar cluster and 0.82 eV on the ad-atom site. The large difference between these two values is unlikely to give an incorrect trend because of cluster-size effects.

Entry E of Table 1 shows the energy barriers for methane dissociation on the step sites of the Rh, Ir and Pt 19-atom clusters. Calculations for the other metals were not concluded on the 19-atom clusters because of optimization convergence difficulties. The results showed that, similarly to the case of the 15-atom clusters, the energy barriers for the 5d metals Ir

and Pt (0.26 and 0.28 eV respectively), were considerably lower than the 4d metal Rh(0.58 eV). The barriers for the step sites for Ir (0.26 eV) and Pt (0.28 eV) do not differ much from those on the ad-atoms Ir (0.17 eV) and Pt (0.31 eV) and are much lower than the barriers for the terrace sites Ir (0.53) and Pt (0.61 eV). Rh was predicted to dissociate methane with a lower barrier on the step site (0.58eV) compared to the adatom site (0.72 eV) whereas for Rh the comparison with the terrace site (0.52 eV) is complicated by the effects of missing nearest neighbor sites on the small cluster used for the terrace sites.

Some general findings can be summarized from the calculations. Collectively, the results on ad-atom and step sites support the conclusions that a) on ad-atom and step sites, 5d metals have smaller energy barriers for methane dissociation than 4d metals b) the adatom and step sites of 5d metals have smaller energy barriers for methane dissociation than terrace sites. Furthermore, the results on the 14-atom planar clusters show that (a) Ru (the 4d metal with the emptiest d-shell among the metals considered) has the smallest barrier among all six metals and (b) the barrier increases within each series as the d-band occupancy increases.

The results obtained from this study can be discussed in relation to actual steam and CO₂ - reforming experimental data. First we note the limitations of such a comparison: a) there exist conflicting experimental results in the literature regarding the reactivity of the catalysts, as discussed in the introduction and in the comparisons below. This can be expected because of the variability of reaction conditions, metal dispersion and its influence on the distribution of different kinds of sites, heat effects, effects of diffusion losses and effects of the supports on the reaction. b) It has not been determined which sites are reactive

and which are not and whether the more reactive sites, such as steps and kinks, are completely inactivated under reaction conditions. c) our methods were aimed at studying trends because of the limited cluster sizes that we used. The accuracy of the values is limited by cluster -size effects. Furthermore, in a previous DFT study⁶ for CH₄ dissociation on Pt, we found a large effect of the functional on the calculation of activation energies: B3LYP gave a higher energy barrier compared to PW91 by 0.25 eV.

We compared the results to experimental work in the literature in which the reactivity of supported transition metal catalysts were assessed for steam and CO₂- reforming under similar experimental conditions. In one set of experiments^{10,1} the results indicated that the order of turnover frequencies is Ru > Rh > Ir > Pt ~Pd. The same order was also obtained for ethane reforming²⁸. The exact order agrees with the results that we obtained for the close-packed terrace sites. This may indicate that the dissociation actually takes place on the terrace sites and that the low-coordination sites are unreactive. In the same set of experiments¹⁰, the formation of carbon deposits on the surface was examined and it was noted that Ru and Rh had low rates of carbon formation compared to the other metals and did not form carbon whiskers. This is qualitatively in agreement with our results because we found that the low-coordinated sites of Ru and Rh are less reactive than those of the 5d metals and adsorb methane less strongly. Thus they would form carbon deposits at a slower rate than the other metals. Two values for activation energies were reported¹, 96 kJ/mol $\approx$ 1.0 eV for Ru and 121 kJ/mol $\approx$ 1.3 eV for Rh which are much higher than the values that we obtained with the 14-atom cluster. One reason for the difference in the range of values is the cluster size effect that was evident by comparing the 14-atom and 26-atom clusters of Pt. Another possible reason is the effect of surface coverage. Our results are relevant to limiting

low coverage. For higher surface coverage that is more likely during experimental conditions the activation energy for methane dissociation would be higher. Still another possibility is the effect of the functional in the calculations (B3LYP gives larger activation energies). It should be noted that the range of energy barriers from periodic slab calculations, given in the introduction, are also much smaller than the experimental range of values. However, the trends would very likely be unaffected by any of the above reasons.

In the second set of experiments methane decomposition, steam reforming and CO₂ reforming was performed on Pt⁸, Ru⁸, Ir²⁹, and Rh³⁰. It was found that the order of turnover frequencies for the reaction on these metal catalysts was Pt > Ir > Rh > Ru, which is different from the aforementioned results. The reported activation energies for methane decomposition were 0.81 eV for Pt, 0.84 eV for Ir and 1.12 eV for Rh. The value for Pt is in good agreement with the value that we obtained for the Pt₂₆ cluster (0.86 eV). However, the trends were more consistent with the first set of experiments. Nevertheless, the fact that the two different experimental studies predicted different trends shows that a different process would control the reactivity in the two experiments. For example, different contributions from uncoordinated sites in the two experiments could be one explanation for their different predictions. Also, adsorbed water and its dissociated species could also influence the rate of adsorption of gas-phase methane on the surface. The energetics of the dissociation of water on transition-metal catalysts is discussed elsewhere³¹.

There also exist many molecular-beam studies of methane dissociation on single-crystal surfaces. Most of them are directed towards discriminating between direct and precursor-mediated modes of methane chemisorption on different surfaces. However the translational

energies used in molecular beams are much higher than catalytic reactors and do not correspond to the conditions of thermal activation in catalytic reactors^{32,33} For this reason we have not discussed the present results in relation to molecular- beam studies.

C. Natural Bond orbital analysis

The DFT calculations identified a large difference in the methane activation energies between 5d and 4d metals on low-coordination sites. In this section we report on the results of an NBO analysis that was performed on selected structures of the reaction path, for methane dissociation on the Pt₁₅ and Ru₁₅ clusters. The energy barrier for methane activation was found to be 0.31 eV for the Pt adatom site and 0.82 eV for the Ru adatom. We chose to perform the NBO analysis of metal cluster-methane complexes for two metals, both in their initial states and in structures along the reaction path that are characterized by a C-H bond length of 1.4 Å. At the transition state the C-H bond length is ~1.6 Å in both cases. We selected a structure prior to the TS because at the TS there are many interacting orbitals and delocalizations that are caused by the simultaneous breaking of the C-H bond and formation of the metal-C bond that make the comparison more complex. Prior to the TS, we can more clearly identify the donation and back-donation effects and the differences between them for the Pt₁₅ and Ru₁₅ clusters. At a C-H separation of 1.4 Å, the energy for the Pt₁₅-CH₄ system was 0.23 eV higher than the initial state, and the energy for the Ru₁₅-CH₄ system was 0.56 eV higher than the initial state. Thus, the energy difference for these structures reflects the large difference in the energy barrier.

The major donor-acceptor interactions are summarized in Table 2. The table shows only the results of the beta spin set. There were no major differences between the results for the alpha and beta spin sets. We can immediately recognize that the initial state of the Pt₁₅-CH₄ cluster-adsorbate pair has a C-H bond length of 1.144 Å, which implies significant orbital interactions between the cluster and CH₄ as one of the C-H bonds is longer than the others. On the other hand, this interaction was not observed for the Ru₁₅-CH₄ pair, that has a C-H bond length of 1.107 Å in the initial state. Donation interactions are characterized by electron transfer from the dissociating $\sigma_{\text{C-H}}$ occupied bonding orbital of methane to an acceptor orbital of the metal cluster that is localized on the adatom. The NBO analysis showed that at the initial state of the Pt₁₅-CH₄ set, there was a deoccupation of the bonding $\sigma_{\text{C-H}}$ of 0.06 electrons, compared to the isolated methane molecule (from 1 to 0.94 electrons). On the other hand, there was only insignificant deoccupation (0.01 electron) of the bonding C-H orbital at the initial state for the Ru₁₅-CH₄ system. When the C-H bond was elongated to 1.4 Å, the occupation of the $\sigma_{\text{C-H}}$ orbital was 0.86 electrons for Pt₁₅-CH₄, whereas it was 0.91 electrons for Ru₁₅-CH₄. Thus the results show a greater donation interaction for Pt₁₅-CH₄ compared to Ru₁₅-CH₄. The acceptor orbital of the Pt₁₅ cluster at the initial state was identified to be an sd-hybridized low-occupation antibonding orbital between the adatom and an underlying Pt atom. At a C-H bond length of 1.4 Å, the acceptor was a low-occupation (non-Lewis) lone pair orbital centered on the adatom. This change in the acceptor orbital is a consequence of the relaxation of the adatom that essentially breaks one of the bonds to increase the interaction between the Pt atom and the adsorbate. A similar result was also observed for dissociation on the Ru₁₅ cluster.

Table 2. Major donor-acceptor interactions for CH₄ chemisorption on Pt₁₅ and Ru₁₅ clusters.

	Pt ₁₅ CH ₄	Pt ₁₅ CH ₄	Ru ₁₅ CH ₄	Ru ₁₅ CH ₄
C-H bond length (Å)	1.144	1.400	1.107	1.400
Donation				
Donor NBO	Bonding C-H	Bonding C-H	Bonding C-H	Bonding C-H
Donor Occupancy	0.94	0.86	0.99	0.91
Acceptor NBO	Antibond Pt-Pt	Lone Pair Pt	Antibond Ru-Ru	Lone Pair Ru
	30% <i>s</i> 70% <i>d</i>	90% <i>s</i> 10% <i>d</i>	30% <i>s</i> 70% <i>d</i>	85% <i>s</i> 15% <i>d</i>
Acceptor Occupancy	0.19	0.34	0.13	0.30
Backdonation				
Donor NBO	Lone Pair Pt	Lone Pair Pt	Bonding Ru-Ru	Bonding Ru-Ru
	100% <i>d</i>	100% <i>d</i>	100% <i>d</i>	100% <i>d</i>
Donor Occupancy	0.98	0.92	0.80	0.76
Acceptor NBO	Antibond C-H	Antibond C-H	Antibond C-H	Antibond C-H
		H		
Acceptor Occupancy	0.02	0.08	0.002	0.08
Natural Charge of CH ₄ group	0.08	0.095	0.03	0.03

A significant back-donation interaction was also identified. In every case, the donor orbital was a d orbital centered on the adatom, that was either a lone pair orbital or a bonding orbital to an underlying atom. At the initial state of the Pt₁₅-CH₄ system the extent of backdonation from a metal orbital to the antibonding $\sigma^*_{\text{C-H}}$ was insignificant (0.02 electrons). However, when the bond length was 1.4 Å, the $\sigma^*_{\text{C-H}}$ orbital was filled by 0.08

electrons. For $\text{Pt}_{15}\text{-CH}_4$, the extent of back-donation was smaller than the extent of donation. For $\text{Ru}_{15}\text{-CH}_4$, the extent of back-donation was similar to the extent of donation. This can be seen in the results by noticing that for $\text{Ru}_{15}\text{-CH}_4$ the $\sigma_{\text{C-H}}$ orbital has been emptied by 0.09 electrons and the $\sigma^*_{\text{C-H}}$ orbital has been filled by 0.08 electrons. The donor orbitals of the metal atom are also being emptied, not necessarily by the same amount as there are also strong electron delocalizations within the cluster. In the final entry of Table 2, the natural charges of the C and H atoms of the metal- CH_4 structures, predicted by NBO- analysis, were summed and reported as the natural charge of the CH_4 group. This charge encompasses both the alpha and beta sets. The net positive charge on CH_4 in the dissociation on Pt reflects the greater extent of donation (electron transfer from the adsorbate to the metal) compared to back-donation interactions. The net positive charge on CH_4 in the dissociation on Ru was small and constant, which shows that both donation and back-donation have an effect on the process.

Table 2 identifies that the reason for the difference in reactivity between the Pt adatom and the Ru adatom is the greater extent of electron donation from the $\sigma_{\text{C-H}}$ orbital to a hybrid sd metal orbital of primarily s character. Thus, we continued the analysis of the donation interactions in terms of orbital energies and perturbative stabilization energies. The results are shown in Table 3.

Table 3. Orbital energies and donor-acceptor stabilization energies for donation interaction from the $\sigma_{\text{C-H}}$ orbital to the metal acceptor orbitals for methane dissociation on Pt_{15} and Ru_{15} clusters.

