Synthesis, Structure, And Catalytic Properties Of Size-selected Platinum Nanoparticles

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SYNTHESIS, STRUCTURE, AND CATALYTIC PROPERTIES OF SIZE-SELECTED PLATINUM NANOPARTICLES

by

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ABSTRACT

The use of heterogeneous catalysis is well established in chemical synthesis, energy, and environmental engineering applications. Supported Pt nanoparticles have been widely reported to act as catalysts in a vast number of chemical reactions. In this report, the performance of Pt/ZrO$_2$ nanocatalyst for the decomposition of methanol, ethanol, 2-propanol, and 2-butanol is investigated. The potential of each alcohol for the production of H$_2$ and other relevant products in the presence of a catalyst is studied. All the alcohols studied show some decomposition activity below 200°C which increased with increasing temperature. In all cases, high selectivity towards H$_2$ formation is observed. With the exception of methanol, all alcohol conversion reactions lead to catalyst deactivation at high temperatures (T >250°C for 2-propanol and 2-butanol, T >325°C for ethanol) due to carbon poisoning. However, long-term catalyst deactivation can be avoided by optimizing reaction conditions such as operating temperature. In addition, the performance of Pt/γ-Al$_2$O$_3$ is evaluated in the oxidation of 2-propanol. Pt nanoclusters of similar size (~1 nm diameter) but different structure (shape) were found to display distinctively different catalytic properties. All the systems studied achieve high conversion (~ 90%) below 100°C. However, flatter particles display a lower reaction onset temperature, demonstrating superior catalytic performance. Acetone, CO$_2$, and water are generated as products indicating that both partial and complete oxidation are taking place. A number of techniques including AFM, XPS, TEM, HAADF-TEM, XAFS as well as packed-bed reactor experiments were used for sample characterization and evaluation of catalytic performance.
To my parents, the rock upon which my life is built
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CHAPTER ONE: INTRODUCTION

1.1 Catalysis and Nanotechnology

Catalysis is the process by which the rate of a chemical reaction is increased without consuming the substance or material that causes such rate increase. Nature’s catalysts, i.e. enzymes, are fundamental in enabling numerous processes that allow many living organisms, including humans, to sustain life [1]. They have also been used for centuries to enhance, for instance, fermentation and coagulation during wine and cheese production, respectively. Thus, even before the concept of catalysis and the details of specific chemical reactions were thoroughly understood, humans have in one way or another made use of catalysts to achieve a great number of tasks. The 19th century saw some of the first attempts to understand and consciously create inorganic catalysts with the intent of enhancing and controlling specific reactions. By 1875, catalyst technology was introduced in industrial applications for the synthesis of sulfuric acid over Pt-based catalysts [2]. Since then, the study and utilization of catalysts have expanded rapidly to the extent that “almost all chemicals, fuels, polymers, and fibers are manufactured in our times by catalytic processes” [2]. Furthermore, they have played a significant role in the development of technologies for controlling the discharge of various gaseous, liquid, and solid pollutants, including CO, NOx, and volatile organic compounds (VOC), among others. They have also played an important role in the energy sector through widely used processes such as petroleum refining [2, 3], and may in the coming years pave the way for development of alternative, non-fossil fuel sources of energy, e.g., fuel cells anodes [4].
A catalyst increases the reaction rate by lowering the activation energy of a reaction. It may not, however, make a thermodynamically unfavorable reaction become favorable, as it has no impact upon the reaction enthalpy [2]. In heterogeneous catalysis, one or more molecules can react by carrying out three basic steps over a solid catalyst: adsorption, reaction, and desorption. The specifics of this process will change depending on the reaction and the type of catalyst. For example, a reactant molecule can undergo either molecular or dissociative adsorption, while surface reactions may involve dissociation or association with molecules physisorbed or chemisorbed on the catalyst surface or even those in the gas phase [5, 6]. Even though each of these processes has an associated energy barrier, a catalyst will be effective provided that the activation energy of each individual step over a catalyst site is lower than that of the uncatalyzed reaction [2]. Thus, the advantages of utilizing catalysts in numerous industrial and pollution control applications are clear and include increased reaction rates even under milder reaction conditions, i.e., lower temperature and pressure, as well as better selectivity for desired products. This may result in significant savings in terms of energy as well as a more efficient utilization of raw materials and decreased impacts upon health and/or the environment [1].

In recent years, another important field of study that has seen increasing interest and a growing number of applications is that of nanotechnology. This is a broad field encompassing different research areas including material synthesis and characterization as well as the study of electronic, magnetic, and biological properties and/or applications. Considering the novel properties and increased number of reactive sites, due to greater surface area found in nanomaterials, their potential applications in catalyst technology become evident. Thus, it is not surprising that advances in field of nanoscience have also led to significant advances within the
field of catalysis through improved development and understanding of materials and processes [1]. For instance, whereas certain metals, e.g. Pt, Fe, have been known to catalytically enhance a number of industrially-relevant reactions, the synthesis of metal nanoparticles (NPs) has resulted in improved conversion rates and selectivities [7]. In addition, novel catalytic properties for materials that were usually thought of as inert in the bulk form, e.g. gold, have also been described [8, 9].

1.2 Alcohol Decomposition

The decomposition of alcohols over metal and metal oxide catalysts has been the subject of numerous studies due to its applicability to a variety of chemical synthesis processes [10-14]. In recent years, this subject has gained particular interest due to growing environmental, economic, and political concerns regarding energy production [11]. Safe and efficient in-situ hydrogen generation from alcohols (i.e. methanol, ethanol, propanol, butanol) can promote the use of fuel cells and other clean technologies as a source of energy for mobile applications. Alcohols can serve as H₂ carriers that are compatible with current infrastructures for liquid fuels and can be catalytically decomposed on-site in order to minimize energy input requirements and operating temperatures [15].

Catalysts that promote methanol (MeOH) and ethanol oxidation processes are key in the improvement and optimization of direct MeOH and ethanol fuel cells [4, 15-21] as well as direct H₂ fuel cells, for which decomposition catalysts are also of great importance. Since ethanol can be produced from the fermentation of biomass [16], it is a potentially renewable fuel that can be reformed on-site to generate H₂. The decomposition of higher order alcohols such as 2-propanol
and 2-butanol can also be of interest for a variety of hydrogen-based energy applications while generating other products, i.e. acetone and butanone, which are of great importance in the chemical synthesis industry [22, 23]. By increasing activity and selectivity, industrial catalysts can decrease the energy input required as well as the output of potentially harmful by-products associated with numerous chemical processes. Furthermore, it has been shown that the addition of H₂ to fuel mixtures enhances the activity and lowers harmful emissions of internal combustion engines [24, 25]. Catalytic reforming of gasoline additives, e.g. methanol, ethanol, and potentially butanol, may serve as an on-board source of hydrogen [26]. Waste streams from industries that make use of solvents may contain significant amounts of alcohols and other organics used for this purpose and may require special treatment. Recent studies have focused on the feasibility of obtaining hydrogen (via steam reforming) from 2-propanol, 2-butanol, and other widely used solvents to be used in stationary fuel cell applications [27, 28]. Dehydrogenation of these higher order alcohols may bring the same benefits (i.e. reduction of waste and H₂ production) while generating other valuable products for industrial applications. Efficient catalysts for the dehydrogenation of higher order alcohols may also contribute to improvements in chemical heat pumps, such as those based on the 2-propanol/acetone/hydrogen cycle [29, 30].

Methanol decomposition has been shown to take place over a variety of metal surfaces and nanocatalysts including Pt, Pd, Au, Rh, Ni, Co, and Cu supported on metal oxides such as Al₂O₃, CeO₂, ZrO₂, ZnO, TiO₂, and SiO₂ [18, 20, 31-51]. In the absence of O₂ and water, MeOH decomposition favors the formation of H₂ and CO, which can be further reacted in the presence of water to form additional H₂ and CO₂ through the water-gas shift reaction. Platinum has been shown to have good activity and selectivity towards H₂ formation. Previous studies from our
group on the decomposition of MeOH over similarly-sized Pt nanoparticles (NPs) deposited on SiO_2, Al_2O_3, CeO_2, TiO_2, and ZrO_2 [37] revealed an enhanced activity for the Pt/ZrO_2 system.

Ethanol decomposition and the associated reactions including ethanol oxidation and steam reforming have also been thoroughly studied over Pt, Pd, Rh, Cu, Co, Ir, Ni, Fe, and other catalysts supported on CeO_2, Al_2O_3, ZrO_2, ZnO, and CuO [16, 21, 26, 52-71], and good selectivity toward hydrogen has been observed in several of these systems. The choice of support and the presence or absence of reactants such as O_2 and water, will determine the reaction’s selectivity. For instance, Pt/CeO_2 and Pt/ZrCeO_2 catalysts tend to promote the formation of H_2 and acetaldehyde [72].

The decomposition of propanol and butanol is carried out in the chemical synthesis industry over Cu-, Zn-, and Ni-based catalysts as well as Pt/Al_2O_3. However, concerns of the fate of some of the most commonly used catalysts for this purpose, such as copper chromite, and their environmental impact have provided a motivation to further study and optimize alternative catalysts that may serve this purpose efficiently. In addition, the opportunity of using these alcohols for hydrogen generation to serve as an energy source has placed particular emphasis on finding catalysts that display high conversion and selectivity towards H_2 formation as well as long term stability. Some studies describing the decomposition of higher order alcohols, i.e. 2-propanol and 2-butanol, over metallic films (Pd-Ag) [73], micrometer-sized powders (Co, Cu, Mg_2Cu, Ni, metal oxides) [74-80], and supported NPs (Pt, Cu, Pt-Cu, copper chromite, W) [81-88] can be found in the literature.

In order to assess the potential of catalyzed alcohol decomposition we have conducted a systematic study of these reactions over size-selected Pt NPs supported on ZrO_2. The objective
of this study is to assess the catalytic performance (activity, selectivity, and lifetime) of novel, micelle-synthesized, Pt catalysts. The conversion and selectivity of each C1-C4 alcohol was evaluated in a packed-bed continuous flow reactor interfaced to a quadrupole mass spectrometer (QMS). Catalyst characterization was carried out before and after exposure to reactants to assess the initial state of our catalyst as well as changes taking place under reaction conditions. Reaction products are also investigated in order to assess the potential emissions associated with these processes as well as opportunities for material recovery in industrial applications.

1.3 Propanol Oxidation

Isopropyl alcohol, or 2-propanol, is a readily available secondary alcohol that is widely used in industry as a solvent and cleaner as well as feedstock in chemical synthesis processes. The production of many industrially-relevant compounds requires selective oxidation to occur in order to prevent complete oxidation to CO₂ and water. Such partially oxidized compounds may include products such as acetone, which is generated via oxidative dehydrogenation of 2-propanol. Traditionally, such reactions were achieved by using metal-based oxidants, e.g., chromium, manganese, selenium, or lead oxides, which under stoichiometric conditions resulted in the selective oxidation of the reactant [7]. However, this method is not preferable due to the hazardous aqueous solutions containing inorganic salts that are generated as part of this process [7]. Other methods involving heterogeneous catalysis have then been developed to carry out this reaction while minimizing environmental impacts. These commonly make use of Cu- and Ag-based catalysts to carry out the reaction in the gas phase while Pt or Pd catalysts are usually preferred for liquid-phase reactions [7]. Although some of these catalysts show significant
activity under relatively mild conditions, controlling selectivity remains a key issue [89]. However, further research into the applicability and performance of Pt-based catalyst for these gas-phase reactions seems sensible as prior studies have shown promising results.

In addition to chemical synthesis applications, another potential application of 2-propanol involves electrooxidation of this compound for fuel cell applications. Liquid-feed direct alcohol fuel cells are considered a promising alternative energy source that do not rely on the combustion of fossil fuels and do not require a pure H₂ feed as in traditional fuel cells. Several alcohols (and other compounds) have been proposed for this purpose, including 2-propanol, which has been reported to perform better than other alcohols, e.g. methanol, for this particular application [90]. The reaction that takes place at the cell’s anode involves electrocatalytic oxidation under aqueous solutions. However, knowledge about catalyst performance even under gas-phase reaction conditions may serve as a reference for potential catalysts to be used in fuel cell applications. Pt has already been reported as performing very well in 2-propanol electrooxidation [90-92], although more inexpensive metals such as Ni have shown comparable performance [92].

On the other hand, emissions of 2-propanol and other VOCs into the atmosphere must be controlled due to detrimental impacts upon health and the environment. VOCs are present in various household and industrial products, including paints, solvents, wood preservatives, cleansers, among others. VOC emissions into the atmosphere contribute, along with NOx, to the formation of ground-level ozone (O₃). Ozone is a criteria pollutant as defined in the National Ambient Air Quality Standards (NAAQS) that can negatively impact crops and ecosystems and, as the predominant constituent of smog, it is responsible for leading to respiratory and other adverse health conditions as well as reduced visibility [93, 94]. Thus, in order to ensure
compliance with NAAQS, regulations are in place which limit the emissions of VOCs into the atmosphere [95]. In terms of indoor air pollution, 2-propanol is one of the most common VOCs. Propanol (and other VOCs) is considered an indoor pollutant because of its potential impact upon the respiratory and central nervous systems and other internal organs as well as their toxicity and/or possible carcinogenicity [93, 94].

A number of technologies have been developed to address these issues by capturing, destroying, or recovering VOCs present in effluent streams, including carbon absorbers, thermal oxidation, biofiltration as well as catalytic oxidation. The applicability and effectiveness of these methods will vary depending on various factors including nature and concentration of contaminant, volume to be treated, as well as desired and/or required removal efficiencies. Deep oxidation, or catalytic incineration, of VOCs presents some advantages over thermal incineration, particularly lower operating temperatures which results in decreased energy costs.

On the other hand, it is important for catalysts used for this purpose to be resistant to deactivation or readily regenerated in order to ensure long catalyst life. This is particularly important for treating streams containing halogenated VOCs, as Cl and S are known to poison catalysts, rendering them ineffective. Thus, research in this area has not been limited to maximizing catalyst efficiency but also considering its resistance to deactivation (or potential for regeneration). Supported Pt and Pd catalysts are known to be very active in oxidation reactions while displaying resistance to poisoning from VOCs, including chlorinated compounds [96].

Numerous reports can be found in the literature describing the catalytic properties of supported Pt NPs in hydrogenation reactions [97] as well as electrooxidation for fuel cell applications [90-92, 97]. As stated above, 2-propanol partial oxidation is usually carried out in
aqueous solutions when Pt-based catalysts are used. Thus, reports of experiments conducted under these conditions are more common than for the gas-phase reactions [97, 98]. In addition, platinum has also been used in a number of environmental applications including catalytic converters for the conversion of CO, NOx, and HCs from mobile sources. However, the performance for gas-phase oxidation of 2-propanol over Pt has not been as thoroughly studied despite holding significant promise due in part to its ability to reversibly absorb/desorb atomic oxygen [7].

This study assesses the potential for γ-Al₂O₃-supported Pt nanoparticles in the gas-phase oxidation of 2-propanol. Particular emphasis is placed on the effect that particle morphology may have upon catalyst performance. Size- and structure-dependent activity and selectivity studies have been reported in the literature. It is clear that decreasing the particle size will affect the characteristics of the NPs surface and will also increase the number of atoms at the surface compared to the bulk. This potentially increases the number of active sites, e.g., atoms with lower coordination, and usually increases the adsorption enthalpies of gas-phase reactants [7]. This change in adsorption energy can be favorable to a degree as it allows the reactants to bind to the surface long enough for reactions to take place. However, decrease of the turnover frequency (TOF) has been observed with particle size decrease due to the inability of products to readily desorb from the surface, thus blocking potential active sites [7]. This phenomenon points to the existence of an optimum adsorption energy range where conversion is maximized, which is examplified by the volcano plot shown in Figure 1. On the other hand, a well studied case of structure sensitivity in catalysis is that of zeolites, particularly as it relates to reaction selectivity, where the porous structure (with pores in the molecular size range) only allow certain molecules
to access the internal active sites and react inside the material. Furthermore, NP faceting (predominance of certain crystalline planes over others) have also been reported to have an impact on a catalyst’s performance on oxidation reactions [99]. In our case, variations in the structure of the Pt NPs (shape, atomic order) may have an impact on its ability to exchange oxygen, as well as influencing the adsorption energy of reactants and their interaction with the support. In order to investigate the effect of particle structure upon catalytic activity, inverse micelle encapsulation will be used to synthesize size-selected NPs, which will be characterized using various techniques including atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray absorption fine structure (XAFS). This combination of complimentary characterization methods should provide a good estimation of the NP size and differences in the structure. Catalyst activity and resistance to deactivation will be evaluated in a packed-bed continuous flow reactor interfaced to QMS and a correlation between particle structure and performance will be described.
Figure 1. Typical volcano plot showing oxygen reduction activity as a function of adsorption energy over various materials. Taken from Nørskov et al. [100]
CHAPTER TWO: EXPERIMENTAL METHODS

2.1 Sample preparation.

A number of methods have been developed over the years with the purpose of fabricating nanomaterials to be studied and used in numerous applications. Some of the methods traditionally used for the synthesis of supported NPs include co-precipitation, precipitation-deposition, evaporation, etc. For the experimental work described in this thesis, we have used a method known as inverse micelle encapsulation [101, 102], which provides a number of advantages over some of the other preparation methods and involves a relatively simple bench-top procedure. The most important among these is the ability to synthesized metallic NPs with a narrow size distribution. Samples prepared this way are thus ideal model systems for the study of material properties, e.g. catalytic activity, including those which are highly dependent on NP size. The method consists of adding a polar/non-polar diblock co-polymer [polystyrene-\textit{block}-poly(2-vinylpyridine)] into a non-polar solvent, toluene. The co-polymer is made up of a polar head and a non-polar tail. Thus, when added to toluene, the polymer self-assembles into inverse micelles made up of a closely packed polar center, formed by the poly(2-vynilpyridine) (P2VP), with non-polar polystyrene (PS) tails stretching radially outward. The polar centers act as nanocages that, upon the addition of a metal precursor, provide sites for the formation of NPs. The metal precursor used was a Pt salt (H$_2$PtCl$_6$·H$_2$O), which binds to the P2VP heads, forming metal clusters of a defined size. The choice of polymer, with a specific polar core molecular weight (chain length), and the amount of metal salt added will determine the particle size while
maintaining a narrow size distribution. After sufficient stirring (usually over two days), the solution is filtered to remove any suspended/undissolved materials.

![Schematic drawing of the micelle formation of poly(styrene)-block-poly(2-vinylpyridine) (PS-b-P2VP) block copolymers in toluene.][1]

The sample is then deposited on two types of supports to conduct different measurements. First, the sample is dip-coated on a SiO₂/Si(001) wafer by slowly (~ 1 cm/min) introducing and retrieving the substrate in the solution, perpendicularly to its surface. This allows for a single layer of particles to be deposited on this planar substrate. Particles display a hexagonal arrangement over the surface due to a relatively uniform inter-particle distance determined by the length of the polymer tails. This arrangement can be particularly useful for studies regarding particle mobility/stability. For this particular study, the dip-coated substrate is utilized in particle characterization via AFM. The smooth surface of a SiO₂/Si(001) wafer containing one monolayer of particles makes this system ideal for AFM imaging. However, since the particles are still encapsulated by the polymer upon deposition, measurements conducted on these samples will tend to overestimate particle size. Thus, polymer removal is carried out by exposing the sample to O₂ plasma under ultrahigh vacuum (UHV) conditions. Following this treatment, AFM images will show particles that are clearly smaller than originally deposited and
removal of the polymeric shell can be confirmed by XPS, since the C-1s photoelectron peak is monitored and lack of a carbon signal indicates the absence of the C-based polymer.

On the other hand, the polymeric solution containing the NPs can be also mixed with an oxide powder to be used as support. In this case, the solution is stirred with the powder allowing the NPs to deposit on the support surface as the toluene evaporates. Samples contain 1% to 2% by weight Pt and are stir-dried overnight (~ 12 h) using a hotplate/stirrer at temperatures of 50-70°C. As in the case of the dip-coated samples, the powder supports contain metal NPs on its surface enclosed in a polymeric shell. These particles do not display any particular arrangement as they would on a planar substrate due to the uneven surface morphology of the powder supports and the fact that the solution is being stirred as the particles attach to the substrate. However, due to the relatively low coverage (low NP loading) on the support surface, it is not expected that significant agglomeration occurs during deposition by means of particle overlap. Due to the considerably greater amount of polymer present in these samples, UHV treatment is not feasible as it would result in significant (and potentially irreversible) contamination of the system.

In order to remove the C and Cl residues present in our samples (from the polymer and metal precursor, respectively), they are annealed at temperatures of 375°C-500°C in an O₂ environment (50% O₂/50% He) at a total flow of 50 ml/min. This procedure is carried out in a packed-bed mass flow reactor, the details of which will be explained in a later section. Removal of the residual C and Cl is confirmed by XPS. In order to conduct these XPS measurements, the treated sample is removed from the reactor and loaded in the UHV chamber. A small amount of powder (~30 mg) is deposited on a sample holder and pressed inside a pocket, making the
powder flat and compacting it to avoid contamination of the chamber due to the loss of powder particles. The transfer should be done as quickly as possible to avoid the deposition of adventitious carbon, water, significant changes in the oxidation state, etc., on the sample prior to characterization. This ensures that the measured sample is representative of that present inside the reactor system at the beginning of each experiment.