	$\text{Pt}_{15}\text{CH}_4$	$\text{Pt}_{15}\text{CH}_4$	$\text{Ru}_{15}\text{CH}_4$	$\text{Ru}_{15}\text{CH}_4$
C-H bond length (Å)	1.144	1.400	1.107	1.400
(a) Energy of C-H Bonding Orbital (a.u.)	-0.508	-0.453	-0.479	-0.415
(b) Sum of energies of occupied CH_4 orbitals (a.u.)	-11.831	-11.821	-11.721	-11.712
(c) Total stabilization energy by electron donation (a.u.)	0.022	0.078	0.002	0.045
(d) Stabilization energy due to main acceptor orbital (a.u.)	0.018	0.066	0.0014	0.037
(e) Donor-Acceptor energy difference (a.u.)	0.35	0.25	0.46	0.38
(f) Overlap element F_{ij} (a.u.)	0.052	0.136	0.027	0.114

Line (a) in Table 3 shows the energy of the C-H bonding orbital for the different structures. It is seen that, for both cases, as the bond length increases the energy of the $\sigma_{\text{C-H}}$ orbital increases, as expected because of the reduction in the overlap between the $\text{C}(\text{sp}^3)$ and $\text{H}(1s)$ orbitals. The rest of the CH_4 occupied orbitals (the core carbon orbital and the three other sigma bonds) decrease in energy and partly compensate for this increase. In line (b) we summed the energies of all the occupied orbitals of methane. Summing NBO orbital energies does not give the total electronic energy of a molecule. However the sum of the

orbital energies is roughly proportional to the total electronic energy, excluding delocalization interactions. We verified this by calculations for an isolated CH₄ molecule. From the entries of line (b) we conclude that the change in the sum of orbital energies of CH₄ between the two states is practically the same (0.01 a.u. different) for Pt₁₅CH₄ and Ru₁₅CH₄. Therefore, the difference in activation energies can be attributed to the 2nd order perturbative stabilization energies of donor – acceptor interactions.

Line (c) of Table 3 presents the total stabilization energy that was obtained by summing-up the energy contributions of all the σ_{C-H} - metal acceptor interactions produced by NBO analysis. The stabilization energy caused by donation changes by 0.056 a.u. between the two states of Pt₁₅CH₄ and by 0.043 a.u. between the two states of Ru₁₅CH₄. This amounts to 0.013 a.u. = 0.35 eV difference between the two cases. The results of the DFT calculations had shown that at a C-H separation of 1.4 Å, the energy for the Pt₁₅-CH₄ system was 0.23 eV higher than the initial state, and the energy for the Ru₁₅-CH₄ system was 0.56 eV higher than the initial state. This amounts to 0.335 eV energy difference between the two cases. Thus we conclude that the difference in activation energies between CH₄ dissociation on Pt₁₅ and Ru₁₅ is caused by the stronger donation interactions from the sigma bond of methane to the acceptor orbitals of Pt₁₅. Furthermore, line (d) of Table 3 suggests that only one NBO acceptor orbital contributes about 80% of the total stabilization energy. The nature of this orbital was given in Table 2 for the different cases.

The final question to be answered in this comparison is if it is the difference in donor and acceptor orbital energies or the overlap coupling element F_{ij} of equation 1 that causes the largest stabilization energy for the Pt(adatom)-CH₄ system. The variations in the overlap

elements reflect the spatial extent and directional differences of the interacting orbitals. Lines (e) and (f) of Table (3) indicate that the $\sigma_{\text{C-H}}$ – metal acceptor energy level difference (line e) is smaller for the Pt adatom case and the orbital overlap element (line f) is larger, for all cases. Both effects are combined to lead to the large difference in activation energies. However, taking into account the actual numbers listed in Table 3 and the fact that the stabilization energy depends on the square of the overlap element, it is concluded that the major fraction of the difference is attributed to the greater overlap between the sigma bond of methane and the unoccupied sd-hybrid orbitals that are localized on the adatom. The results of the NBO analysis are only valid for the comparison between the adatom sites of Pt and Ru, which can be taken as being representative of the low-coordination sites of 5d and 4d metals.

3.4 Conclusions

The present DFT study of CH_4 dissociation on Ru, Rh, Pd, Os, Ir and Pt transition metal clusters resulted in the following conclusions:

1. Surface relaxation was significant at the structures of the transition states. The metal atom that forms the metal – carbon bond was displaced outwards by 0.34-0.52 Å.
2. CH_4 was initially molecularly chemisorbed on adatoms and steps with significantly larger binding energy than for terrace sites of the same metals.
3. Among the six metal clusters that modeled the close-packed terrace sites, the energy barrier for CH_4 dissociation was found to be smallest for Ru. The energy barrier increased as the d-band occupancy of the metal increased.

4. Among clusters that modeled the ad-atom sites, the energy barrier was found to be smallest on iridium. The energy barriers for the 5d metals Os, Ir, Pt were significantly smaller than for the 4d metals Ru, Rh, Pd and also significantly smaller than the barriers on the terrace sites.

5. For the three metal clusters that modeled step sites of the metals Rh, Ir and Pt, the order of the energy barriers was the same as for the ad-atom sites.

6. A natural bond orbital analysis of the chemisorption of methane on a Pt ad-atom site (Pt/Pt(111)) and on a Ru-adatom site (Ru/Ru(0001)) identified electron donation from a bonding orbital of CH₄ to an sd –hybrid orbital of the metal ad-atom and electron back – donation from a d orbital of the ad-atom to an antibonding orbital of methane. The different reactivity of the two metal sites was caused by the greater overlap of the Pt acceptor orbital with the donor methane orbital that resulted in greater electron donation, compared to Ru.

7. The activation energies that have been measured in steam reforming experiments are in better agreement with the calculated energy barriers for methane dissociation on terrace sites than on uncoordinated sites.

8. The barrier for dissociation of methane on terrace sites to adsorbed methyl and hydrogen increased in the order Ru < Os < Rh < Ir < Pt $\approx$ Pd. This order agrees with one set of experiments published in the literature for steam – reforming of methane on transition metal catalysts. However, other experiments with different reactivity order for the catalysts have also been published. Different reactivity orders in actual steam – reforming experiments may reflect the different contributions of uncoordinated sites or the effect of water dissociation on the reaction rate³¹.

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CHAPTER 4: Cluster DFT study of the adsorption and dissociation of water on Ru, Rh, Pd, Os, Ir, Pt and Pt-Ru.**

George Psfogiannakis^{†L}, Alain St-Amant[‡] and Marten Ternan^{*†§L}

Department of Chemical Engineering and Department of Chemistry, University of Ottawa,
Ottawa, ON, K1N 6N5, Canada, Centre for Catalysis Research and Innovation, University
of Ottawa, ON, K1N 6N5, Canada and EnPross Inc., 147 Banning Road, Ottawa, ON, K2L
1C5, Canada

*Corresponding author. E-mail:ternan@sympatico.ca Phone: (+1) 613-8318080

[†] Department of Chemical Engineering, University of Ottawa

[‡] Department of Chemistry, University of Ottawa

^L Centre for Catalysis Research and Innovation

[§] EnPross Inc.

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Abstract

Ab-initio DFT cluster calculations were performed to estimate the binding energies of H₂O, OH and H on transition metals and the activation energy barriers for the dissociation of adsorbed H₂O to form adsorbed OH and H. 14-atom planar clusters were used to model the close-packed surfaces of Ru, Rh, Pd, Os, Ir, Pt and a Pt-Ru alloy. Reaction coordinate calculations were performed and the results identified trends in the calculated energy barriers and binding energies. It was found that for H₂O dissociation the energy barriers were linearly correlated with the overall reaction energy change. The energy barrier was smaller for Ru and Os, and increased for metals with increased d-band occupancy. The binding energy of OH was lowest on Pt and Pd and decreased with increased d-band occupancy. The results were combined with a previous cluster-DFT study of methane dissociation on the same surfaces. The implications of the results for the reactivity trends of transition metals used as steam-reforming catalysts and fuel cell electrocatalysts are discussed.

Keywords: water, chemisorption, transition metals, density functional theory, clusters

4.1 Introduction

The interaction of water with transition metals is significant in a wide variety of applications in heterogeneous catalysis and electrochemistry. A very large amount of information has been summarized in extensive reviews^{1,2} of theoretical and experimental aspects of the interaction of water with transition metals and metal surfaces in general. At low coverage, water monomers adsorb weakly on transition metals while at high coverage water can form adsorbed monolayers, bilayers or water clusters². Water can also dissociate on a metal surface, either to form OH and H or completely dissociate to O and H atoms². The mode of water adsorption (dissociative versus non-dissociative) and the structure of water at a metal surface depend on the nature of the metal and the particular system temperature and pressure². For electrochemical systems, the magnitude of the electrical field at the metal electrode also has a significant effect². Furthermore, the coadsorption of any other chemical species will interfere with the adsorption and dissociation of water.

Among the wide variety of processes that involve the interaction of water with transition metal surfaces, our primary interest lies in two systems that involve the coadsorption of water and methane. In particular we are interested in a) steam reforming of natural gas on transition metals^{3,4,5} and b) fuel cell anodes that operate with aqueous electrolytes and electrooxidize methane⁶⁻¹⁴. To this end, we have previously done a DFT study¹⁵ of the mechanism of methane oxidation on Pt(111), as well as a DFT study¹⁶ of the adsorption and dissociation of methane on Ru, Rh, Pd, Os, Ir and Pt. In these investigations, more extensive introductions to the catalytic aspects of these processes have been given. In steam-reforming, methane and steam are converted catalytically to a mixture of hydrogen, carbon

monoxide and carbon dioxide³⁻⁵. In a direct methane fuel cell, methane and water are converted electrochemically to CO₂ and partially oxidized hydrocarbons with simultaneous generation of electric current. These processes are vastly different: steam reforming is of immense industrial significance and is an existing well-established process. On the other hand, the direct electro-oxidation of methane in fuel cells is currently of no practical significance because the generated current densities are too small for any useful application. However, both of these processes involve the simultaneous interaction of water and methane on a metal catalyst. For steam reforming, nickel is usually the preferred catalyst for economic reasons³ but late transition metals are also effective in catalyzing the reaction. In direct methane fuel cells, it has been found experimentally that among transition metal catalysts, only Pt is effective in the generation of appreciable current densities¹⁴.

In the present work, we extended the previous studies by examining the role of water adsorption and dissociation in these processes. In particular we studied the adsorption and dissociation of a single water molecule on clusters that model the most close-packed surfaces of ruthenium, rhodium, palladium, osmium, iridium, platinum and a platinum-ruthenium alloy. The binding energies of a water molecule, a hydroxyl group (OH) and a hydrogen atom on the surfaces and the energy barrier for water dissociation were calculated. We used small planar 14-atom clusters and a single water molecule in the calculations because our interest was in trends and because an extensive number of calculations was required. The basic assumption in this work is that the effect of the metal atoms underneath the surface is similar for the different metals and does not change the trends in energy. To test this assumption, some comparisons with trends obtained from periodic slab calculations are discussed in the results section. Similarly, the interaction of the adsorbed species (H₂O,

OH, H) with surrounding water molecules, either in the vapor or liquid phase, is assumed to be similar for the various metals. For example¹⁷, periodic slab DFT calculations showed that the order in the binding energies of a single water molecule on the close-packed surfaces of Pt, Rh, Ir, Pd was the same as the order in the binding energies of adsorbed water bilayers on the same surfaces. Furthermore, for the conditions of catalytic reactors, at high temperatures and pressures and with co-adsorbed species and surface reactions, it is very unlikely that ordered water structures are formed on the surface. Generally, despite the simplifications in the model system, the results indicated that it can capture the main features of the differences in reactivity among these transition metal surfaces.

4.2 Computational methods

The binding energies of H₂O, OH and H on transition metals and the activation energy barriers for the dissociation of adsorbed H₂O to adsorbed OH and H were estimated in this study by performing DFT cluster calculations. 14-atom symmetric planar clusters were used to model the close-packed surfaces Ru(0001), Rh(111), Pd(111), Os(0001), Ir(111), and Pt(111). The cluster is shown in the figures of the results section. The structure of the (111) surface of the fcc metals Rh, Pd, Ir, Pt is equivalent to the (0001) surface of the hcp metals Os, Ru. The interatomic distance in the metal clusters was kept fixed in the optimizations at the experimental bulk values¹⁸, 2.775 Å for Pt, 2.714 Å for Ir, 2.734 Å for Os, 2.750 Å for Pd, 2.689 Å for Rh and 2.706 Å for Ru. No further constraints were imposed in the reaction coordinate calculations. The adsorbed water molecule and the dissociated fragments, OH and H, were bonded to internal sites of the 14-atom cluster, so that edge effects were minimized. Calculations were also performed for a 14-atom Pt cluster in which one of the

internal atoms was replaced by Ru. This cluster aimed to model the reaction on a Pt-Ru surface. The Ru atom was the site that bound the adsorbed water molecule of the initial state and the hydroxyl group of the final state, because Ru was found to adsorb H_2O and OH more strongly than Pt.

Density functional theory (DFT) calculations were performed using GAUSSIAN 03 software¹⁹. We employed the generalized gradient approximation functional of Perdew and Wang²⁰ (PW91) to describe exchange and correlation effects. For the transition metal atoms, we used the Los Alamos National Laboratory basis set of double-zeta quality (LANL2DZ)²¹ and the corresponding scalar relativistic effective core potential that replaces the inner-shell electrons. The outer-shell s,p and d electrons (18 for Pt and Pd, 17 for Rh and Ir and 16 for Ru and Os) were treated explicitly. The 6-31G** basis set was used for the hydrogen and oxygen atoms. No significant spin contamination was found. For geometry optimizations, the convergence criteria corresponded to a maximum step size of 0.01 au and an RMS force of 0.0017 au.

For each reaction, the initial state was taken to be the minimum-energy molecularly-adsorbed state of H_2O and was optimized in a separate calculation. Reaction coordinate scans were done for all reactions by selecting the O-H bond length as the internal coordinate to scan through the potential energy surface. We performed constrained energy minimizations for various fixed values of this coordinate. The TS energy was estimated as the maximum energy of the reaction scan. In a previous work¹⁵, we obtained the exact TS saddle point of many reactions on Pt(111) using analytical frequency methods. We observed that, as long as enough points were included in the reaction energy scans, the energy of the

maximum point in the scan was in all cases very close to the exact TS energy. Thus, the electronic activation energy was taken to be the energy difference between the maximum point in the scans and the molecularly-adsorbed initial state. Zero-point energy (ZPE) corrections to the activation energies could not be calculated without vibrational frequencies. Because the water dissociation reaction is very similar on different metals, ZPE corrections should also be very similar.

The binding energies of H₂O, OH and H were calculated after optimizing the adsorbed species on the metal clusters. The binding energy for each of the adsorbates was found by subtracting the energy of the cluster-adsorbate system from the sum of the energies of the isolated cluster and the adsorbate at infinite separation from the cluster. For the optimization of OH and H, the calculations were performed for on-top sites only, because it was observed in the reaction energy scans that the final state of the dissociation had OH and H bound on-top.

The effect of the spin state of the cluster-H₂O systems was included in all calculations. In each case, the spin multiplicity (SM) that minimized the total energy (the ground state) was found by performing calculations for several different spin multiplicities (SM=1+ number of unpaired electrons). Reaction paths were followed for the ground-state spin of the initial state for each reaction. We performed calculations on some reaction pathways with two and more different spin multiplicities and found that there is no change in the spin state from the initial state to the TS. In general, we found that the ground states of the clusters are high-spin and vary significantly between metals. The effect of the spin-state on the electronic

energy of Pt clusters has been previously examined²² and the preferred high-spin states were explained by a model that predicts the bonding orbitals within the cluster.

4.3 Results and discussion

Figure 1 shows the optimized structure of a water molecule adsorbed on a Ru₁₄ planar cluster. This cluster was used to model the (0001) close-packed surface of ruthenium. The binding energy of the H₂O molecule to the cluster was 0.66 eV. The spin multiplicity of the minimum was 29. The water molecule was adsorbed on top of a ruthenium atom. The Ru-O bond length was 2.18 Å. This structure was taken to be the initial state for the dissociation of H₂O to adsorbed OH and H. For all other metals, the initial state was similar and consisted of a water molecule adsorbed on an on-top site of the cluster. The molecular plane was nearly parallel to the surface. Periodic DFT slab calculations also predict that water is adsorbed on atop sites and parallel to the surface²³.

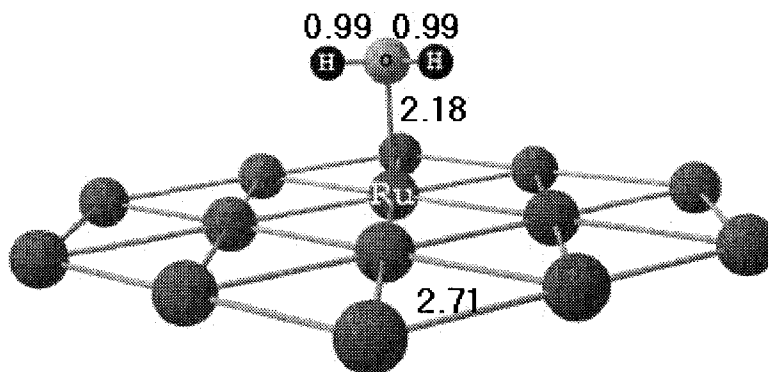


Figure 1. Optimized structure of adsorbed H₂O on the Ru₁₄ planar cluster (Distances in Å)

Figure 2 shows the transition-state for the dissociation of water on the Ru₁₄ cluster. The cluster was rotated in Figure 2, compared to Figure 1, to obtain a better view. The dissociation occurred over the central Ru-Ru bond of the cluster. The O atom remained nearly on-top all through the reaction. The dissociating O-H bond was elongated from 0.99 Å at the initial state to 1.42 Å at the transition state. The Ru-O bond length was reduced from 2.18 Å at the initial state to 2.05 Å at the TS. For all other metals, the transition state had a similar geometry. However, the O-H distance varied at the TS among the various clusters. The final state of the reactions was not optimized for all metals, because we were interested in the energy barriers for the forward direction of the dissociation reaction. For Pt, however, a final state optimization resulted in OH and H bonded on-top of the two adjacent central Pt atoms. The OH remained on top of the metal atom that initially bound H₂O.

The cluster that was used to model the reaction on a Pt-Ru alloy consisted of a single ruthenium atom surrounded by platinum atoms. The Ru atom was the atom labeled Ru in Figure 1. The water molecule was initially bound on top of the Ru atom as water is more strongly bound on Ru. The H atom dissociated towards the adjacent Pt atom and the transition state was similar to that of Figure 2.

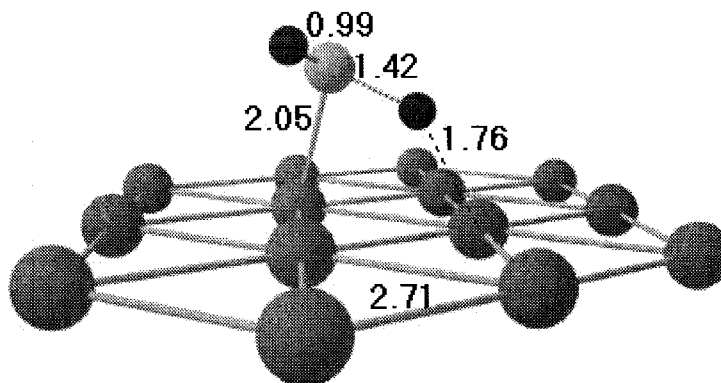


Figure 2. Transition state for the dissociation of H₂O to OH and H on the Ru₁₄ planar cluster

Figure 3 shows the reaction coordinate-energy curves that were prepared by choosing the O-H bond length to represent the reaction coordinate. The electronic energy shown on the y-axis is relative to the initial state. In all cases, constrained optimizations were performed by fixing the O-H bond length to several values. The graphs presented are those for the spin multiplicity of minimum energy, which was 29 for Ru, 19 for Rh, 7 for Pd, 25 for Os, 19 for Ir, 11 for Pt and 13 for the Pt-Ru cluster. The curves were harmonic at the TS and closely spaced points allowed for accurate determination of the TS structure and energy. For Pd and Pt, the results showed a very flat profile around the TS, the energy being only slightly reduced after the TS. For these metals, the energy barrier was the highest and the reaction was very endothermic. The curves show that the O-H bond length at the TS was longer for metals that had larger energy barriers for the water dissociation reaction.

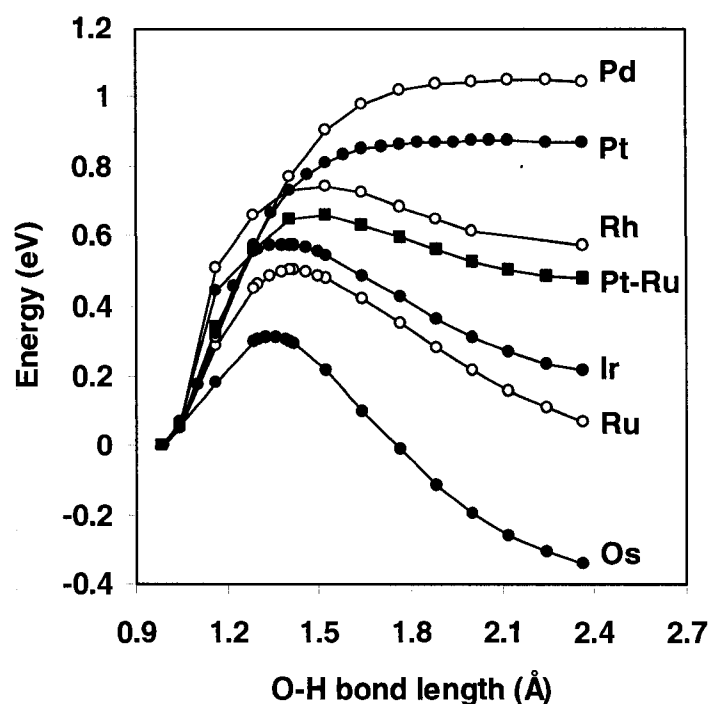


Figure 3. Electronic energy, relative to the initial state energy, versus O-H bond length for the dissociation of H_2O to adsorbed OH and H on transition metal clusters.

Table 1 summarizes the energy barriers for the dissociation of water on the various metal clusters. These were the energies of the maxima of the curves of Figure 3 relative to the initial state. The position of the metals in the first two rows of Table 1 corresponds to their respective locations in the periodic table. The first line contains the 4d- series metals and the second line contains the 5d-series metals. The smallest energy barrier was found for osmium. Within each row, the energy barrier increased as the d-band occupancy of the metal increased, moving towards the right of the periodic table. Thus, the lowest barrier among the examined 4d metals was found for ruthenium and the lowest barrier among the 5d metals was found for osmium. Furthermore, the energy barriers were lower for the 5d

metal series, compared to the 4d metal series. The electronic configuration of the valence shell for a 5d metal atom is equivalent to the 4d metal that is directly above it in the periodic table. Therefore, the size of the atom and the increased spatial extent of the electron density of the 5d metal surface, result in a reduced energy barrier for H₂O dissociation. This reduction was similar in magnitude for the pairs Ru and Os, Rh and Ir, Pd and Pt. For the Pt-Ru cluster, the energy barrier (0.66 eV) was found to be larger than that of the Ru cluster (0.50 eV), but smaller than that of the Pt cluster (0.87 eV). This indicates that both metals have an effect on the magnitude of the barrier.

Table 1. Electronic energy barriers (eV) for the dissociation of H₂O to OH and H on 14-atom planar clusters

Ru 0.50	Rh 0.74	Pd 1.05
Os 0.31	Ir 0.57	Pt 0.87
Pt-Ru 0.66		

In order to gain more insight into the trends suggested by Figure 3 and Table 1, we performed additional optimizations to calculate the binding energy of the reactant and product species of the dissociation reaction. These are the binding energies of a water molecule, a hydrogen atom and a hydroxyl group on the metal clusters. In a previous study²⁴ it was found by examining a large amount of data from periodic slab calculations, that for the dissociation of N₂, CO, NO and O₂ a linear relationship exists between the activation energy for dissociation on different metals and the binding energy of the dissociated species. This is called a Brønsted-Evans-Polanyi (BEP) type of relationship. In a different study²⁵ a

list of more than 50 elementary steps were examined. A BEP linear relationship was found to relate the activation energy of different classes of dissociation reactions on surfaces to the enthalpy change between the reactant and dissociated products.