2.2 Atomic Force Microscopy

The use of optical microscopes, consisting of a series of lenses that magnify an image, is widespread in numerous areas of research. However, since the images obtained derive from visible light (wavelength≈390-750nm) reflected on the objective, the resolution of these devices cannot exceed this size range by a great degree. Therefore, the characterization of nanomaterials requires the use of other methods in order to obtain real-space images of different samples and materials. A number of devices that do not rely on visible light to image materials have been developed, including AFM, TEM, scanning electron microscopy (SEM), scanning tunneling microscopy (STM), among others.

In the case of AFM, this type of microscope makes use of short- and long-range interactions among materials. Short-range (< 1 nm) interactions include chemical forces (e.g., van der Waals) while long-range (up to 100 nm) interactions include electrostatic as well as magnetic forces. The respective magnitude of these forces will vary depending on a number of factors, including tip shape, distance to the sample, tip and sample composition, etc., thus making some forces dominant over the others. The relative magnitude of these forces as a
function of distance is illustrated in Figure 3. In general, an AFM consists of a cantilever, providing stability in the x-y plane while allowing for oscillation in the z-direction, and a sharp tip which interacts directly with the measured sample. Over the years, a number of AFM operation modes have been developed depending on the applications and type of samples to be measured. However, they all share the basic aspects of operation including a sharp tip (down to ~7-15 nm end radius), e.g. inverted pyramid, brought close enough to a sample as to interact based on one or more of the forces described above and a method for monitoring such interactions and creating a real-space image of the surface. For instance, contact mode operation involves scanning the sample with the tip positioned close enough to the surface as to generate a deflection in the cantilever corresponding to the sample morphology. Such deflection originates from the short range repulsion forces and its magnitude will depend upon the spring constant, k, of the cantilever as described by Hooke’s law. Contact AFM can also be operated in constant-deflection mode where a feedback system responds to surface corrugation as the cantilever moves up or down in order to maintain the same deflection at all times. Other modes of operation, such as dynamic AFM, involve the oscillation of the cantilever with a certain frequency and amplitude. These non-contact modes of operation allow the tip to scan the surface at a distance where long-range attractive forces are present. These forces will have an impact upon the amplitude and phase of the cantilever oscillation which can be correlated with surface characteristics.
Figure 3. Relative magnitude of short- and long-range forces as a function of distance [103].

Our AFM measurements were conducted under intermittent-contact or “tapping mode” using a Digital Instruments AFM. Tapping mode AFM is a form of dynamic AFM that is operated with oscillations that are close enough to the surface at the point where the tip will “feel” the shorter-range repulsive atomic forces. Changes in the cantilever oscillations in terms of amplitude or phase, which relate to changes in surface height, are measured by reflecting a laser on the top of the cantilever and collecting the reflected beam on a split photodiode. By measuring the difference in the intensity of the signal collected by the two halves of the photodiode, the cantilever angle and its deflection can be monitored at any point on the x-y plane, and information about the surface morphology can be extracted. For our studies, the dip-coated planar substrates [SiO₂/Si(001)] containing the monodispersed Pt NPs are measured using AFM in order to determine the particle height. The collected images can be analyzed in order to obtain the sample size distribution, i.e., average height and standard deviation.
The main advantage of AFM over other microscopic techniques is that it does not require vacuum environment for operation as it can operate in air and even liquid media. Also, it works over conducting and non-conducting samples. However, one limitation of AFM is that it cannot accurately determine the diameter of NPs due to artifacts related to the finite size of the AFM tip (~ 7-15 nm) which can be much larger than our NP size.

2.3 X-ray Photoelectron Spectroscopy

XPS is a powerful technique that allows for the characterization of samples with respect to composition, oxidation state, alloy formation, etc. The basis of this technique is the photoelectric effect. This phenomenon was first observed, although not fully understood at the time, by Heinrich Hertz in the late 19th century and expanded by J.J. Thompson and Albert Einstein near the turn of the century. It denotes the process by which an incoming photon excites an atom within a material causing the emission of an electron, as illustrated in Figure 4. This process will take place as long as the energy of the incoming photon is greater than the binding energy of the electron. If this is the case, the emitted electron, called the photoelectron, will possess a kinetic energy equal to the difference between the incoming photon and the initial binding energy of the excited electron, as such:

\[ E_k = h\nu - E_b - \varphi \quad (1) \]

where \( E_k \) denotes the kinetic energy of the photoelectron, \( h\nu \) is the energy of the incoming photon (described as the product of its frequency, \( \nu \), multiplied by Planck’s constant, \( h \)), \( E_b \) is the binding energy of the electron in its initial non-excited state, and \( \varphi \) is the work function of the spectrometer.
Figure 4. Illustration of the photoelectric effect [104].

In our instrument, the electrons are excited by using a monochromatic Al Kα X-ray source (1486.6 eV) and the kinetic energy of the photoelectrons is measured by a hemispherical analyzer which monitors the electrons emitted at each energy. The excited electrons travel in vacuum, passing through the entrance tube where they are retarded (and filtered based on their energy) to what is known as the pass energy, and into the analyzer where a series of electrostatic plates deflect the trajectory of the incoming electrons forming an arc that leads to the detector. The detector measures the electron counts (current) at each kinetic energy and amplifies the signal to a measurable current. This technique is conducted under UHV in order to ensure that the mean-free path of the incoming photons and extracted electrons is adequate by minimizing interference with gas molecules present in the region between the sample and the detector.

XPS measurements are usually plotted as intensity (a magnitude proportional to electron counts in arbitrary units) versus binding energy (BE). When scanning across the energy spectrum, each material, depending on its chemical state, has a particular set of peaks (even
though some peaks of one material will overlap with peaks from another) corresponding to the binding energies of electrons initially found at the different atomic orbitals. Thus, measuring the energy spectrum of a sample provides information about all the materials present in a sample. Information regarding the oxidation state of the sample is also contained in the spectrum as a shift to higher energies or the appearance of higher energy peaks. This shift is due to the electronegativity of the oxygen atoms which tend to make metallic atoms more positive. The removal of additional electrons from a positively charged atom is more difficult, thus increasing the binding energy of the remaining electrons. Similar behaviors may be observed due to alloy formation or interactions with the NP support, e.g., positive BE shifts when charge is transferred from the NPs to the support.

Since this technique relies on the removal of electrons from the sample, direct contact between the sample and its holder, which should be grounded, will prevent conducting materials from becoming positively charged (this refers to the overall net charge on the sample, not to charge transfer among atoms in the sample as described above). However, our samples consist of Pt NPs deposited on oxide supports with low conductivity, which make up 99% of the material being probed (only 1% Pt), thus dominating the properties of the samples during measurement with respect to conductivity. In order to compensate for the net loss of electrons and the resulting positive charging of the sample, a stream of low energy electrons is applied by using an electron flood gun. The electron energy and current (electrons emitted per unit of time) is established so that positive binding energy shifts are minimized and a clear signal, e.g. well-defined peaks, is obtained. In those cases where only small amounts of materials are present, the magnitude of certain peaks may be in the order of the measurement noise. Multiple high-resolution scans can
be conducted over a region where peaks are expected to appear in order to improve the signal-to-noise ratio and improve the quality of the data. The obtained data can then be analyzed by using the software CasaXPS which allows fitting the data obtained based on the known position of the XPS peaks.

XPS plays an important role in characterizing our samples as it allows us to ensure proper removal of residues associated with the NP synthesis process and thus optimize pretreatment and annealing conditions. As described above, the oxidation state of the sample can be estimated and different components, e.g. Pt, PtO, and PtO$_2$, can be identified. This analysis allows us to identify the species present at the initial stage of the reactivity experiments as well as the final composition. Furthermore, it may allow for the identification of poisoning species on the catalyst surface following deactivation.

2.4 Scanning Transmission Electron Microscopy

Another imaging method that presents an alternative to optical microscopes is TEM. This method is used as a complement to AFM as it allows us to acquire images on our Pt NPs after deposition on the nanocrystalline powder support (which is not possible by use of AFM). The basic process involved in TEM is relatively simple. It involves projecting a stream of electrons through a specimen which then get collected on a detector screen, while STEM is a mode of TEM that uses a focused beam of electrons so that the sample can be raster-scanned. More electrons get absorbed by the sample in the thicker or denser parts, while more electrons pass through the thinner or less dense regions. Thus, the transmitted atoms are focused and allowed to reach the detector. The real-space image formed in the detector will be darker in the areas that
transmit the least electrons (thicker/more dense), and brighter in the thinner/less dense regions. In the case of Pt NPs supported on oxide supports, the NPs possess a greater density than the support and thus appear as dark spots on the support, the crystallinity of which can sometimes be observed in the form of atomic rows.

The instrument was first developed by Max Knoll and Ernst Ruska in the early 1930s and was commercialized by the end of that decade. Even though some of the basic principles can also be applied to optical imaging (by shining light through an object as with a projector), the significantly shorter wavelength of electrons allows to obtain resolutions that are several orders of magnitude greater. As in the case of XPS, operation in vacuum increases the mean free path of electrons by minimizing interactions with air molecules and, in the case of TEM, prevents high-voltage arcing. The electron source usually involves a filament that is set up in such a way that a portion of the electrons will be emitted and directed through the instrument column and sample. Electron lenses are used along the way in a manner similar to those in an optical microscope to guide the path of the electrons from the source, through the sample, and to the detector as well as focusing the electron beam.

The images obtained can also be useful in conducting size analysis. First, the Pt particles should be identified. As mentioned above, they are recognizable as well-defined darker (more dense) areas that contrast with the support. The appropriate software can be used to determine the diameter of the particles and calculate the average particle size. The images also provide proof of successful deposition of the Pt NPs on the support and provide an estimate on the dispersion over its surface. Furthermore, the real-space images collected can be used to extract lattice parameters which can help understand alloy formation, NP-support interactions (e.g. strain
effects), etc. These measurements can be conducted before and after exposing the catalyst to the reactants in order to observe any changes that may have occurred in the process (e.g. C poisoning).

TEM images of our prepared samples used in this project were obtained by collaborators Prof. Helge Heinrich at the Advance Material Processing and Analysis Center (UCF) and Long Li and Prof. Judith C. Yang at the University of Pittsburgh. The particle size analysis was carried out in part by our group.

Another mode of operation used in electron microscopy, includes high angle annular dark field (HAADF) imaging. In general, dark field imaging is used in a variety of applications and can be carried out with an optical microscope. In this case, the microscope is arranged in such a way that the direct light from the source does not reach the objective lens but only a portion of the light scattered by the sample itself will become visible. This creates an image with a dark background and superior contrast as compared to a traditional optical microscope. HAADF imaging is based on the same principle but is carried out in a STEM setup. Thus, it is an electron beam (rather than light) that gets scattered by the sample and collected by the detector. If an annular detector is placed around the beam/sample (rather than in-line with it), only scattered electrons can be collected without detecting the main beam that passes through and around the sample. Thus, as is the case of optical dark field images, the background (where there are no scattered electrons) will be dark while the regions of the sample from which more electrons are scattered appear brighter. Collecting electrons scattered at high angles can aid in elemental analysis. This is due to the fact that the degree by which electrons are scattered from a material, particularly those at high angles, depends on the atomic number (Z) of this material. For this
reason, this technique is also known as Z-contrast imaging. In our studies, HAADF images allow
us to clearly identify the Pt NPs as bright spots (rather than dark areas as in the case of TEM)
over the oxide supports due to the fact that Pt has a higher Z number than our oxide supports.
The measurements were conducted by our collaborators and the particle size analysis was
primarily conducted by our group.