In the present work, we examined the relationship between the activation energy barrier and the reaction energy change for water dissociation on the clusters. The reaction electronic energy change, ΔE , was obtained in terms of the binding energies of H_2O , H and OH on the metal clusters. We can initially write the reaction energy as the difference in absolute DFT energies between the final and initial states of the reaction:

$$\Delta E = E_{M-H-OH} - E_{M-H_2O} \quad (1)$$

where E_{M-H-OH} is the energy of the metal cluster with H and OH co-adsorbed on different metal atoms and E_{M-H_2O} is the energy of the metal cluster with an adsorbed water molecule. Subsequently, we can write the term E_{M-H-OH} as:

$$E_{M-H-OH} = E_{M-H} + E_{M-OH} - E_M \quad (2)$$

where $E_{M-H} + E_{M-OH}$ is the sum of the energies of two metal clusters, one with adsorbed H and one with adsorbed OH. E_M is the energy of a bare metal cluster and is subtracted to equate the number of metal clusters on the two sides of the equation. Equation 2 assumes that the interaction energy between H and OH when they are co-adsorbed on the metal is negligible. We can now use the following relations for the binding energies of H, OH and H_2O :

$$E_{b,H} = E_M + E_H - E_{M-H} \quad (3)$$

$$E_{b,OH} = E_M + E_{OH} - E_{M-OH} \quad (4)$$

$$E_{b,H_2O} = E_M + E_{H_2O} - E_{M-H_2O} \quad (5)$$

Equations (3)-(5) define the binding energies, $E_{b,H}$, $E_{b,OH}$, and E_{b,H_2O} , of H, OH and H_2O respectively as the energy change upon adsorption, with a positive sign. When equations (3)-(5) are substituted into (2) and (2) is substituted into (1), we finally obtain:

$$\Delta E = E_{b,H_2O} - E_{b,H} - E_{b,OH} + \Delta E_{dis,H_2O} \quad (6)$$

where the last term in equation (6) is the energy required to dissociate an isolated H_2O molecule into OH and H. This term is a constant.

$$\Delta E_{dis,H_2O} = E_H + E_{OH} - E_{H_2O} \quad (7)$$

Equation (6) expresses the electronic energy change for the reaction in terms of the binding energies of H_2O , H and OH and assumes negligible interaction between the adsorbates in the final adsorbed state, which is valid for the limiting low coverage that is inherent in the cluster method.

In the present work, the OH and H were optimized separately at on-top sites of the metal clusters because for all geometries in the reaction scan, OH was bound on-top and H dissociated towards an on-top site. For OH the adsorption site was the same as for the H_2O molecule. For the H atom, the adsorption site was the adjacent on-top site, which is an equivalent site due to the symmetry of the cluster. We could have alternatively optimized both the H and OH atoms co-adsorbed on adjacent metal sites to represent the final state of the reaction. However, calculating the binding energies for OH and H separately allowed as to quantify the effect of each of them on the energy barriers. For each adsorbate, the

ground-state spin multiplicity was found by repeating the optimization for several spin states and finding the minimum.

Table 2 shows the binding energies of H₂O, OH and H on the metal clusters. For the Pt-Ru cluster, H₂O and OH were adsorbed on the Ru atom while H was adsorbed on a Pt atom. The results indicated some general trends for the binding energies of the species. Among the pure metals, H₂O was more strongly bound on Rh and Ir. Thus, there was a maximum in the binding energy of water for the 4d and 5d metal series at an optimum d band occupancy. The binding energy of water was slightly lower for the 5d-metal series, compared to the 4d. Water was found to bind more strongly on the Ru atom of the Pt-Ru cluster, compared to pure Ru. For the pure metal clusters, the range in the binding energies of H₂O was 0.57-0.74 eV. Periodic DFT calculations²⁶ predict somewhat smaller binding energies, in the range 0.33-0.42 eV for 0.25 monolayer coverage on Pt(111), Pd(111), Rh(111) and Ru (0001).

Table 2. Binding energies (eV) of H₂O, OH and H on 14-atom planar clusters

H₂O			
Ru	0.66	Rh	0.74
Os	0.57	Ir	0.73
Pt-Ru	1.02	Pd	0.66
		Pt	0.62
OH			
Ru	3.12	Rh	2.78
Os	3.12	Ir	2.70
Pt-Ru	2.97	Pd	2.24
		Pt	2.10
H			
Ru	2.85	Rh	2.87
Os	3.13	Ir	3.20
Pt-Ru	2.93	Pd	2.64
		Pt	2.93

The binding energy of OH decreased considerably when moving towards the right in each transition metal series. It was also decreased for the 5d metal series compared to the 4d metal series. OH was bound more strongly on pure Ru than on the Ru atom of the Pt-Ru cluster. Experimental data²⁷ obtained by laser-induced fluorescence for OH desorption from Pt indicate a binding energy 2.04 eV, which is in good agreement with the value 2.10 eV from the cluster model. The binding energy of H was highest for Rh among the 4d metals, and for Ir among the 5d metals, indicating a maximum within each series. H was found to bind considerably more strongly on the 5d metals, compared to the 4d metals. The binding energy of H on the Pt cluster and on a Pt atom of the Pt-Ru cluster were equal. The heat of adsorption per H₂ molecule dissociating on Pt(111) has been measured experimentally by thermal desorption spectroscopy²⁸⁻³¹ and was found to be in the range 0.70 to 0.83 eV. When the dissociation energy of H₂ calculated with the PW91 functional (4.65 eV) is added to this and the result divided by 2 (because two adsorbed H atoms are produced per H₂ molecule), the binding energy of a H atom is calculated to be in the range 2.67-2.74 eV. Our calculated value is 2.93 eV, which is in reasonable agreement.

Comparisons with periodic slab DFT calculations can also be made. Calculations³² for Pt(111) results found that OH binds on atop sites with binding energy 2.12 eV and H binds on atop sites with binding energy 2.71 eV. These values are in generally good agreement with the binding energies that we obtained with the small planar cluster, 2.10 and 2.93 eV respectively. In a previous periodic DFT slab calculation³³ the reaction energies for the reaction $\text{H}_2\text{O}_{(\text{gas})} + \text{metal} \rightarrow \text{OH}_{\text{ads}} + 0.5\text{H}_{2(\text{gas})}$ for the close-packed surfaces of Ru, Rh, Pd, Ir and Pt were computed. The trends for these energies correspond to the trends in the

binding energies of OH, because the energies of H₂O and H₂ were calculated in the gas-phase. The greater reaction energies correspond to smaller OH binding energies. The authors found that the reaction energy increases in the order Ru < Rh < Ir < Pd < Pt. Thus, the OH binding energy increases in the reverse order, in excellent agreement with our results. The fact that the order of binding energies is the same for both our cluster calculations and period slab calculations, indicates the suitability of our methods for studying trends.

The binding energies of Table 2 were used to calculate the electronic energy changes for the reaction (reaction energies) on the various clusters using equation (6). Subsequently, the dissociation energy barrier was plotted against the reaction energy. The plot is shown in Figure 4. The results suggested that a linear relationship exists between the energy barrier and the reaction energy. Thus the BEP relationship for the dissociation of water to OH and H was confirmed in the present cluster study. The equation of the best-fit line was $E_{\text{act}} = 0.480(\Delta E) + 0.502$. The R^2 value was 0.975. The figure also shows that the reaction energy was negative only for Os and Ru, indicating an exothermic dissociation reaction on these metals. The reaction energies can also be seen to correspond to those in Figure 3. In Figure 3, however, the final state of the reaction was not optimized, but the energies for the last points in the scans are fairly close to the reaction energies shown in Figure 4. For both the reaction energies and the energy barriers, previous periodic slab DFT calculations³⁴ for fcc(211) surfaces have also found the same trend: Ru < Ir < Rh < Pt < Pd.

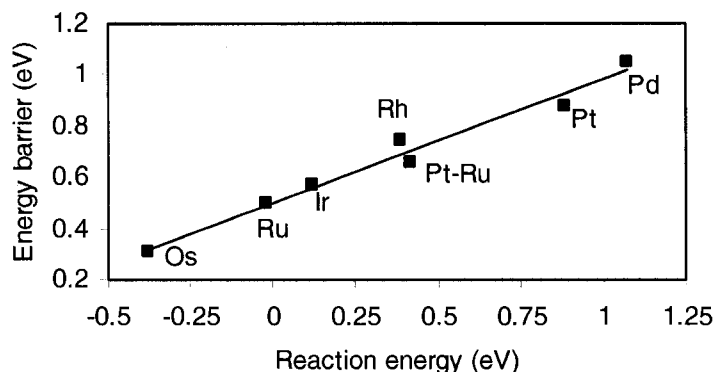


Figure 4. Energy barrier for the dissociation of water versus the reaction energy. The reaction energy is defined by equation (6).

The variation in the binding energies shown in Table 2 suggests that the trend in the energy barrier within each series is determined by the binding energy of OH, which decreased substantially towards the right of the periodic table. To justify this, a plot of the energy barrier versus the binding energy of OH is shown in Figure 5. Within each series, 4d and 5d, the energy barrier varied linearly as a function of the binding energy of OH. Two different and close to parallel lines were obtained for the 4d and 5d metals. However, when comparing the energy barriers between the 4d (Ru,Rh,Pd) and the 5d metals (Os,Ir,Pt), we have to take into account the differences in the binding energies of H. Table 2 shows that H binds stronger on the 5d metals compared to the 4d metals. This reduced the energy barrier on the 5d metals. The variations in the binding energy of H₂O were not as significant among the pure metals. However, for the Pt-Ru cluster, the increased barrier compared to pure Ru, was a consequence of the stronger binding of water on Pt-Ru. The binding energy of H₂O was 1.02 eV on the Ru atom of Pt-Ru and 0.66 eV on the Ru cluster. The energy difference in the final state (OH and H) was smaller.

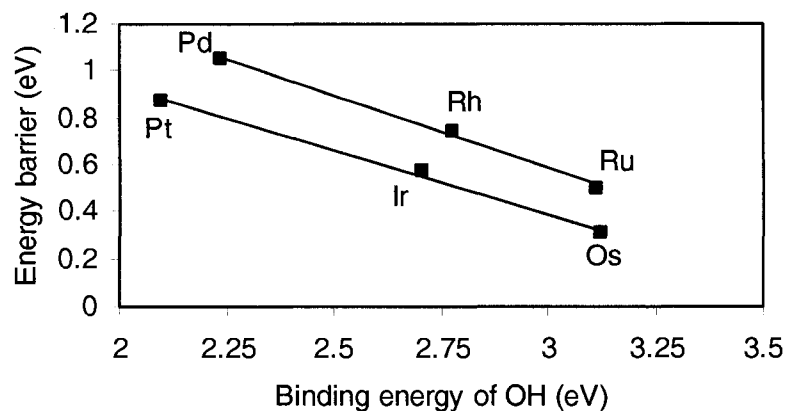


Figure 5. Energy barrier for the dissociation of water versus the binding energy of OH. The two lines correspond to the 4d (top) and 5d (bottom) metal series.

As mentioned in the introduction, we are interested in the consequences of these results in relation to steam reforming and fuel cells, particularly direct hydrocarbon fuel cells. The above findings were combined with a previous study¹⁶ that we performed for the dissociative chemisorption of methane ($\text{CH}_{4(\text{ads})} \rightarrow \text{CH}_{3(\text{ads})} + \text{H}_{(\text{ads})}$) on transition metals, in which the same methods and clusters were used. Table 3 shows the binding energies for methane on 14-atom clusters of Ru, Rh, Pd, Os, Ir and Pt. The clusters and adsorption sites were the same as those used for H_2O . Table 3 shows that CH_4 binds very weakly on the transition metals. The binding energies for all metals are within the range 0.058-0.08 eV. On the other hand, Table 2 shows that the binding energies of a H_2O molecule on the transition metals are within the range 0.57-0.74 eV. Thus, the binding energy of a water molecule on all transition metals is approximately 10 times greater than that of methane. This indicates that a transition metal surface in contact with a methane-water mixture will be preferentially

covered by water. This comparison is more appropriate for the vapor-phase adsorption of water. For aqueous systems, water molecules either adsorbed or in solution interact through hydrogen bonds with the surrounding water molecules. The binding energy of water would thus be also affected by the change in the hydration shell of the adsorbing water molecule as the molecule adsorbs. DFT calculations³⁵ have shown that the binding energy of water is decreased when the hydration shell is taken into account. Since our calculations have only a single water molecule, this effect can not be further explored.

Table 3. Binding energies (eV) of CH₄ on 14-atom metal clusters.

Ru 0.058	Rh 0.059	Pd 0.067
Os 0.067	Ir 0.075	Pt 0.080

Table 4 shows the energy barriers for the dissociation of methane on the 14-atom Pt clusters that were obtained in our previous work¹⁶. These clusters were similar to those of the present study and the results of Table 4 were obtained by using the same methods as for water dissociation. These results were compared to experimental work reported in the literature, in which the reactivity of supported transition metal catalysts were assessed for steam reforming under similar experimental conditions. In one set of experiments^{3,36} the results indicated that the order of turnover frequencies is Ru > Rh > Ir > Pt ~Pd. The same order was also obtained for ethane reforming³⁷. This order agrees with the results that we obtained for the energy barriers of methane dissociation on close-packed terrace sites shown in Table 4. Pre-exponential factors are not expected to affect the order of turnover frequencies because the reaction is similar on different metals.

Table 4. Energy barriers (eV) for the dissociation of methane on 14-atom metal clusters

Ru 0.58	Rh 0.67	Pd 0.72
Os 0.67	Ir 0.71	Pt 0.71

However, in another set of steam reforming experiments that was performed on Pt³⁸, Ru³⁸, Ir³⁹, and Rh⁴⁰, it was found that the order of turnover frequencies for the reaction on these metal catalysts was Pt > Ir > Rh > Ru. This order is different from the order of energy barriers shown in Figure 4. Based on the results of Table 2, it seems probable that in this case the order of reactivity is determined by the binding energy of OH. For steam reforming OH will probably dissociate to O and H atoms at the high temperatures involved in the process. However, the binding energy of oxygen atoms has been found with slab calculations³³ to follow the same trend as OH for the closed-packed surfaces (Ru < Rh < Ir < Pd < Pt). That should also be expected, as OH binds through the oxygen atom on the metals. Table 2 shows that the binding energy of OH increases in the order Pt < Ir < Rh < Ru. Because OH (or O) is more weakly bound on Pt, it will also be more reactive. Thus, it will oxidize more efficiently the adsorbed carbonaceous species that form by dissociation of methane. Also, the fraction of sites not covered by OH (or O) would be larger on Pt. These sites would be available for adsorption and dissociation of methane. Therefore, it is probable that in this set of experiments the order of reactivity is determined by the availability of sites for the chemisorption of methane, which is in turn determined by the

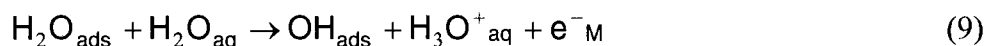
binding strength of the dissociation products of water and their reactivity. The two cited experiments were performed with different supports, different steam to methane ratios and at different temperatures and pressures. All of these may be responsible for the different order of turnover frequencies in the two cited experimental studies. More experiments would be required to assess the order of reactivities of transition metals towards steam reforming of methane and the effect of the variables that could affect the turnover frequencies.

The results on the binding energy of OH and H₂O on the metal surfaces can also be used to assess the extent of OH formation at the electrochemical interface. It has been previously proposed and experimentally verified in the literature^{41,42} that the reversible potential for OH formation on a metal electrode is linearly related to the difference between the binding energies of H₂O and OH on the surface. The difference between the binding energies of H₂O and OH determines the relative reaction energies for OH formation on the surface of different metals. We can examine why this is so for the case of an anode electrode in contact with acid electrolyte. On the surface of the electrode, the reaction that is responsible for OH formation is⁴³:



where H⁺_{aq} denotes a proton in solution and e⁻_M denotes an electron in the metal. Thus, OH is formed by the deprotonation of H₂O adsorbed on the electrode. In this elementary electron transfer reaction, the H atom is transferred from the adsorbed water molecule to another water molecule in solution, resulting in a proton in solution, and simultaneously the electron is transferred into the metal. Quantum mechanical calculations⁴⁴ have shown that,

for aqueous systems, the direct transfer of the H atom of a water molecule to an adjacent water molecule is energetically favorable compared to the homolytic dissociation of a water molecule to H and OH adsorbed on the metal surface. To facilitate the discussion we can write reaction (8) explicitly for a metal in contact with an aqueous solution.



where $\text{H}_2\text{O}_{\text{aq}}$, $\text{H}_3\text{O}^+_{\text{aq}}$ denote a water molecule and a proton in the solution that are interacting with the adsorbed water molecule. The energy change for reaction (9) is given as the difference between the initial and final states of the reaction:

$$\Delta E = E(\text{OH}_{\text{ads}}) - E(\text{H}_2\text{O}_{\text{ads}}) + E(\text{H}_3\text{O}^+_{\text{aq}}) - E(\text{H}_2\text{O}_{\text{aq}}) + \Delta E(\text{e}^-_{\text{M}}) \quad (10)$$

The quantity $\Delta E(\text{e}^-_{\text{M}})$ denotes the energy change associated with the transfer of a single electron to the metal. If we consider the components of the electronic energy change, ΔE , given by equation (10), for two different metal electrodes that are at the same electrochemical potential, $\Delta E(\text{e}^-_{\text{M}})$ will be the same for the two metals because it is determined by the electrode potential. If the electrode operates at steady-state the quantity $\Delta E(\text{e}^-_{\text{M}})$ should be taken in the limit of constant electrical potential. Furthermore, if the metals are in contact with the same aqueous solution, the energies of a proton and a water molecule in solution would be the same. Thus the difference in the reaction energy between the two metals is determined by the first two terms of equation (10). In terms of binding energies (considered positive), the quantity $E_{\text{b}}(\text{H}_2\text{O}) - E_{\text{b}}(\text{OH})$ determines the difference in reaction energy between different metals. For the same value of the electrochemical potential, metals for which this quantity is large and negative will have a greater concentration of OH on the surface, as the equilibrium of reaction (9) will be more shifted

to the right. These metals will also have lower activation energy barriers for OH formation since the reaction energy and the activation energy are generally linearly related. This model was used in previous periodic DFT studies^{41,42} of the water deprotonation reaction on Pt(111) and Pt₃Co(111) and Pt₃Cr(111). According to the model, the difference in the quantity $E_b(\text{H}_2\text{O})-E_b(\text{OH})$ in eV is equal to the shift in the reversible potential (in volts) for reaction (8) on two different metals⁴¹. When the term is large and negative, OH will be formed at lower anodic potentials.

Table 5 shows the values of the quantity $E_{b, \text{H}_2\text{O}}-E_{b, \text{OH}}$ for the various transition metal clusters and was calculated from the binding energies of Table 2. The trends are mostly determined by the binding energies of OH, since the binding energy of water does not vary substantially among the various metals. The results indicate that OH will be formed at lower anode electrode potentials on Ru and Os, and at higher potentials on Pt and Pd.

Table 5. Difference in binding energies (eV) between H₂O and OH, $E_b(\text{H}_2\text{O})-E_b(\text{OH})$, on 14-atom planar clusters

Ru -2.46	Rh -2.04	Pd -1.58
Os -2.54	Ir -1.97	Pt -1.48
Pt-Ru -1.95		

The availability and reactivity of adsorbed OH species on a fuel cell anode electrode is significant for the majority of fuel cells. Hydrogen fuels usually contain trace amounts of CO that poison the reaction sites. Organic fuels such as methanol or hydrocarbons form CO

and other carbon-containing species as part of the reaction mechanism. Most researchers agree that CO is oxidized through reacting with adsorbed OH species⁴⁵. This is based on the fact that CO is oxidized at anode electrode potentials at which OH is formed on the surface. Table 5 indicates that OH will be available at lower potentials on Ru and Os. However, the reactivity of OH would also have a significant influence. The greater the binding energy of OH, the less reactive it is and thus it will oxidize CO less efficiently. Furthermore if OH is strongly bound on the surface, its coverage will be high, thus prohibiting the initial adsorption of the reactant molecules. Table 2 indicated that the binding energy of OH is greatest for Ru and Os and smallest for Pt and Pd. Among all metals, OH would be most reactive on Pt. Experimentally, among all pure metals, fuel cell anodes of platinum generally have the highest reactivity. The present results suggest that this is because OH is less strongly bound and thus more reactive on Pt.

The binding energy of CO would also have a significant effect and this is not examined in the present study. However, a large amount of experimental information on CO binding energies have been collected in the literature⁴⁶. The binding energy of CO varies in the order Pt(111) (1.37 eV) < Rh(111) (1.45 eV) < Pd (111) (1.48 eV) < Ru(0001) (1.49 eV) < Ir(111) (1.58 eV). However, the uncertainties in the experimental measurements were quite large compared to the differences in their mean values (~0.13 eV standard deviations were reported, based on various different measurements). In the same work⁴⁶, the binding energies were also calculated with periodic slab calculations, and the order was found to be Pt(111) (1.22 eV) < Pd (111) (1.36 eV) < Rh(111) (1.58eV) < Ru(0001) (1.62 eV) < Ir(111) (1.67 eV). Both the experimental and calculated results indicate that Pt(111) binds CO less strongly than the rest of the transition metals, which indicates that CO would also be more

reactive on platinum. Nevertheless, for the metals studied, the differences in CO binding energies for the metals within each row in the periodic table, are smaller than the differences in the calculated OH binding energies. This suggests that OH binding energies will largely determine the trends within each row. These results, however, also suggest that the reactivity of Pt compared to Pd will be also be influenced by the binding energy of CO, which is smaller on Pt.

As mentioned in the introduction, we are also interested in the consequences of these results on the direct electrochemical oxidation of hydrocarbon fuels on transition metal electrodes and liquid electrolytes. Our results can be used to explain the major experimental findings regarding the electrooxidation of methane. These are: a) The current densities are much smaller than fuel cell anodes operating on other fuels, such as hydrogen or methanol⁶⁻¹⁴. b) only platinum catalysts produce any appreciable current density while all other transition metals are virtually inactive^{10,14}. For example, a study of the electrooxidation of methane on Pt, Pd, Ir, Ru, Os and a Pt-Ru alloy¹⁰ concluded that at 80°C in H₂SO₄ electrolyte, measurable current densities were observed only on Pt. Pt is also the most effective electrocatalyst among the pure metals for the oxidation of ethane and propane¹⁴. c) Adsorbed CO has been detected⁴⁷ as an intermediate in the electro-oxidation of methane on Pt, Pd, Ru and Rh using in-situ infrared spectroscopy. Results from our previous DFT study¹⁵ indicated that, for the part of the reaction mechanism from the initial CH₄ adsorption up to adsorbed CO, the dissociative chemisorption of methane is rate-limiting on Pt(111) because of the high energy barrier required for chemisorption and also the small pre-exponential factor that is caused by the loss of entropy upon adsorption. As shown in Table 4, based on the results on planar close-packed models of Ru, Rh, Pd, Os, Ir and Pt

catalysts, the lowest barrier was found for Ru (0.58 eV) while the barrier for Pt was higher (0.71 eV). If we consider that the current density is determined by the dissociation of methane on close-packed terrace sites, we note that despite this trend, only platinum has any appreciable reactivity in the electro-oxidation of methane. On the other hand, if the current density is determined by the dissociation of methane on low-coordination sites, then according to previous DFT calculations¹⁶ the current density should be highest for Ir, which is also in conflict with experiment. The results of the present study can explain the observation that Pt is superior. For the electro-oxidation to proceed, OH has to be present on the surface to oxidize the adsorbed dissociated fragments on methane and CO that is formed on the surface. If we compare Ru and Pt, even though OH is formed on Ru at lower anode potentials, it is much more strongly bound to the surface of Ru than Pt. This suggests that on Ru, OH will be less reactive and will have high coverage on the surface. Because methane binds very weakly on the surface (Table 3), its adsorption would be severely hindered by strongly adsorbed unreacted CO and OH. On the other hand, OH on Pt is less strongly bound, its coverage will be smaller and will be more reactive towards oxidizing CO, thus leaving a fraction of sites available to chemisorb and dissociate methane. Among the transition metals used in these calculations, OH was found to bind more weakly on Pt. Therefore Pt should be the most efficient catalyst for the electro-oxidation of methane, even though its reactivity is too small for practical applications.

We note also that a major difference between the catalytic and electrocatalytic oxidation of methane is that in the former CO desorbs from the surface as a product, while in the latter CO is strongly bound and can only be further oxidized to CO₂ at high anodic potentials (>0.45 V). In steam-reforming, the energy required for desorption of strongly bound CO is

available because of the high temperature of the process. However, in low-temperature fuel cells, experiments have measured close to 100% CO₂ yields from the electro-oxidation of methane on Pt^{6-8,11}. CO₂ was also the only product⁴⁷ in the electrooxidation of methane on Pd, Ru and Rh. One study⁴⁸ has also reported that partially oxidized organics (formaldehyde and methanol) were also produced in the electrooxidation of methane on a Pt-Ru alloy. As with any fuel that contains or forms CO on a fuel cell electrode, adsorbed CO from methane can act as a poison in a fuel cell by blocking the reactive surface sites. Thus, the requirement for highly reactive oxygen-containing species is enhanced in the electrocatalytic system. It is this requirement that is better satisfied by platinum, among all transition metals.