2.5 Packed-Bed Reactor/Quadrupole Mass Spectrometer

In order to measure the catalytic properties of our prepared samples our group has
designed, built, and improved over time a packed-bed continuous flow reactor, illustrated in
Figure 5. This instrument allows us to measure the rate of conversion of the reactants of our
choice under “real-world” conditions, i.e. atmospheric pressure and elevated temperatures. Mass
flow controllers (up to four) are used to introduce the desired gases into the system. In addition
to the desired gases, a controlled amount of alcohol vapor can be introduced to the system by
using a bubbler. The bubbler consists of an SS vessel containing the desired alcohol in liquid
state. A perforated pipe acts as a sparger and is introduced in the fluid in such a way that all the
perforations are covered by the liquid. A carrier gas, He in our case, flows through this pipe,
down into the liquid, and bubbles up becoming saturated. This stream of gas containing the
alcohol vapor is introduced into our system. The amount of vapor carried by the gas stream as it
leaves the bubbler (and entering our system), can be calculated based on the equation,

\[ F_v = \left( \frac{P_a}{P_h - P_a} \right) F_c \quad (2) \]
where, \( F_v \) represents the volumetric flow of the alcohol vapor being introduced in the systems, \( P_a \) represents the vapor pressure of the alcohol at equilibrium, \( P_h \) is the total pressure in the bubbler headspace (assumed to be 1 atm), and \( F_c \) is the volumetric flow of the carrier gas through the bubbler. Thus, controlling the flow and maintaining the temperature of the vessel relatively constant (room temperature) provides a steady flow that can be adjusted as desired by adjusting either of these two parameters, i.e. carrier gas flow rate or bubbler temperature. The gases and vapors flow through SS pipes that are kept slightly heated in order to avoid condensation of reactants or products on the walls and to keep water levels as low as possible within our system.

Figure 5. Illustration and photographs of the packed-bed continuous flow reactor and QMS

The reactor itself consists of a tube with an inner diameter of 7.4 mm. containing the powder sample supported by a quartz wool plug. The gases flow through the catalyst bed which is heated to the desired temperature during operation. A capillary tube collects a portion of the gases leaving the reactor in order to introduce it in our mass spectrometer. The QMS monitors the composition of the gases leaving the reactor tube and provides quantitative information about
the partial pressure of each component at any given point in time and temperature. Since the gases are continuously analyzed by the QMS, real-time information (in the order of 1-2 minutes) about the components exiting the system can be obtained. The capillary tube connecting the reactor outlet to the QMS, which should also remain heated, serves the purpose of collecting just a small sample of the total gas flow in order to provide the necessary pressure reduction for QMS operation (vacuum must be maintained inside the MS system at all times), while the remainder gas is directed to the exhaust. This setup is advantageous because it allows the integration of a precise measuring technique typically operated in vacuum (QMS) with a system operating under continuous flow at atmospheric pressure (packed-bed reactor).

Gases introduced in the QMS are ionized by electron bombardment, resulting in a stream of positively charged molecules. These ions travel through the quadrupole, i.e. a set of four circular metal rods positioned in parallel. Oscillations in the electric fields applied to the rods alter the trajectory of the ions to the point where they may become unstable and collide with the rods themselves. Only ions possessing a certain mass-to-charge ratio (m/z\(^1\)) will have stable trajectories and escape the quadrupole. These ions are captured by the detectors and their signal amplified to measurable levels. By varying the voltage applied to the rods, and thus the nature of the resulting electric field, ions possessing different m/z ratios are able to reach the detectors and be counted. The relative concentration of different ions, which is representative of partial pressures in the gas stream, can then be assessed using this method.

A number of considerations must be taken into account when analyzing QMS data, including sensitivity factors, fragments, and satellite peaks. First, it must be noted that different

---

1 Note that this charge value, z, should not be confused with atomic number, Z.
molecules possess different probabilities of being ionized when first introduced into the system. Thus, even in cases when two compounds are introduced in equal amounts, the compound with a greater probability of ionization will display a greater partial pressure. In order to compensate for this measurement artifact, sensitivity factors (SF) can be introduced. For this, N$_2$ is commonly used as a standard (SF=1) and it is introduced into the system with a known flow. At the same time, another compound can be introduced with the use of a mass flow controller (MFC) or a bubbler. If the signal (partial pressure) of the second compound is, for instance, half of what it is expected to be based on its flow rate compared to that of N$_2$, then a SF of 0.5 is assigned, indicating that this compound it twice less likely than N$_2$ to be ionized. This SF can be applied directly by calibrating the software or manually during data analysis. Either way, a SF of 0.5 indicates that the value obtained by the QMS must be multiplied by 2 (divided by 0.5) in order to obtain the appropriate value. SF for reactants and products must be carefully established for any system. The values used in our work were either taken from a standard library (MASsoft, Hiden Analytical Inc.) or specifically determined in separate experiments under our experimental conditions.

In addition, as molecules travel through the ionization chamber they can be altered in a number of ways, resulting in what are known as fragments. Several different fragments can originate from a single compound (more so for bigger molecules) having different m/z values and thus appearing at different positions in the spectrum. The fragments may originate from changes in z (charge), which are related to different degrees of ionization, or from changes in m, as the total mass of a molecule can change depending on how it breaks within the ionization chamber. The summation of all fragments of a compound should add up to the total number of
ions originally formed and they typically appear on a certain proportion, i.e., the fraction of each fragment with respect to the main ion is usually known. The presence of these fragments serves an important role in the identification of unknown compounds by QMS. On the other hand, mass overlap of reactants and product fragments can make mass spectral analysis difficult. However, each gas has a unique fragmentation pattern, and although some of the species studied here have common ion fragments, they also have unique fragments that make their distinction unequivocal. To address this point, a total of 16-22 different masses were monitored simultaneously during each experiment. The main fragments used to identify the reactants include m/z 31 for the methanol and ethanol experiments, and m/z 45 for 2-propanol and 2-butanol. A partial list of the products being monitored to establish selectivity (and the m/z values of some of their main fragments) includes H₂ (2), CO (28), CO₂ (44), H₂O (18), CH₄ (15, 16), acetaldehyde (29, 43), acetone (43, 58), propene (41, 39), butanone (43, 72), and butene (41, 56).

The appearance of satellite peaks is another phenomenon observed during MS measurements. These originate because every compound has a certain probability of possessing an isotope, which will have a higher mass than the most common isotope, e.g. carbon atom with a mass of 13 instead of 12, due to the presence of a greater number of neutrons in the nucleus. Thus, satellite peaks are those that appear usually at one or two m/z values higher than the main fragment of a compound. Bigger molecules, i.e. those that consist of a greater number of atoms, have a greater probability of displaying satellite peaks.

In order to operate the reactor all the lines are first flushed with He to get rid of any air or other gases present in the lines. All flows are established by using MFCs including that of the alcohol vapor. All levels are monitored with the QMS at the beginning of the experiment to
establish the background conditions before any reactions take place. This is done by flowing the gases through a bypass line that does not contain the catalyst sample. After all levels have become stable, the gases are switched to the reactor line (containing the catalyst bed) and any changes in the partial pressure of the reactants or products are assessed. Since the reactants first come into contact with the catalyst at relatively low temperature, no activity is expected to occur when the reactants are first exposed to the catalyst. Thus, the initial flow through the reactor pipe can also be used during the data analysis as the background conditions. The temperature is then increased to the desired value with the help of a temperature controller and a heating element surrounding the reactor tube. The temperature is increased step-wise and held constant at each value until the levels (gaseous partial pressures) of all the components being monitored by the QMS have stabilized. During annealing, only He and O₂ flow through the system and no monitoring of the effluent gases is required.

The main parameter used to measure catalytic activity is the conversion of reactants. This is done by calculating the decrease in the relative levels of reactant(s) at any given temperature with respect to the background levels. Normalizing by the initial conditions, we obtain the conversion as,

\[
\text{Conversion} \text{ (\%)} = \left( \frac{P_i - P_T}{P_i} \right) \times 100 \quad (3)
\]

where, \(P_i\) represents the initial (background) pressure of the reactant and \(P_T\) is the pressure of that reactant at some temperature, T. Also, by using the proper SF and establishing a constant flow for our carrier gas (He), partial pressures obtained by the QMS provide a direct measure of the volumetric (or molar) flow of each gas in the system. Thus, conversion can also be expressed, for instance, as a rate in units of mol/g·s (conversion rate normalized by catalyst mass).
2.6 X-ray Absorption Fine Structure Spectroscopy

XAFS spectroscopy measurements provide information regarding the physical and chemical state of a material based on a sample’s X-ray absorption spectrum. Depending on the region of the spectrum being considered, XAFS measurements can be classified as X-ray absorption near edge spectroscopy (XANES) for measurements at and near the edge, while extended X-ray absorption fine structure (EXAFS) involves the study of phenomena above the edge, as will be explained below. Since this technique requires the use of a strong (i.e., high flux) and well-defined (monochromatic) X-ray beam, measurements are typically carried out at synchrotron facilities. Data were collected by our group, alongside our collaborators at the National Synchrotron Light Source of the Brookhaven National Laboratory (BNL). The samples measured were prepared the same way as those used in the packed-bed reactor experiments except that the powder is compressed into a pellet.

The fundamental physical phenomenon occurring during XAFS measurements is similar to that of XPS, namely the photoelectric effect, yet both techniques provide different information about the sample. During XPS, the sample is irradiated with an X-ray at a fixed energy and the binding energy of the electrons of atoms present in a sample is obtained based on the kinetic energy of the emitted electrons. As mentioned before, composition and oxidation state information (but not structure) can be obtained from this technique. In the case of XAFS, the incoming X-ray is varied over a range of energy around the absorption edge of the material being studied. As the energy of the X-ray is increased to the point where it surpasses the binding energy threshold, a clear, sudden increase in the absorption is observed known as the absorption edge, as shown in Figure 6. Above this edge, photons that make up the X-ray have a greater
probability of being absorbed by the sample and generate the corresponding photoelectrons. A photoelectron being emitted can be thought of as a propagating wave carrying energy to its surrounding. If an isolated atom is considered, then the absorption probability of an X-ray moving through the sample increases sharply at the absorption edge as described above and decreases in a fairly linear fashion with increasing energy of the incoming beam. However, in reality, the propagating wave will encounter and interact with those atoms around the emitting atom. Thus, the emitted electron may backscatter from the neighboring atoms and return to the absorbing atom. The outgoing waves can interact with the backscattered ones in the form of constructive or destructive interference. Such conditions may increase (e.g. E₂ in Figure 6) or decrease (e.g. E₁ in Figure 6) the probability of a new incoming photon being absorbed as compared to that of being absorbed by an isolated atom. These fluctuations in the absorption probability are the origin of the “fine structure” observed in the above-edge absorption coefficient. They depend on the frequency (energy) of the propagating wave (which in turns depends on the energy of the incoming X-ray) as well as the amplitude and phase of the backscattered wave. The nature of this backscattered wave is dependant on the physical and chemical environment surrounding the central atom with respect to, among other factors, interatomic distance, coordination number, oxidation state, nature of neighboring atoms, degree of crystallinity/atomic disorder, particle-support interactions, etc. It must be noticed that the propagating/backscattered waves not only interact with the immediate neighboring atoms but also with those further away, either directly or by means of intermediate atoms. In our studies, EXAFS measurements were useful as they provided the basis for determining the structure of our supported NPs.
Figure 6. Typical X-ray absorption spectrum, in this case, for manganese. "A" represents the absorbing atom and "S" as the scattering atom [105].

XANES measurements are carried out under the same conditions as EXAFS, but the region of interest is limited to the range at or near the absorption edge. This means that the emitted photoelectrons will carry less energy than those affecting the higher regions of the spectrum. These lower-energy photoelectrons will have a longer wavelength (greater than the interatomic distance), which leads to phenomena dominated by multiple rather than single scattering. In general, the absorption of the X-ray requires the existence of an unoccupied state for the photoelectron to occupy upon excitation. Thus, XANES can be a useful tool in probing unoccupied states, for instance, in transition metals which possess a partially-filled d-band. The peak found at the absorption edge is known as the white line (WL) and a greater intensity is indicative of a greater number of empty states. In our measurements, the Pt-5d states are probed and an increase in WL intensity indicates a greater degree of oxidation. This phenomenon can be explained by oxygen’s ability to withdraw electrons from the metal atoms, thus enhancing the
density of unoccupied electronic states. By comparing the intensity of the WL in our samples to a known metallic standard, i.e. Pt foil, the degree of oxidation/reduction can be estimated.

The energy of the incoming X-ray is tuned by use of a monochromator consisting of two Si crystals placed in a certain angle with respect to the incoming beam, thus allowing only the fraction of the beam of a certain wavelength to go through while the rest of the beam is filtered out (see Figure 7 for a schematic of the XAFS measurement setup). Changing the angle of the Si crystals with respect to the incoming beam allows for different wavelengths to reach the sample, thus exposing the sample to an X-ray beam of narrow wavelength band and tunable energy. During measurements, the scan region of the desired element is selected and the monochromator crystals are positioned in such a way that an X-ray beam is produced at energies ranging from below to above the material’s absorption edge in small increments. In our case, the Pt L₃ edge was used, which is found at ~ 11562 eV. Below this absorption edge energy, the X-rays travel through the sample relatively unaltered. However, above this energy, the X-rays can be absorbed by the sample by means of the photoelectric effect. The extent of the X-ray absorption taking place can be measured using the transmission or fluorescence modes. Such measurements can also be carried out simultaneously with the proper arrangement as shown in Figure 7. Transmission mode measurements rely on the changes on intensity in the transmitted X-ray beam as a function of energy while fluorescence mode measures the photons being emitted during the atomic decay following the absorption process. Both of these modes are described in more detail below.
Figure 7. Schematic of XAFS measurement setup at a synchrotron facility for transmission and fluorescence modes (modified from Ref. [106]).

The beam intensity is measured by a detector consisting of a chamber in which gas molecules are ionized by the entering beam and subject to a voltage that directs them toward the chamber’s wall. The current generated by this process (ionized gas molecules flowing across a voltage difference) indicates the intensity of the beam. The detectors can be filled with different gases (including mixtures), e.g. He, N₂, Ar, depending on the energy range being measured as each gas will be ionized by the X-ray beam to a different degree. A total of three detectors are used during measurements, namely I₀, I₁, and I_ref. The first chamber, I₀, is positioned before the sample to measure the intensity of the initial beam. After the beam passes through the sample pellet, the intensity of the transmitted beam is measured by the chamber I₁. Finally, the remainder of the transmitted beam goes through a foil (thin sheet) of the material being measured (thus a Pt foil was used for our measurements). The foil presents the properties of the material in the bulk and serves as a reference for the edge position. The beam transmitted through the foil is measured at the third and last chamber, labeled I_ref. The degree of ionization in the gas within
each chamber, which correlates with the beam intensity, is measured at each of the positions described above in order to monitor the degree of absorption. In the transmission mode, the absorption coefficient, $\mu$, as a function of energy, $E$, can be calculated as:

$$\mu(E) = \ln \left( \frac{I_0}{I_t} \right)$$

where, $I_t$ is the intensity of the transmitted X-ray and $I_0$ is the intensity of the incoming beam before interacting with the sample. These values are measured by the ionization chambers of corresponding names. The key parameter that can be obtained from these measurements is thus the absorption coefficient, $\mu$. For measurements conducted under the fluorescence mode, an additional phenomenon that should be considered is the process by which an atom in the excited state (following the absorption of an X-ray and possessing a core hole) decays back to its ground state. This decay involves an electron dropping from a higher level to fill up the hole left by the emitted electron. This process results in some energy being released either in the form of an electron (Auger process) or in the form of a photon (Figure 8). Photons being emitted can be collected by a fluorescence detector and, since this photon emission is a secondary process, it provides information about the degree to which X-rays were absorbed in the first place, considering

$$\mu(E) \propto \frac{I_f}{I_0}$$

where $I_f$ denotes the intensity of fluorescence measured by the detector.
Figure 8. Illustration of the origin of fluorescence in the decay of the excited atom [104].
3.1 Experimental Details

Pt NPs supported on a crystalline ZrO$_2$ support were synthesized following the procedure described above (section 2.1) and with a Pt loading of 2% by weight. The Pt/ZrO$_2$ catalyst powder was then annealed in an oxygen environment (50% O$_2$, 50% He) in our packed-bed reactor at 500°C for a total of 8 hours. TEM images of our powder samples were acquired after annealing in O$_2$ as well as after exposure to reactants under the experimental conditions. For these measurements, the powder sample is deposited on a fine copper grid which is then placed in a removable arm to be introduced in vacuum. Additionally, chemical characterization of our Pt NP catalysts, including their oxidation state, was conducted by XPS before and after the exposure to different alcohols. Our Al K$_\alpha$ X-ray source was operated at an energy of 350W. A flood gun was used to compensate for sample charging and the Zr-3d$_{5/2}$ core level of ZrO$_2$ (182.6 eV) [107] was used as the binding energy reference. The Pt-4f core level region of our NPs was fitted with three different spin-orbit doublets (Pt-4f$_{7/2}$, -4f$_{5/2}$) corresponding to metallic Pt (Pt-4f$_{7/2}$ at ~71.7 eV), PtO (~73.0 eV), and PtO$_2$ (~75.3 eV). A Shirley background was subtracted from the raw data and slightly asymmetrical line shapes (asymmetry factor = 0.2) were used. Estimated errors of peak positions and spectral area are ± 0.2 eV and ± 3%.

The catalytic performance of our zirconia-supported Pt NPs in the decomposition of C1-C4 alcohols was evaluated in our packed-bed mass flow reactor. The reactor consists of a SS tube where 100 mg of the catalyst sample is placed and supported by quartz wool. The
temperature of the reactor tube is monitored by a K-type thermocouple placed in contact with the reactor wall. The total flow in each experiment was 50 ml/min (at standard conditions) resulting in an alcohol flow of 38 µmol/min. Changes in the partial pressures of the alcohols and their associated products were used to determine activity (alcohol conversion) and selectivity over temperatures ranging between 100°C and 300°C. Each reactant and product was monitored via mass spectrometry based on the m/z ratios of their ionized fragments.

Measurements taken at a catalyst temperature of 100°C were used as reference to ensure that vapors were not condensing within the reactor. In addition, reactivity experiments were also conducted on the Pt-free ZrO₂ support and on the blank SS reactor (containing only quartz wool) for each alcohol. The blank SS reactor tube was found to display low conversion below 300°C (<7-17 % for all alcohols), and such data have been subtracted from the reactivity of the Pt/ZrO₂ and ZrO₂ samples in Figure 14 and Figure 15. Each experiment was carried out two times in order to test the reproducibility of the reactivity results obtained, and the average values, along with error bars, are shown in the figures. The error was calculated as the difference between the minimum and maximum values obtained from the repeated experiments. The error margins shown in Figure 14(a) and (b) represent the error in the blank experiments plus the error in the Pt/ZrO₂ data and the Pt-free ZrO₂ data, respectively. In order to study the potential deactivation of our catalysts under reaction conditions, the reactor temperature was elevated up to 400°C and indications of deactivation (i.e. decreased activity) were monitored. Above 300°C, accurate quantitative estimations of catalyst performance become difficult due to the convolution of the catalytic activity of our samples with that associated with the SS reactor walls as well as gas-phase reactions. Therefore, our discussion related to the activity in the 300°C-400°C temperature
range is limited to a qualitative description of clearly discernable trends in catalytic activity. Long-term stability was determined by exposure to the alcohols under reaction conditions for a period of 17 hours as described in the stability section.

3.2 Results

3.2.1 Catalyst Characterization

3.2.1.1 Morphology (AFM, TEM)

The AFM image in Figure 9 reveals the narrow size distribution of our as-prepared Pt NPs when dip-coated on SiO$_2$/Si(001). This micrograph was acquired after polymer removal in UHV by O$_2$ plasma. The average NP height was found to be 2.1 ± 0.4 nm.

![Ex-situ AFM image of Pt NPs synthesized by encapsulation in PS(27700)-PV2P(4300) and dip-coated on SiO$_2$/Si(001). The polymer shell was removed by an O$_2$ plasma treatment for two hours at 4.5 x 10$^{-5}$ mbar O$_2$.](image)

Figure 9. Ex-situ AFM image of Pt NPs synthesized by encapsulation in PS(27700)-PV2P(4300) and dip-coated on SiO$_2$/Si(001). The polymer shell was removed by an O$_2$ plasma treatment for two hours at 4.5 x 10$^{-5}$ mbar O$_2$.

The TEM images shown in Figure 10 (overview) and Figure 11 (high resolution) show the as-prepared Pt NPs deposited on the ZrO$_2$ support after annealing in O$_2$ and before reaction.
with the different alcohols [Figure 10(a) and Figure 11(a)], and after reaction with methanol [Figure 10(b) and (c) and Figure 11(b)], ethanol [Figure 10(d) and Figure 11(c)], 2-propanol [Figure 10(e) and Figure 11(d)], and 2-butanol [Figure 10(f) and Figure 11(e)]. Our TEM images demonstrate a narrow particle size distribution over the zirconia surface before and after the different reactions.