4.4 Conclusions

This study of the dissociation of water on clusters of transition metals has resulted in the following conclusions:

- 1) Water is initially bound on top of a metal atom through the O atom. The OH group remains on top throughout the dissociation reaction and the H atom dissociates towards an adjacent on-top site.
- 2) Among the closed-packed surfaces of Ru, Rh, Pd, Os, Ir, Pt and a Pt-Ru alloy, the energy barrier for dissociation increases in the order Os < Ru < Ir < Pt-Ru < Rh < Pt < Pd. The energy barrier is smaller for metals with the most empty d-band Ru and Os, and increases with increased d-band occupancy. Also, the barrier is lower for the 5d metals Os, Ir and Pt compared to the corresponding 4d metals that have the same electronic

configuration and are directly above them in the periodic table Ru, Rh, Pd. The barrier for the Pt-Ru alloy is smaller than pure Pt but larger than pure Ru.

3) The energy barrier for dissociation is linearly related to the reaction energy. Among the metals, the reaction energy increases in the same order as the activation energy. The dissociation is exothermic only for Os and Ru. For metals in the same series, trends in the reaction energy are determined by the binding energy of OH. The binding energy of H also has an effect when comparing the 4d with the 5d metals.

4) The reaction energy and activation energy for the deprotonation of water at the metal-solution interface, which happens by direct transfer of a H atom to an adjacent water molecule, increases in the order Os < Ru < Rh < Ir < Pt-Ru > Pd < Pt. Thus, at the metal-solution interface, the fractional coverage of OH would be the smallest for Pt and increase in the opposite order.

5) The binding energy of OH increases in the order Pt < Pd < Pt-Ru < Ir < Rh < Ru < Os. Thus, OH would be more reactive on Pt and its reactivity would decrease in the opposite order.

When the results of this study are combined with the results of a previous study¹⁶ in which the energy barriers for methane dissociation were obtained, the following conclusions can be made.

6) The relative reactivity of the transition metals towards steam-reforming of methane may be either determined by the trends in the dissociation barrier for CH₄, or the trends in the binding energy of OH (or O). In the first case, metals that have a low energy barrier for methane dissociation would be better. In the second case, metals that bind OH more weakly would be better, because OH is more reactive, can oxidize the adsorbed C-fragments easier

and will leave free sites for hydrocarbon adsorption. Based on these results, in the first case, Ru would be the better catalyst, while in the second case Pt would be the better catalyst. Both cases have been observed experimentally in comparative studies of methane steam reforming on transition metals.

7) The relative reactivity of the transition metals towards the electrochemical oxidation of methane at the metal solution interface is determined by the trends in the binding energy of OH. Metals that bind OH weakly would be more efficient in oxidizing methane because of the increased reactivity of OH towards oxidizing the adsorbates and the availability of more sites for the adsorption and dissociation of methane. Based on the results of this model, the best catalyst for the electrochemical oxidation of methane would be platinum. Experimental results have shown that only Pt can electrooxidize methane, in agreement with the present results. The energy barrier for the methane dissociation reaction $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ at the metal – vacuum interface does not determine the trends in the reactivity of transition metals in the case of fuel cells. It is the metal-OH binding energy that does.

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CHAPTER 5: Overall research contributions, conclusions and recommendations

5.1 Contributions to knowledge

The following can be regarded as the major contributions of this work to scientific knowledge:

a) Cluster DFT methods were used for the first time to obtain the activation energies of the elementary surface reactions of a general reaction network for the oxidation of methane on platinum. The reaction mechanism and rate-limiting step were identified. (Chapter 2)

b) Cluster DFT calculations were performed for the first time to obtain, using the same methods, the energy barriers for the dissociation of methane and water on six different transition metal surfaces. The results identified trends in the intrinsic reactivity of the transition metals towards dissociating methane and water. (Chapters 3 and 4)

c) Cluster DFT methods were used for the first time to explore the structure sensitivity of the CH_4 dissociation reaction to adsorbed CH_3 and adsorbed H, on transition metals. Calculations on close-packed terrace sites, adatoms and step sites, identified trends in the energy barriers with respect to both the type of reaction site and the identity of the metal. (Chapter 3)

d) Cluster DFT methods were used for the first time to discuss reactivity trends for the transition metals towards the direct electro-oxidation of methane in fuel cells as well as for the steam reforming of methane on transition metals. The results were found capable of explaining the trends found in literature experimental work. (Chapters 3 and 4)

e) Cluster DFT methods were used for the first time to show a linear correlation between activation energies and reaction energies for the dissociation of water on a variety of transition metal surfaces. (Chapter 4)

f) The DFT calculations demonstrated the efficient use of cluster methods to obtain trends in the energy barriers of a series of reactions on the same metal surface, or of the same reaction on different metal surfaces.

5.2 Conclusions and discussion

The main conclusions from the entire thesis are summarized below and the implications for both methane electro-oxidation and steam reforming are discussed.

1) A study of the electro-oxidation of methane on Pt(111) showed that the reaction proceeds according to the mechanism: $\text{CH}_4 \rightarrow \text{*CH}_3 \rightarrow \text{*CH}_2 \rightarrow \text{*CH} \rightarrow \text{*CHOH} \rightarrow \text{*CHO} \rightarrow \text{*CO} \rightarrow \text{CO}_2$, where * denotes an adsorbed species. In the sequence of adsorption intermediates, dehydrogenation reactions happen by dissociation of the reactant species on

the surface and oxidation reactions happen by combination of the reactant species with adsorbed OH. (Chapter 2)

2) The rate determining step for the pathway from CH_4 to $^*\text{CO}$ is the dissociative chemisorption of CH_4 . The rate of this elementary step is slow because it has a relatively large electronic energy barrier and it is accompanied by a large entropic loss. (Chapter 2)

3) As a result of (2), the only two possible rate-determining steps for the overall reaction of methane electro-oxidation on Pt(111) are the dissociative methane chemisorption step and the $^*\text{CO}$ oxidation step. This conclusion is supported by the experimental observation in the literature of no adsorbed organic adlayer at electrode potentials above about 0.4 V. At these potentials, adsorbed OH that is formed on the surface by the deprotonation of water oxidize adsorbed CO on the Pt surface. (Chapter 2)

4) As a result of (3) the relative reactivities of transition metals for the electro-oxidation of methane can be determined either by the rate of the dissociative chemisorption of methane or by the oxidation rate of adsorbed CO on the surface. The latter is related to the electrode potentials at which OH forms on the surface and the binding energy of OH (see also conclusion 9). (Chapter 2)

5) An investigation of the dissociative chemisorption of methane to produce adsorbed methyl ($^*\text{CH}_3$) and $^*\text{H}$ on the most close-packed surfaces of Ru, Rh, Pd, Os, Ir and Pt showed that the energy barrier is lowest for Ru(0001). The barrier increased in the order Ru

$< \text{Os} < \text{Rh} < \text{Ir} < \text{Pt} \approx \text{Pd}$. Surface relaxation was found to have a significant effect in the magnitude of the energy barriers, but not in their relative order.(Chapter 3)

6) A study of the dissociative chemisorption of methane on low-coordination sites (step sites and adatoms) showed that for the 5d metals Os, Ir and Pt, the energy barrier for dissociation is significantly decreased, compared to the close-packed terrace sites. The energy barrier was lowest for Ir. For the 4d metals, Ru, Rh and Pd, the energy barrier for low-coordination sites is larger than the 5d metals. (Chapter 3)

7) A study of the dissociation of adsorbed water to adsorbed OH and H on the most close-packed surfaces of Ru, Rh, Pd, Os, Ir, Pt and a Pt-Ru alloy revealed that the energy barrier increases in the order $\text{Os} < \text{Ru} < \text{Ir} < \text{Pt-Ru} < \text{Rh} < \text{Pt} < \text{Pd}$. The energy barriers for dissociation are linearly related to the total energy change for the reaction. The binding energy of OH determines the trend within the 4d and 5d metal series. The binding energy of H affects the relative energy barriers between the 4d and the 5d metals. (Chapter 4)

8) The binding energy of OH increases in the order $\text{Pt} < \text{Pd} < \text{Ir} < \text{Rh} < \text{Pt-Ru} < \text{Os} \approx \text{Ru}$. This has the following implication for fuel cells in which adsorbed OH participates in the reaction network through oxidizing adsorbed CO, including the anode reaction in a direct methane fuel cell: more weakly bound OH is more reactive towards electro-oxidizing adsorbed CO, it will enhance the net rate of reaction and will also consequently leave a larger fraction of the surface available for adsorption of the reactant. (Chapter 4)

9) As a consequence of (4), (6) and (8) in combination with the experimental observation that methane is electro-oxidized at an appreciable rate only on Pt electrodes, it is the low binding energies of both OH and CO on Pt, compared to the other metals, that determines the relative trend. The smaller binding energies of OH and CO on Pt would make the activation energy for the reaction of CO and OH to form CO₂ smaller than the rest of the transition metals. If it was the intrinsic reactivity of the close-packed catalyst surfaces towards dissociating methane that determined the trend, the rate should have been highest on Ru, according to the present calculations [see (5) above]. Also, if it was the intrinsic reactivity of methane dissociation on uncoordinated sites that determined the trend, the rate should have been highest (or, at least, similar) on Ir. These possibilities are excluded based on the experimental literature. (Chapter 4)

10) A comparison of steam reforming data with the model results reveals that the trends in the reactivity of transition metals towards catalyzing the reaction may be either determined by the energy barrier for methane dissociation on the most-close packed surfaces of the metals, or by the binding energy of the dissociation products of water (adsorbed OH or O). In the first case, according to the present calculations, the rate should be highest on Ru. In the second case, the rate should be highest on Pt. Experiments have been found in the literature that conform to both possibilities. (Chapters 3, 4)

11) The experimental activation energy for steam reforming on Pt is closer in magnitude to the DFT-calculated activation energy on the close-packed surface. This indicates that uncoordinated and therefore more reactive sites are likely inactive under reaction conditions. (Chapter 3)

12) A natural bond orbital analysis of the chemisorption of methane on a Pt ad-atom site (Pt/Pt(111)) and on a Ru-adatom site (Ru/Ru(0001)) identified electron donation from a bonding orbital of CH₄ to an sd –hybrid orbital of the reaction site and electron back – donation from a d orbital of the metal site to an antibonding orbital of methane. The different reactivity of the two metal sites is caused by the greater overlap of the acceptor orbital with the donor methane orbital, for Pt, compared to Ru. That results in greater electron donation for Pt compared to Ru. (Chapter 3)

13) A linear relationship was found to exist between the energy barrier for water dissociation on transition metals and the overall energy change for the reaction. Such Bronsted – Evans- Polanyi relationships have been demonstrated before using DFT calculations for metal slabs, but the present cluster calculations also confirm the validity of such a linear correlation for the water dissociation reaction.(Chapter 4)

14) Concerning low-temperature direct methane fuel cells, this study suggests that a catalyst that would have superior performance to Pt would be one that forms less strongly bound (more reactive) OH by deprotonating water to oxidize adsorbed CO at low potentials, and at the same time would be effective in dissociating methane. Also the catalyst should be stable in the acidic environment of a fuel cell. (Chapter 4)

We could also discuss further at this point the use of alloys in fuel cell anodes that operate with carbon-containing fuels in general, and with methane in particular. As mentioned above, for pure metal catalysts the trend in the oxidation rates is determined by

the binding energy of OH, as well as that of CO, which are both lowest on Pt (conclusion 9). The electro-oxidation of CO, that is formed on the surface when the feed contains carbon (such as for methanol or methane fuels), is believed to happen according to the reaction^{1,2}:



Thus, the smaller binding energies of OH and CO on Pt would make the activation energy of reaction (1) smaller than the rest of the transition metals. Furthermore, if we compare, for example, Pt and Ru metals, adsorbed OH on Ru is likely to severely hinder the adsorption of the reactant, as the binding energy of OH on Ru is large.

However, the situation with alloys is somewhat different. For example, it is known¹ that a Pt-Ru alloy has superior performance compared to either pure Pt or pure Ru in the electro-oxidation of methanol. The reason for this is believed to be^{1,2} that CO and OH, that are formed on the surface in the process, occupy different metal sites. CO occupies Pt sites and OH occupies Ru sites. The present calculations (chapter 4) show that OH has a strong energetic preference for Ru, compared to Pt. The binding energy of OH on Ru is 3.12 eV, compared to 2.10 eV on Pt). Thus, on a Pt-Ru alloy, OH will bind on the Ru sites, leaving the Pt sites available for adsorption of the reactant and formation of CO. Because of the large binding strength of OH on Ru, it will be formed at low anodic potentials (compared to Pt), which is beneficial¹ because it would reduce the overpotential of the fuel cell. This happens without OH blocking the entire surface and thus preventing the adsorption of the reactant, because Pt sites would be available. It has also been found² that there is an additional beneficial electronic effect, which consists of a reduction of the binding energy of CO on Pt, when OH is co-adsorbed on a neighboring Ru site. Furthermore, we also found in this study a small reduction of the binding energy of OH on the Ru atom of the Pt-Ru alloy,

compared to pure Ru (2.97 versus 3.12 eV). These two effects lead to a lowering of the activation energy for the oxidation of CO according to equation (1).

The above discussion justifies why the reactivity of the Pt-Ru alloy is not simply determined by the binding energies of OH or CO and the corresponding trends found in Chapter 4 (see Table 5 of Chapter 4 and text). The question that arises is whether a Pt-Ru alloy would have any beneficial effect in the direct oxidation of methane, as it is known to have in the oxidation of methanol. No answer can be given on the basis of this work. The issues that were discussed in the previous paragraph should be valid also in the case of the electrooxidation of hydrocarbons. One experimental investigation³ of the electro-oxidation of methane from acid electrolyte on a Pt-Ru alloy found that the performance was worse than on pure Pt catalyst. Another study⁴ with a PEM fuel cell found that the performance was better on Pt-Ru compared to pure Pt, but there were also products other than CO₂ that were formed on Pt-Ru, such as formaldehyde and methanol. Thus, the mechanism may be very different on an alloy catalyst. Further experimental work would certainly be beneficial in answering this question.

A further point in question regarding the mechanistic conclusions of Chapter 2 (conclusion 1) is the possibility that the reaction network that was examined did not include all possible reactions that can take place on the platinum surface. In particular, the possibility arises that, at anode electrode potentials for which the OH coverage of the surface is substantial, the dehydrogenation steps of the hydrocarbon intermediates may happen by a transfer of the H atom from the CH_x or CH_xO species to adsorbed OH, rather than by dissociation of the H atom to an adjacent surface metal atom. There appears to be no prior discussion in the literature for this alternative pathway. For example, the dissociation

of the methyl radical was consider in the mechanism that we examined to take place in the following way:



However, it might also happen in the following way:



A similar mechanism is possible for all other dehydrogenation reactions, including the initial dissociative chemisorption of methane.

In order to study these reactions and their relevance, an extended set of calculations would have to be performed. If the reactions did happen in this way, then the binding energy of OH would also be expected to have an effect on the energy barriers for the dehydrogenation elementary steps. In particular, if OH is weakly bound on the surface, it would provide a better acceptor molecule for the H atoms . The opposite would be true if OH is strongly bound. To explain this, we note that during the reaction, adsorbed OH is converted to H₂O. If OH is strongly bound then the energy of the reactants, compared to the products, is decreased. Correspondingly, the reaction energy change is increased and the activation energy should also increase. Based on the conclusions of Chapter 4 (conclusion 8), among all metals that were studied, OH binds more weakly on Pt. Therefore, Pt would catalyze these reactions with a lower energy barrier. This would therefore provide additional reasons for the superiority of Pt among transition metals in catalyzing the electro-oxidation of methane.

5.3 Recommendations

The following are recommendations for future work:

a) In the majority of the calculations that were performed in this work, one layer clusters were used to simulate the surface. Identification of trends, rather than accurate energy barriers, justified the use of small clusters. More accurate results can be obtained using larger clusters, for example 3-layer clusters. For the entire sequence of calculations that were performed in this work, the computation times with larger clusters would be prohibitive. The choice of cluster size depends on the computing resources, time constraints and extent of calculations required for the project under investigation. It is expected that in the near future such calculations will continue to become progressively more time-efficient. The larger cluster sizes that could be afforded would increase the accuracy of the models. It is recommended that the calculations are repeated with larger clusters when the computation times are not prohibitive for this task.

b) Despite the fact that the methods that were used in the present work were suitable for predicting trends, the accuracy of the absolute values is questionable because of the use of small clusters and the inherent accuracy of DFT methods. One approach that can potentially improve the accuracy of the present calculations is to implement embedded-cluster methods⁵⁻⁸. These methods treat the metal surface as consisting of two distinct regions: a region that contains the reaction site and some metal atoms in its immediate environment (the cluster) and a region that consists of the surrounding metal lattice. The embedded cluster and the surrounding lattice are treated with different methods. The objective is to use a very accurate method for the cluster while taking into account the surrounding lattice in an effective way that is not very computationally demanding. The

main advantage of the embedded-cluster methods compared to the finite cluster approach is that it takes into account the effect of the long-range interactions between the adsorption / reaction site and the metal atoms further away in the lattice. If compared to periodic slab methods, embedded-clusters methods are advantageous in that very accurate *ab initio* methods can be used for the cluster, such as perturbation methods (MPn), configuration interaction and coupled-cluster techniques. On the other hand, these methods, that are more accurate than DFT methods, cannot be practically used in calculations with large metal clusters or with periodic slabs, because of the prohibitive scale of computational resources that would be required.

Various implementations of embedded cluster methods have appeared in the literature. For example, an early model⁵ consisted of a cluster embedded in a crystal charge density and was implemented as a DFT-cluster in a DFT-slab that is periodically repeated in space. A cluster-in-cluster approach utilizing the configuration interaction method for the primary region was another early approach⁹. Various variations of this method have appeared more recently, including cluster-in-slab approaches, DFT implementations and second-order perturbation theory¹⁰⁻¹². Other approaches include the perturbed cluster technique of Pisani and Green's function formulations^{13,14}.

A recent implementation^{15,16} of an embedded-cluster technique is well-suited for improving the accuracy of the present calculations and is recommended for further work. In this method, periodic DFT theory is used for the surrounding metal region and very accurate correlation methods (configuration interaction and Møller-Plesset perturbation methods) are used for a small cluster that contains the adsorption site. The interaction of the

cluster with the surrounding extended metal is taken into account by an effective embedding potential. This potential is calculated with periodic DFT and is used as an one-electron operator in subsequent very accurate cluster calculations. The success of this approach was manifested by benchmark calculations that included the CO/Cu(111) system¹⁵ and the CO/Pd(111) system¹⁶. Because the adsorption of CO is known to be a problematic case in DFT methods, and is often used a prototype molecule for experimental adsorption studies, the reliability of the computational approach is increased. Good agreement with experiment was demonstrated for predicted adsorption geometries and energies as well as for excitation energies within the adsorbed CO molecule. This methodology could therefore also be used to extend the present calculations by including the reaction of the oxidation of CO on transition metal catalysts, and improve the accuracy of the calculation that were performed. However, the approach has not been explicitly included in commercial quantum-mechanical software and would have to be implemented by appropriately modifying existing codes.

c) The present work focused on DFT methods to explain the observations of catalytic aspects of the electro-oxidation of methane in low-temperature fuel cell anodes. Direct hydrocarbon fuel cells would also benefit from the application of modern experimental methods of surface science and electrochemistry. It should be noted that the majority of experimental work on direct hydrocarbon fuel cells was performed during the 1960s. Since that time, experimental surface science and electrochemistry have greatly advanced. In the present work, many conclusions have been drawn on the basis of theoretical DFT calculations. It is recommended to also use experimental surface science methods to probe the electrochemical interface and collect much needed information on the anode processes of a direct hydrocarbon fuel cell.

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Appendix A: Brief Introduction to Quantum Mechanics (QM) and QM methodology

This section is a very brief introduction to Quantum Mechanics. It is by no means a comprehensive introduction. It was written for purposes of completeness, in an attempt to explain such terms as density functional theory, exchange-correlation functionals, basis sets, geometry optimization, effective core potentials etc., that appear in the document, and are part of the Quantum Mechanics terminology. The discussion is based on references 1-3.

A.1 The Schrödinger Equation and ab-initio methods

The theory of quantum mechanics (QM) postulates that the total energy E of a molecule is the eigenvalue of the Hamiltonian operator acting on the molecular wavefunction.

$$\hat{H}\Psi = E\Psi \quad (1)$$

Equation 1 is the Schrödinger equation. The wavefunction Ψ is an eigenfunction of the Hamiltonian and uniquely determines the state of the molecule. This means that the value of any molecular property can be calculated if the molecular wavefunction is known. The Hamiltonian operator contains terms that correspond to the kinetic and potential energy of the molecule. For a molecule of M nuclei and N electrons, the Hamiltonian is:

$$\hat{H} = -\sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{A=1}^M \frac{\hbar^2}{2m_A} \nabla_A^2 + \sum_{i=1}^N \sum_{A=1}^M \frac{q_i q_A}{4\pi\epsilon_0 r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{q_A q_B}{4\pi\epsilon_0 r_{AB}} \quad (2)$$

The first term is the kinetic energy of the electrons, the second is the kinetic energy of the nuclei, the third is the attractive electrostatic interaction between the electrons and the nuclei, the fourth is the repulsive electrostatic interaction between the electrons and the fifth is the repulsive electrostatic interaction between the nuclei.

The Born – Oppenheimer approximation is used in quantum mechanical methodology to simplify the complicated Hamiltonian. The motion of the nuclei is much more sluggish than the motion of the electrons and therefore the electrons are assumed to adjust instantly to the position of the nuclei. Thus, the electronic energy is calculated for fixed nuclear positions and the repulsive internuclear potential energy is a constant added to the result. This reduces the terms in the electronic Hamiltonian, the operator that yields the electronic energy as the eigenvalue when applied to the electronic wave function:

$$\hat{H}_{el} = -\sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i=1}^N \sum_{A=1}^M \frac{q_i q_A}{4\pi\epsilon_0 r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (3)$$

$$\hat{H}_{elec} \Psi_{elec} = E \Psi_{elec} \quad (4)$$

Ab-initio QM methods are computational methods that solve the electronic Schrödinger equation in order to calculate the energy of a collection of atoms to various levels of accuracy. Ab-initio methods have been implemented in several computer codes. Computational chemists use the term “x level of theory”, where x is the name of the method used, in order to stress the fact that each method corresponds to a different level of accuracy. The computational time and disk space required to perform a QM calculation increases with the accuracy of the method used. The least accurate is the Hartree-Fock (HF)

level of theory. Various levels of post-HF and the various implementations of Density Functional Theory are progressively more accurate. The computational time and resources required to perform a QM calculation depend very much on the number of atoms in the system. CPU time is often proportional to the third or fourth power of the number of atoms. The scaling problem is worse for the more accurate methods.

A.2 The Potential Energy Surface, geometry optimization and vibrational frequencies

The most common task of ab-initio methods is to explore the potential energy surface (PES) of a chemical system. The PES is the ‘plot’ of the energy of a collection of atoms with respect to the coordinates of the atomic nuclei i.e. the geometry of the molecule. The coordinates can be Cartesian or internal coordinates (bond lengths, bond angles and dihedral angles). If specification of two coordinates is sufficient to describe the molecule, the PES is a 2D surface and can be shown pictorially. Otherwise it is a hyper-surface in $3N-6$ coordinates for a molecule of N atoms or $3N-5$ for linear molecules. The concept of the PES is a consequence of the Born – Oppenheimer approximation, because it allows a one-to-one mapping of the molecular energy and the molecular geometry.

Minima and saddle points on the PES are called stationary states. Actual molecules, such as the reactants and products of a chemical reaction, are energy minima on the PES. The intrinsic reaction coordinate (IRC) is the lowest energy path between two minima. This is the path on the PES that the reacting system follows. A transition state is a saddle point on the PES. It is the maximum energy structure along the IRC direction and it is a minimum in

all other directions. Mathematically, for stable structures on the PES (reactants, products and intermediates), the second derivatives of the energy with respect to all molecular coordinates are positive. For transition states, the second derivative of the energy along the reaction coordinate is negative.

Geometry optimization is the process of locating stationary points on the PES and is one of the main features of computer codes for computational chemistry. The optimization process requires the user to enter a guessed structure. The guessed structure should not be too different from the minimum or transition state searched for, in order to avoid common pitfalls such as locating local instead of global minima. Within each step in a geometry optimization routine, the electronic Schrödinger equation is solved to obtain the absolute energy of the collection of atoms and electrons with the nuclei fixed at a specific location.

Geometry optimizations require the calculation of the first and second derivatives of the energy with respect to all molecular (internal or Cartesian) coordinates. First derivatives form the gradient matrix and second derivatives form the Hessian matrix. Much of the difficulty in geometry optimizations is in estimating the Hessian matrix because analytic second derivatives are computationally demanding for most ab-initio methods. Finding transition states is also much more challenging than optimizing to minima.