Figure 10. Low magnification TEM images of the Pt/ZrO₂ catalysts: (a) as-prepared (only exposed to a pre-treatment in O₂ at 500°C for four hours) and after exposure to methanol (b,c), ethanol (d), 2-propanol (e), and 2-butanol (f), at 400°C for up to 10 hours.

Based on the high resolution TEM images (Figure 11), the average particle diameter in these samples is 4.8 ± 1.0 nm. The difference between the NP height obtained from AFM images and the diameter observed in the TEM images may result partly from morphological changes (NP coarsening) occurring upon annealing as well as from non-spherical cluster shapes. No significant change in the average NP size is observed when comparing samples before and after
Figure 11. High resolution TEM images of the Pt/ZrO$_2$ catalysts as-prepared (only exposed to a pre-treatment in O$_2$ at 500°C for four hours) (a) and after exposure to methanol (b), ethanol (c), 2-propanol (d) and 2-butanol (e), at 400°C for up to 10 hours. The arrows point to the presence of an amorphous layer, most likely C deposits, present on some sample after exposure to reactants (with the exception of methanol)
exposure to reactants at temperatures up to 400°C (Figure 11), indicating that coarsening is not taking place during the different reactions. However, an amorphous layer not present in the fresh sample [after O₂ annealing, Figure 11(a)], is observed by TEM in the catalyst sample exposed to ethanol, Figure 11(c), and to a certain extent also in those exposed to 2-propanol and 2-butanol [Figure 11(d) and (e), respectively]. This layer is believed to be the result of carbonaceous species deposited during C2-C4 alcohol decomposition, as will be shown in connection with XPS data.

3.2.1.2 Chemical Composition (XPS)

XPS measurements were used to determine the oxidation state of the as-prepared Pt nanocatalysts and to monitor possible changes in this state after reactions. Figure 12 displays fitted XPS spectra of the Pt-4f core level region of the Pt/ZrO₂ catalyst before and after reactions with alcohols (at temperatures up to 400°C) as given by the right-hand side labels. Vertical lines in Figure 12 denote the approximate position of the Pt-4f₇/₂ components of Pt⁰ in metallic Pt at 71.7 eV (solid line) [36], Pt²⁺ in PtO at 73.0 eV (dashed line) [44], and Pt⁴⁺ in PtO₂ at 75.3 eV (dotted line) [44]. A shift with respect to the position of bulk metallic platinum from ~ 71.1 eV to ~ 71.7 eV is observed for the metallic Pt component, which is consistent with previous observations by our group [36] and is attributed to particle size effects [108-111] and/or the formation of Pt-Zr, Pt-Zr-O alloys [112]. Catalyst exposure to all alcohols, and the associated sample heating up to 400°C, resulted in a strong reduction of Pt oxide species, although complete reduction was never observed. Table 1 shows the relative content of the different Pt species before and after alcohol exposure as determined by the area under the corresponding fitted doublets (Pt 4f₇/₂ and 4f₅/₂ core levels). It can be observed that Pt oxides make up over 50 % of
the total platinum species in the as-prepared sample (after annealing in O₂) and at least 10 % of those present after exposure to reactants.

Table 1. Pt, PtO and PtO₂ content (%) of our as-prepared Pt/ZrO₂ catalysts after annealing at 500°C in oxygen for 4 hours and subsequent exposure to methanol, ethanol, propanol and butanol obtained from the analysis of XPS data.

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Pt²⁺ B.E. (eV)</th>
<th>Pt⁰ (%)</th>
<th>PtO (%)</th>
<th>PtO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 hrs O₂</td>
<td>72.0</td>
<td>46</td>
<td>42</td>
<td>12</td>
</tr>
<tr>
<td>Methanol</td>
<td>71.7</td>
<td>86</td>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>71.4</td>
<td>89</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>71.5</td>
<td>90</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>71.7</td>
<td>85</td>
<td>9</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 12. XPS spectra of the Pt-4f core level region of a fresh Pt/ZrO₂ sample after a pre-treatment in oxygen at 500°C for 4 hours (as prepared sample), and analogously synthesized samples after subsequent exposure to methanol, ethanol, 2-propanol and 2-butanol at a maximum temperature of 400°C for up to ten hours. The reference lines indicate the binding energy of the 4f⁷/₂ core level of metallic Pt (solid line), PtO (dashed line), and PtO₂ (dotted line).
XPS measurements from the C-1s region conducted on the Pt/ZrO₂ catalyst and the Pt-free ZrO₂ support are displayed in Figure 13(a) and (b), respectively. The bottom spectra in these figures represent the fresh Pt/ZrO₂ and ZrO₂ samples and the remaining spectra correspond to measurements conducted after exposure to the different alcohols as indicated by the left-hand side labels. All spectra are plotted using the same scale but are displaced vertically for clarity. Only a very small C signal, associated with adventitious carbon, is observed in the fresh samples (labeled “as prepared”), indicating the removal of the encapsulating polymer from the Pt/ZrO₂ sample by the O₂ annealing pre-treatment [113]. Interestingly, after exposure to MeOH, the ZrO₂ and Pt/ZrO₂ samples remain carbon-free, while a large increase in the C-1s intensity is observed after ethanol, 2-propanol, and 2-butanol exposure. The C-1s spectra of all the samples were fitted using three different photoelectron peaks, Figure 13. The first peak at ~285 eV corresponds to the presence of carbon species predominantly containing bonds of the type C-C and C-H (e.g. hydrocarbons, C₅H₉) [114, 115]. The second peak at ~286 eV is assigned to the presence of oxygenated carbonaceous species (C-OH/C-OR) [115], and the third peak at ~289.8 eV is assigned to carboxyl and/or carbonate species over the catalyst surface [114-117]. The C signals detected in the Pt/ZrO₂ samples exposed to C2-C4 alcohols are in agreement with the amorphous thin layers observed in the TEM images of some of these samples, Figure 11, and they also correlate to the trends in activity and selectivity that will be discussed in the next sections. Based on a literature comparison, possible origins for the carbonaceous species detected by XPS are included in the discussion section.
Figure 13. XPS spectra of the C-1s core level region of (a) our nanoscale Pt/ZrO$_2$ catalysts and (b) the Pt-free ZrO$_2$ support, as-prepared (only exposed to a pre-treatment in O$_2$ at 500°C) and after exposure to methanol, ethanol, 2-propanol and 2-butanol.
3.2.2 Catalyst Performance

3.2.2.1 Activity

The conversion for each of the alcohols as a function of temperature is shown in Figure 14(a) for the Pt NPs supported on ZrO$_2$, and in Figure 14(b) for the Pt-free nanocrystalline ZrO$_2$ support, both after exposure to an identical thermal pre-treatment in oxygen. As expected, based on previous studies by our group on similarly prepared catalysts [35, 37], methanol was efficiently decomposed over the Pt/ZrO$_2$ catalyst, Figure 14(a). The onset of methanol conversion occurs at a temperature of about 175°C, and the activity was found to increase with temperature, reaching over 90% conversion at 300°C. Beyond that temperature, complete conversion and no deactivation for at least 10 hours (time frame of our reactivity experiment) were observed. Ethanol conversion over Pt/ZrO$_2$ was found to start at ~150°C, increasing with increasing temperature up to about 47% conversion at 300°C, Figure 14(a). Catalytic activity decreases sharply above 325°C (not shown). The reactants 2-propanol and 2-butanol displayed the lowest reaction onset temperature of ~125°C and were effectively decomposed throughout the entire temperature range showing similar trends in terms of conversion, Figure 14(a). After reaching maxima in activity at ~250°C, some catalyst deactivation takes place as demonstrated by a decrease in the conversion activity of both alcohols with increasing temperature up to 300°C. The conversion of the different alcohols over the Pt-free ZrO$_2$ support was relatively low (2-20%) as compared to the activity observed in the presence of Pt (47-92%).
Figure 14. Temperature-dependent alcohol decomposition data obtained in a packed-bed continuous flow reactor interfaced to a QMS. The data in (a) correspond to Pt NPs deposited on nanocrystalline ZrO$_2$ while (b) displays the reactivity of the Pt-free ZrO$_2$ support.

3.2.2.1 Selectivity

Catalyst selectivity was monitored with a particular interest in its ability to generate H$_2$ from C1-C4 alcohols. The dominant reaction pathways observed in the decomposition of each of
the alcohols studied are described below. Reactions (6-9) correspond to methanol decomposition, (10-14) to ethanol, (15-16) to 2-propanol, and (17-18) to 2-butanol decomposition.

Methanol decomposition and related reactions include:

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{CO} + 2\text{H}_2 \quad (6) \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 3\text{H}_2 \quad (7) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad (8) \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (9)
\end{align*}
\]

Ethanol decomposition and related reactions include:

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CO} + \text{CH}_4 + \text{H}_2 \quad (10) \\
\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{CH}_4 + 2\text{H}_2 \quad (11) \\
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2 \quad (12) \\
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad (13) \\
\text{C}_2\text{H}_4\text{O} & \rightarrow \text{CH}_4 + \text{CO} \quad (14)
\end{align*}
\]

2-propanol dehydrogenation and dehydration are described as:

\[
\begin{align*}
\text{C}_3\text{H}_7\text{OH} & \rightarrow \text{C}_3\text{H}_6\text{O} + \text{H}_2 \quad (15) \\
\text{C}_3\text{H}_7\text{OH} & \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} \quad (16)
\end{align*}
\]

2-butanol dehydrogenation and dehydration are described as:

\[
\begin{align*}
\text{C}_4\text{H}_9\text{OH} & \rightarrow \text{C}_4\text{H}_8\text{O} + \text{H}_2 \quad (17) \\
\text{C}_4\text{H}_9\text{OH} & \rightarrow \text{C}_4\text{H}_8 + \text{H}_2\text{O} \quad (18)
\end{align*}
\]
Figure 15. Rate of alcohol decomposition (dashed lines) and production of corresponding products over Pt NPs supported on nanocrystalline ZrO$_2$ (solid lines and closed symbols). The data in (a) correspond to methanol, (b) to ethanol, (c) to 2-propanol, and (d) to 2-butanol decomposition. The rates are normalized by the weight of Pt/ZrO$_2$ catalyst (in grams) present in each sample (~0.1 g).
Selectivity towards the different products was determined based on our mass spectrometry data. Figure 15 shows the rate of (a) methanol, (b) ethanol, (c) 2-propanol, and (d) 2-butanol conversion in units of $\mu$mol/s g catalyst (0.1 g Pt/ZrO$_2$) (dashed lines) together with the rate of production of H$_2$ and a variety of reaction by-products (methane, acetone, butanone, etc., solid symbols connected by solid lines).

In the case of methanol, Figure 15(a), the direct decomposition reaction described by eq. (2) was greatly favored, with H$_2$ and CO accounting for nearly 100% of the products generated up to 300°C. The conversion data for ethanol and the associated reaction by-products are shown in Figure 15(b) and may be explained in terms of the pathways suggested above. Ethanol decomposition shows significant H$_2$ production accompanied by the generation of CO, CH$_4$, as well as smaller amounts of CO$_2$, water, and acetaldehyde (C$_2$H$_4$O) for temperatures up to 300°C. This suggests that reaction (10) is dominant for this temperature range, while pathways (9), (11) and (12) may also occur to a lesser degree.

The selectivity of 2-propanol and 2-butanol decomposition are shown in Figure 15(c) and (d), respectively. For temperatures below 250°C high selectivity for H$_2$ production is observed. The reactions observed in this temperature range result in the generation of acetone (C$_3$H$_6$O) in the case of 2-propanol [reaction (15)], and butanone (C$_4$H$_8$O) for the decomposition of 2-butanol [reaction (17)]. However, the formation of water is observed above 250°C, indicating the onset of the dehydration reactions [reactions (16) and (18)] for both reactants.

3.2.2.3 Catalyst Deactivation and Stability

The peak in activity in the decomposition of 2-propanol and 2-butanol (T $\sim$ 250°C) and the drop in activity that follows is an indication of catalyst deactivation. In the case of ethanol, a
similar behavior was observed at $T > 325^\circ\text{C}$ (not shown). On the other hand, the catalytic activity for methanol decomposition remained steady after reaching a conversion $> 95\%$ for the remainder of the temperatures studied (from $T \sim 300^\circ\text{C}$ up to $400^\circ\text{C}$). Therefore, the temperature at which our Pt/ZrO$_2$ catalyst deactivated was found to be a function of the alcohol being decomposed, possibly related to the temperature at which C-C bond scission takes place, as well as the formation of specific reaction intermediates. In order to distinguish between temperature and time-on-stream effects, stability experiments were conducted where the catalysts were exposed to the reactants for $\sim 17$ hours at temperatures below which short-term deactivation was observed for each alcohol. The temperatures selected for these experiments were $225^\circ\text{C}$ for methanol, $250^\circ\text{C}$ for ethanol, and $200^\circ\text{C}$ for both 2-propanol and 2-butanol. The catalyst’s activity in the decomposition of all the alcohols remained constant throughout the duration of each experiment. In addition, selectivities were similar to those reported in the low temperature region ($<250^\circ\text{C}$) of Figure 15.

3.3 Discussion

As described in Figure 14(a), all the alcohols studied displayed some conversion over the Pt/ZrO$_2$ catalyst below $200^\circ\text{C}$. Within the $100^\circ\text{C}$-$200^\circ\text{C}$ range, 2-propanol followed by 2-butanol display the greatest conversion. At $225^\circ\text{C}$, over $70\%$ of the 2-propanol and 2-butanol introduced is being catalytically converted. Over the Pt-free ZrO$_2$ support [Figure 14(b)], 2-propanol and 2-butanol display higher conversion than methanol and ethanol over the entire temperature range, although at lower rates as compared to the activity over the platinum catalyst. This result may seem unexpected if we consider that it requires more energy to break the C-C bonds present in
the higher order alcohols. However, when we consider the products of these reactions in Figure 15(a-d) we observe that the conversion of all the alcohols is dominated by hydrogen production. This means that 2-propanol and 2-butanol may undergo dehydrogenation through reactions that do not require C-C bond scission. This assertion is supported by the predominance in the generation of acetone and butanone derived from the 2-propanol [equation (15)] and 2-butanol [equation (17)] reactions, respectively.

For methanol and ethanol the addition of Pt to the ZrO$_2$ support does little to improve the activity below 200°C. However, above this temperature ethanol shows a steady increase in conversion while methanol displays the greatest overall improvement in the range of 200-300°C. From this we can see that the Pt NPs play a significant role in the decomposition of these alcohols in this temperature range. Our conversion rates and onset temperatures for methanol decomposition are in agreement with previous literature reports [22, 32, 40-42, 44, 48]. Selectivity for H$_2$ and CO appears to depend on the choice of NP support, and other catalyst properties (e.g. composition, particle size) and such high selectivity as observed in our experiments has been shown to occur over Pt- and Pd-based catalysts supported on ZrO$_2$ and CeO$_2$ as well as activated carbon [22, 40, 42, 44, 48]. Supported Pt and Pd particles have been reported to display greater conversion in ethanol over a similar temperature range [54] or displaying slightly lower (~150°C) onset temperatures for this reaction [53]. Acetaldehyde has been reported to be the dominant product over Pt/CeZrO$_2$ [55] while ethene is mostly formed over Pt/Al$_2$O$_3$ [54]. These products can be formed without C-C bond scission, which is not the case for the products observed in our experiments. It must be noted that significantly greater
conversion rates have been observed over the catalysts mentioned above in the presence of oxygen or steam [52, 53, 55, 56, 58, 62, 63, 72].

After reaching > 90% conversion at T ~ 300°C, the rate of MeOH decomposition remains constant for the entire range of temperatures (up to 400°C), indicating that significant catalyst deactivation is not taking place. XPS data obtained after exposing the Pt/ZrO$_2$ catalyst to MeOH under reaction conditions up to 400°C indicate that no detectable amounts of carbon are present on the catalyst surface in excess of those observed before the reaction, Figure 13. This is interesting in light of the well known poisoning effects of CO on Pt and may be related to the nature of the strong particle-support interaction in this system and the possible formation of Pt-Zr and/or Pt-Zr-O alloys. Such strong Pt-ZrO$_2$ interaction has also been revealed by recent EXAFS data acquired by our group on this system showing lack of complete PtO$_x$ reduction of our ZrO$_2$-supported Pt NPs upon H$_2$ annealing at 375°C, while NPs of analogous size deposited on γ-Al$_2$O$_3$ were found to be completely reduced.

The conversion of ethanol also shows a steady increase in activity up to 300°C over the Pt/ZrO$_2$ catalyst, Figure 14(a). The detected products indicate that that C-C bond scission is taking place over the catalyst surface and that reaction (10) may compete with the formation and/or desorption of acetaldehyde (C$_2$H$_4$O) [equation (12)], keeping this latter pathway from becoming more prevalent as demonstrated by the smaller amounts of C$_2$H$_4$O being formed. CO and H$_2$ may react to form methane and water, and in turn, promote the water-gas shift (8) and ethanol steam reforming (11) reactions. The catalyst undergoes significant deactivation at temperatures greater than 325°C and similar behaviors have been reported following the poisoning of Pt/Al$_2$O$_3$ catalysts [54] and at T ~ 350°C over a CuO/Al$_2$O$_3$ [65].
TEM images taken before and after the reactivity experiments (Figure 10 and Figure 11) indicate that particle sintering is not taking place over the range of temperatures studied. Therefore, increased particle size is not a viable explanation for catalyst deactivation. However, an amorphous layer on the catalyst surface, visible in Figure 11(c), indicates the presence of contaminants that may block active sites. These deposits consist mainly of carbonaceous species generated during the decomposition of ethanol as indicated by our XPS measurements of Figure 13(a) and (b).

It should be noted that without the use of in-situ surface analysis techniques (e.g. FTIR or DRIFTS) that allow the determination of intermediate absorbed species, a quantitative mechanistic description of the reaction pathways or detailed catalysts deactivation phenomena cannot be established. Therefore, we have referenced well-established, related literature to discuss plausible explanations for our experimental observations. In order to understand the deactivation mechanism, the possible reactions taking place must be considered. Ethanol is believed to adsorb on the ZrO$_2$ surface either molecularly [54] or through dissociative adsorption forming ethoxy species [55]. Loss of hydrogen can lead to the formation of acetaldehyde or acetate species through interaction with the support’s oxygen. Interfacial sites in contact with the ZrO$_2$ support have been proposed as promoters of acetate demethanation and acetaldehyde decomposition [55], both of which may lead to the products observed by us in the case of ethanol decomposition [Figure 15(b)], namely methane, CO, and H$_2$. The accumulation of by-products and/or intermediate species, such as acetate and other oxygenated species, over the catalyst surface can be seen in Figure 13(a) and (b) represented by peaks located at ~ 286 eV and ~ 289.8 eV. The high energy peak at 289.8 eV has been associated with carboxyl moieties or other
carbonaceous deposits on the acid sites known as “acidic coke”, which would likely form over the ZrO₂ surface. It has been previously proposed that these adsorbed species hinder the migration of other intermediates over the metal oxide support and prevent them from reaching the catalytically active Pt-ZrO₂ interface [54, 118], resulting in their accumulation over the catalyst surface. This explanation satisfies both the deactivation observed over the Pt/ZrO₂ catalyst and the accumulation of oxygenated carbon species over both the Pt/ZrO₂ and the ZrO₂ support. The rate limiting step in this model (i.e. migration of molecules to interfacial sites) precedes the interaction of intermediate species with the Pt particles. Thus, the origin of CₓHᵧ species formed and stabilized in the presence of platinum [peak observed at ~285 eV, Figure 13(a)] could be attributed to species formed through the interaction of the ethanol molecules directly on the Pt surface. De Lima et al. [55] have recently proposed that the accumulation of oxygenated species over the support surface is not the cause but rather the result of catalyst deactivation caused by the accumulation of CHₓ species at the Pt-support interface. Contamination of these active sites reduces intermediate turnover and causes the build-up of these species over the catalyst surface. This mechanism explains the presence of oxygenated carbon deposits on both the ZrO₂ and the Pt/ZrO₂ catalyst, while the CₓHᵧ are mainly observed when Pt is present.

The conversion activities of 2-propanol and 2-butanol reach their maxima ~ 250°C. Rioux et al. [87, 88] studied 2-propanol dehydrogenation over C-supported Cu, Pt, and Cu-Pt nanoparticles with the intent of finding high selectivity and conversion comparable to currently used industrial catalysts, yet at lower metal loadings. Our Pt/ZrO₂ catalyst displays higher conversion than their Pt-based catalysts at similar metal loadings and particle size (~4 nm),
possibly due to the synergistic interaction between our particles and oxide support, while maintaining very high H$_2$ selectivity (>90%). The dehydrogenation of 2-butanol has also been investigated mostly over supported copper catalysts [75, 82, 84, 86], which display high selectivity toward H$_2$ and butanone but lower conversion rates than those observed over our Pt/ZrO$_2$ catalyst. The performance of the Cu/SiO$_2$ catalyst in the decomposition of 2-butanol displays structure dependence, as larger particles (> 8nm) show greater activity than smaller ones [86]. Such size- and structure-dependence in the performance of our Pt NP catalyst is the subject of the studies described in the next chapter for the oxidation of 2-propanol.