The Hessian matrix also holds all information about the vibrational frequencies of the molecule (the normal modes). Vibrational frequencies are obtained by diagonalization of the Hessian ($\mathbf{H} = \mathbf{P}\mathbf{k}\mathbf{P}^{-1}$). The matrix $\mathbf{P}$ is composed of the eigenvectors of the Hessian and contains all information about the directions of the normal mode vibrations. The elements of

the diagonal matrix $\mathbf{k}$ are the eigenvalues of the Hessian and supply the vibrational frequencies, when mass-weighted. For a maximum on the PES, all eigenvalues of the Hessian are positive. For a transition state, there is only one negative eigenvalue. Equivalently, the Hessian corresponding to a transition state has exactly one imaginary vibrational frequency, because calculating the vibrational frequencies involves taking the square root of the eigenvalues. This process of finding the normal mode frequencies is implemented within the available computer codes. In this work we have made use of the requirement concerning the sign of the eigenvalues to confirm that transition states have been properly located.

A way of testing the proper location of a transition state is by using computer programs capable of animating the vibrational modes. The imaginary frequency should follow the reaction coordinate. Another way is by doing an IRC calculation. This is a process that generates a series of structures from the transition state to the reactants or products. These tests are used to make sure that the located transition state does not correspond to a different reaction than the one that was intended for.

Frequency analysis also provides zero-point energies (ZPE's). These are the vibrational energies of molecules at absolute zero. After a geometry optimization process has concluded, the stationary point found does not contain the finite vibrational energy at 0K. The ZPE's are sometimes found by frequency analyses and added to the results to obtain enthalpies or free energies at 0K. In most cases, we are interested in energy differences rather than absolute energies. For example, we are seeking energy changes between

reactants and products or between reactants and transition states. Usually, these are only slightly affected by ZPE's.

A.3 The wave function and the Hartree-Fock method

The wavefunction of the electronic Schrödinger equation can not be analytically obtained for any system other than the hydrogen atom. For the H atom the solution is the familiar 1s, 2s, 2p_x, 2p_y etc. atomic orbitals. For any other atom or molecule, approximate methods have been devised to solve the equation.

Electrons are properly described by four coordinates. The three space coordinates (x, y, z) and a spin coordinate (spin α or spin up and spin β or spin down). The value of the spin coordinate is the additional fundamental property of the electron that, coupled with the requirement of antisymmetry gives rise to the quantum mechanical effect called “exchange correlation” or simply “exchange”. The wavefunction of the Schrödinger equation is a function of the 4N coordinates of the N electrons in the system. Electrons must satisfy a principle called antisymmetry: if the four coordinates corresponding to one electron in the wavefunction are interchanged with the four coordinates of another electron, the wavefunction changes sign. The simplest wavefunctions that satisfy this requirement are called Slater determinants. For example, for the 1s² wavefunction of the singlet state of the He atom, a Slater determinant can be written as:

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} \quad (5)$$

where $1s(1)$ is the molecular orbital (the space function) associated with electron 1 and $\alpha(1)$ is the spin coordinate of electron 1 ($1s(1)\alpha(1)$ is a spin orbital). The Slater determinant is an antisymmetric wavefunction. In the Hartree-Fock method (HF) the wavefunction is represented as a single Slater determinant. As shown above for He, the wavefunction is written in terms of the known atomic orbitals (s, p, d, f...) of the hydrogen atom.

Exchange correlation is the quantum mechanical interaction of electrons of same spin among themselves. The consequence of exchange correlation is that the density of like-spin electrons around a given electron in the molecule is depleted (Fermi hole). Electrons of like spin cannot be at the same point in space. Exchange correlation decreases the energy of the molecule. A wavefunction that satisfies the antisymmetry requirement, such as the Hartree-Fock wavefunction, takes full account of exchange.

The Hartree-Fock (HF) method is based on the variational principle. The variational principle states that for any trial function Ψ_0 :

$$\int \Psi_0 \hat{H} \Psi_0 d\tau \geq \int \Psi \hat{H} \Psi d\tau \quad (6)$$

where Ψ is the true (real) wavefunction, so that the second term is the energy of the molecule. Use of this theorem is made by writing the trial wavefunction Ψ_0 in parametric form and then minimizing the quantity on the left-hand side of Equation 6, and in this way approach the true energy of the molecule. Thus, the HF method is an optimization process in which the parameters of the trial function (a set of molecular orbitals forming a Slater determinant) are optimized such as to minimize the molecule's energy. The mathematics of the process is very complicated and will not be discussed here. The computational difficulty

in the process is that it requires the time-consuming computation of many integrals. It will be acknowledged in this short description that the HF method is an iterative scheme in which the parameters of a trial set of molecular orbitals, which form a Slater determinant, are optimized to minimize the energy of the molecule.

A.4 Basis sets and effective core potentials

Within the mathematical implementation of the HF scheme, the molecular orbitals are expanded using a set of K basis functions, called the basis set.

$$\psi_i = \sum_{v=1}^K c_{vi} \phi_v \quad (7)$$

This mathematical trick of replacing the molecular orbitals by linear combinations of a given set of orbitals reformulates the problem into optimizing the coefficients c_{vi} to the values that minimize the energy. Therefore, it is required by the user of any program that does ab-initio calculations to select a basis set. The functions of the basis set are chosen in such a way that their linear combinations can approximate the atomic orbitals of the H atom. The true atomic orbitals of the hydrogen atom (the Slater functions) are not used in the HF method because they yield a set of very hard-to-compute integrals.

Sets of Gaussian functions are used instead. Primitive Gaussian functions are proportional to $e^{-\alpha(r-R_0)^2}$, where R_0 is the position of the atomic nucleus around which the orbital is located. Contracted Gaussian functions are linear combinations of primitive Gaussian functions. The orbital exponents α of contracted Gaussians are chosen so that the shape of the function resembles that of Slater functions. For example, an STO-3G basis set (Slater

Type Orbitals - 3 Gaussians) has three primitive Gaussians for each contracted Gaussian and has the ability to represent quite well the “diffuse” shape of the Slater function’s tail away from the nucleus. Contracted Gaussians are named after the Slater functions they represent. For example, s, p d, f contracted Gaussians are used to represent the s, p, d, f H-atom orbitals. A minimal basis set contains the minimum number of basis functions that is able to represent the atomic orbitals of an atom. That contains all contracted Gaussians of the valence shell.

A basis set is a set of parametric functions, the parameters of which are optimized within the variational scheme of ab-initio methods. Thus, several basis sets that vary in their effectiveness are currently used. For example, split-valence double-zeta basis sets, replace each contracted Gaussian by two contracted Gaussians in the valence orbitals, so that the two orbital exponents allows greater flexibility in the size of the orbitals. Thus, a 6-31G basis set has 6 primitive Gaussians for each contracted Gaussian in the core orbitals, while the valence orbitals are split to two Slater-Type orbitals, one composed of three primitive Gaussians and one with one. These two contractions have different orbital exponents. A 6-31G** basis set is a split-valence basis set that contains polarization functions for all atoms. For example, s and p Gaussians are used for the H atom in the 6-31G** basis set even though the H atom electronic configuration (when not in a molecular environment) is $1s^1$. However, if the electronic density surrounding the H atom in a molecule tends to drift away from the spherical symmetric shape of the 1s orbital, polarization functions are able to accommodate this. Diffuse functions may also be added to the basis set to describe situations of very diffuse electronic density, such as for anions.

Effective core potentials (ECPs), named also pseudopotentials, are commonly used for the heavier elements of the periodic table, usually from the 3rd row and below. Within the mathematical implementation of an ab-initio method, if pseudopotentials are used, the core electrons are not treated explicitly. The effect of the core electrons on the valence electrons is treated in an “average” way. Thus, a large amount of electron-electron interactions (and their associated integrals) do not have to be calculated explicitly. Valence electrons are treated explicitly. The use of ECPs allows for faster calculations that involve the heavier atoms, in reasonable amounts of time. If ECPs are not used for the heavier atoms that contain many electrons, the computation time required is often prohibitive for reasonable applications of the theory.

Another requirement for accurate calculations involving heavier atoms is the use of methods that take into account relativistic effects. The Schrödinger equation is non-relativistic. The masses of the electrons in the inner-most orbitals of heavy atoms are greater than the electron rest-mass because of their high velocity. This sometimes has significant effects on the calculated energies. Because ECPs and relativistic corrections are both required for the heavier atoms, most ECPs and their basis sets (such as the LANL2DZ basis set) take into account relativistic effects.

A.5 The Hartree-Fock limit and post-HF methods

Within the HF method, the interelectronic repulsions are treated mathematically in such a way that each electron experiences the average electrostatic repulsion of a charge cloud made up of all the other electrons. The electrons do not have a particular position in the

molecule at any instant of time but their position is characterized by the probability distribution that gives rise to a mean electrostatic field. The smeared-out electrostatic field exerts a force on any electron. In reality, this is an incomplete approach because each electron actually feels each instantaneous pair-wise interaction between itself and all the other electrons in the molecule. As a consequence, HF overestimates the interelectronic repulsions because in reality the electrons avoid each other more than the estimation of the HF method. This discrepancy is called electron correlation or simply correlation (not to be confused with exchange correlation, which is a quantum mechanical effect). Correlation energy is the difference between the true energy of a molecule and the lowest possible HF energy. Thus, even with the most accurate basis set, the HF calculation converges to an energy that is always greater than the true energy. This is the Hartree-Fock limit.

In order to solve the problem of electron correlation and obtain more accurate results, different approaches that require greater CPU times are possible. Perturbation theory and configuration interaction are the two most effective approaches. Mathematically, these two methods are very different. Physically, they both can yield more accurate results by allowing the electrons to be partly excited to higher-energy orbitals. In this way, they are allowed to avoid each other more as they are not restricted to the orbitals of the Hartree-Fock determinant.

The first method, configuration interaction (CI), is based on using a wavefunction that is a linear combination of Slater determinants. The Hartree-Fock solution yields a set of N spin orbitals that are occupied, where N is the number of electrons. It also yields virtual (unoccupied) spin orbitals. In the CI approach, spin orbitals of the Hartree-Fock determinant

are replaced by virtual orbitals to give ‘excited determinants’. Replacing occupied orbitals with virtual ones yields a large number of determinants. In practice, only a few excitations are allowed. This approach has been implemented in a series of CI methods (CID, CISD, QCISD, QCISD(T) etc.).

Another approach is Moller-Plesset (MP) perturbation theory. This method is based on a mathematical technique that provides 1st, 2nd and higher order corrections to the known wavefunction and energy of a Hamiltonian that is similar but not exactly the same as the true Hamiltonian. Because a mathematical treatment of the perturbation theory is beyond the scope of this document, no further discussion will be made here. The method has been implemented as the various Moller-Plesset schemes that become progressively more accurate and more computationally demanding as higher-order corrections are computed for the unperturbed system (MP2, MP3, MP4 etc. form the series of MP methods).

A.6 Density Functional Theory (DFT) methods

Density Functional Theory is fundamentally different from the rest of the methods mentioned so far. Instead of aiming at finding the wavefunction, it aims at describing the molecule using the electron density function. The electron density function $\rho(r)$ (or the probability function) is the square of the wavefunction and is depends only on the three spatial coordinates. On the contrary, the wavefunction of a molecule with N electrons is 4N-dimensional. Thus each point in space is associated with the probability of finding an electron at it. So the dimensionality of the problem is greatly reduced. This approach is relatively new because until 1964 it had not been realized that it is possible to calculate

electronic densities without first calculating wavefunctions. At that time, two important theorems were proven [Hohenberg and Kohn (1964), Kohn and Sham (1965)]. The first theorem states that the energy of a ground-state molecule is uniquely determined by its electronic density function. Otherwise stated, the energy is a functional of the electronic density function, $E = E[\rho_0(\mathbf{r})]$. A functional is a one-to-one mapping of a function (the argument) with a number (the result). The second theorem states that this functional will yield a higher energy for any density $\rho(\mathbf{r})$ other than the true density of the ground state ($E[\rho(\mathbf{r})] > E[\rho_0(\mathbf{r})]$); the functional is variational.

The form of the functional remains unknown. In practice, the density is expressed in terms of a set of orbitals, the Kohn-Sham orbitals, which depend only on the three space variables. The functional is decomposed into three different functionals: the kinetic energy functional, the potential energy functional and the exchange-correlation (XC) functional. The last one is the only one that is not known. All of the difficulty in DFT methods is in the exchange-correlation functional, which describes the phenomena of exchange and electron correlation.

Over the years, many different XC-functionals appeared. In many of them, both the density and its gradient are used (The Generalized Gradient Approximation functionals). The most popular exchange-correlation functional today is the B3LYP functional. This is a parametric functional and has been parameterized against a set of reliable experimental thermochemical data. The mathematics of the DFT method will not be discussed here. As with HF and post-HF methodology, basis sets are used to expand the Kohn-Sham orbitals. The results of DFT calculations are of comparable accuracy to some of the most advanced

post-HF methods and DFT is less computationally demanding. For this reason DFT has become very popular in the computational chemistry community.

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