During our 2-propanol and 2-butanol experiments, some catalyst deactivation becomes evident at temperatures greater than 250°C. The deactivation is a function of increased temperature and not time-on-stream alone as demonstrated by our stability tests. Coke formation due to the deposition of carbonaceous species on the metal surface has been reported at temperatures similar to those where conversion is hindered in our study [75, 77], and is a possible source of catalyst deactivation at higher temperatures. Furthermore, XPS of the C-1s region indicate that both oxygenated carbon species and hydrocarbon species are present in the Pt/ZrO$_2$ after exposure to 2-propanol and 2-butanol, Figure 13(a); however the Pt-free support that has been exposed to the same reactants contains carbon deposits predominantly associated with the oxygenated species, Figure 13(b). 2-propanol has been shown to adsorb over the ZrO$_2$ surface in a similar fashion to that of ethanol (i.e. molecular and dissociative adsorption) and to further decompose over this surface leading to the reactions observed in our studies [119, 120], while the decomposition activity is enhanced in the presence of Pt [88, 120, 121]. A parallel could then be drawn between the deactivation mechanism during the ethanol experiments and
those involving higher order alcohols, where Pt-ZrO₂ interfacial sites become blocked by CₓHᵧ species, reducing intermediate turnover and leading to the accumulation of oxygenated carbon species over the catalyst surface. Our TEM images [Figure 11(d) and (e)] display some evidence of carbonaceous deposits over the catalyst surface after 2-propanol and 2-butanol exposure but to a lesser degree than those observed after ethanol exposure [Figure 11(c)]. These images also rule out the agglomeration (coalescence) of Pt particles as a deactivation mechanism, since the particle size remains constant after deactivation.

The decrease in activity observed at temperatures higher than 250°C for 2-propanol and 2-butanol coincides with the onset of water formation. Acidic sites on the ZrO₂ have been reported to enhance the dehydration reactions [74, 75, 83, 85, 88, 122-125], namely reaction (16) for 2-propanol and reaction (18) for 2-butanol. These reactions would result in the formation of water and the corresponding alkenes, i.e. propene and butene. Therefore, it is possible that as our Pt catalysts become poisoned by carbon deposits, some of the alcohol decomposition activity observed at higher temperatures (T>250°C) can be attributed to the nanocrystalline ZrO₂ support alone.

The potential use of these reactions may be studied according to the specific application being considered. The dehydrogenation of 2-propanol will occur at the lowest temperature over the Pt/ZrO₂ catalyst as compared to the other reactions, generating H₂ and acetone. This makes 2-propanol a viable candidate for energy applications, particularly in stationary sources as well as industrial settings where both acetone and hydrogen could be recovered and reused. 2-butanol displays similar properties, generating butanone. However, at approximately 300°C, methanol decomposition will generate more than twice the amount of hydrogen from the same amount of
reactant as any of the other alcohols studied here. Since this reaction generates almost exclusively carbon monoxide for this temperature range, the CO generated could be utilized as a reactant in the water-gas shift reaction, generating even more H₂ and CO₂. Oxidation and steam-reforming reactions involving the alcohols included in this study will most likely continue to grow in importance in the coming years due to their applicability in a wide range of industrial processes, e.g. chemical synthesis and emissions control/material recovery.
CHAPTER FOUR: 2-PROPANOL OXIDATION

4.1 Experimental Details

Pt NPs were synthesized using the inverse micelle encapsulation procedure described above. Two different polymers (containing different head lengths) and various metal-salt/polymer-head ratios were employed to synthesize particles of different sizes/shapes, the details of which can be found in Table 2. The polymeric solution was dip-coated prior to evaporation for the purpose of conducting AFM measurements. The powder samples (S1-S3) were prepared by impregnating the nanocrystalline $\gamma$-Al$_2$O$_3$ support with each of the different solutions, resulting in samples containing 1% Pt by weight (except sample S1 used for EXAFS measurements which contained 2% Pt). After drying, these samples were annealed in an O$_2$ environment (50% O$_2$ in He, except S3 which was annealed in 70% O$_2$) in our packed-bed reactor or in a system with a similar configuration. The annealing temperatures ranged from 375°C to 425°C for up to 24 hours to ensure that all synthesis residues (Cl and C) had been removed. This removal was monitored by conducting XPS measurements on the annealed powder samples. The Al-2s peak in $\gamma$-Al$_2$O$_3$ at 119.2 eV was used as a binding energy reference during analysis.

TEM-HAADF measurements were conducted on these samples by our collaborators at the University of Pittsburgh (Long Li, Prof. Judith Yang). The samples were prepared for TEM by adding ethanol to create a suspension of the catalyst powder and depositing it on a C grid, where it was allowed to air-dry. The size analysis was conducted on these images where the
Table 2. Description of synthesis parameters and size information of our micellar Pt NPs supported on nanocrystalline $\gamma$-Al$_2$O$_3$. The value “L” denotes the metal-salt/polymer-head ratio used during NP synthesis. The values in parenthesis represent the error margins in the average NP diameter.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Polymer</th>
<th>L</th>
<th>Annealing T (°C)</th>
<th>TEM diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>PS(27700)-P2VP(4300)</td>
<td>0.2</td>
<td>375 [50]</td>
<td>1.0 (0.2)</td>
</tr>
<tr>
<td>S2</td>
<td>PS(16000)-P2VP(3500)</td>
<td>0.05</td>
<td>375 [50]</td>
<td>1.0 (0.2)</td>
</tr>
<tr>
<td>S3</td>
<td>PS(16000)-P2VP(3500)</td>
<td>0.1</td>
<td>425 [70]</td>
<td>1.0 (0.2)</td>
</tr>
</tbody>
</table>

Diameter of each particle was measured. EXAFS measurements were conducted at BNL by pressing the powder samples into pellets by applying a pressure of 3 metric tons. These pellets were then loaded into a cell that allowed the transmission measurements as well as heating and cooling of the sample. The sample environment could also be controlled by introducing the desired gases into the cell, which were monitored via QMS. The Pt L$_3$ edge was measured at room temperature for the “as-prepared” (oxidized) samples and then for the reduced ones. Sample reduction was carried out in-situ by flowing 50% H$_2$ in He and heating the cell up to 375°C. XANES measurements (which provide a clear indication of the sample’s oxidation state) were conducted during this treatment to ensure that samples were fully reduced. EXAFS measurements were conducted on the samples while a Pt foil (presenting a bulk Pt spectrum) was measured simultaneously to use as a reference. Multiple scans were acquired and averaged to obtain a better signal-to-noise ratio.

The catalytic properties of our Pt/$\gamma$-Al$_2$O$_3$ samples were evaluated in our packed-bed reactor for the oxidation of 2-propanol, placing the catalyst sample inside a quartz tube where it
was held by a quartz wool plug. The heating source used during these experiments consists of a split furnace connected to a temperature controller. The gas flows were set to 20 ml/min of He through the bubbler containing 2-propanol (liquid), 20 ml/min of He through a direct line in order to dilute the stream, and 10 ml/min of O₂. Under these conditions (room temperature and atmospheric pressure), the 2-propanol content in the stream is approximately 2% while the 20% O₂ content approximates its content in air to represent reaction conditions using air as an oxidant. This O₂ content is well in excess of the stoichiometric requirements for complete oxidation of 2-propanol (and of course, more so for the partial oxidation). Conversion of 2-propanol under these conditions was measured in 10°C increments in the range of 40°C-100°C. The temperature was held constant at each value for approximately two hours to allow sufficient time for the levels of all the measured components to stabilize. A total of 16 different m/z values were simultaneously monitored over time by the QMS, including the main fragments of all the relevant reactants and products.

4.2 Results

4.2.1 Sample characterization

Sample characterization was carried out by using a variety of complementary techniques that provided in-depth information about our catalysts’ properties. The first step in the size analysis of our prepared NPs consisted of AFM measurements on a dip-coated SiO₂/Si(001) substrate. The measured particle height is 1.2 ± 0.5 nm for sample S1. However, due to the small particle sizes (~ 1 nm according to TEM) present in these samples, AFM measurements appeared
to be close to the limits of the instrument’s resolution. Therefore, reliable images, and the associated particle size distributions, could not be obtained for all samples based solely on AFM.

Following the deposition of Pt on the $\gamma$-Al$_2$O$_3$ support and the annealing treatment described above, XPS measurements were conducted on the samples. Figure 16(a) shows the XPS data from C-1s region before and after the O$_2$ annealing treatment. Significant amounts of C are present on the sample upon impregnation due to the polymeric shell surrounding the particles. After the annealing treatment, it is clear that the carbon has been effectively removed. The Cl region (sample S1) is also shown to demonstrate that our sample is clear of such residue [Figure 16 (b)]. The Pt-4d core level region is also depicted in Figure 16(c). The position of the peak suggests that the Pt present in our samples is oxidized, predominantly as PtO (Pt$^{2+}$). In general, a better resolution of the Pt species present could be obtained by measuring the Pt-4f core level region of the spectrum. However, this region overlaps with that of the Al-2p orbital peak present in the $\gamma$-Al$_2$O$_3$, thus making the Pt contribution virtually undetectable due to the fact that it is only 1% of the total content. All the XPS measurements shown were obtained from sample S1, but they are representative of the results obtained for all samples in terms of both removal of synthesis residues and oxidation state.
Figure 16. XPS spectra from the (a) C-1s, (b) Cl-2p, and (c) Pt-4d core level regions of micellar Pt NPs supported on γ-Al₂O₃ (S1) acquired before (open circles) and after (solid lines) polymer removal by annealing in O₂ at 375°C. No residual C or Cl was observed on this sample after annealing. PtO species are present after the treatment in O₂. The reference lines in (c) correspond to the Pt-4d₅/₂ level of metallic Pt, PtO (Pt²⁺) and PtO₂ (Pt⁴⁺).

Figure 17 shows HAADF-STEM images of the Pt NPs deposited on nanocrystalline γ-Al₂O₃ (after annealing treatment in O₂) obtained by our collaborators (Long Li, Prof. Judith Yang, Pittsburgh University) as well as the particle size distribution (diameter) for each of the samples. The images show Pt as brighter, relatively round spots over the γ-Al₂O₃ support. Even though these NPs do not display any arrangement over the powder supports, good dispersion is observed. The accompanying histograms give clear evidence that the narrow size distribution is maintained through the deposition and annealing processes for all samples as there is no evidence of particle sintering (usually recognizable by a broadening of the particle size distribution). Furthermore, it can be seen that all samples display very similar sizes among them (virtually undistinguishable within the error). It is important to consider the fact that the HAADF-STEM measurements and analysis only provide information regarding the particle diameter, not its height or shape. Therefore, although all samples appear to be uniform in terms of size based solely on diameter, other morphological parameters may play a role with respect to some other properties, including catalytic activity, as will be described below.

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Figure 17. HAADF-STEM images of micellar Pt NPs on γ-Al2O3: (a) S1, (b) S2, (c) S3. The images were taken after polymer removal by annealing in O2 at 375ºC-425ºC. Histograms of the NP diameter distributions are shown next to the corresponding image.
The data derived from the EXAFS measurements on the reduced samples, along with that of the Pt foil, are shown in Figure 18(a), as analyzed using the software Athena and Artemis [126, 127]. The k-space data are obtained after subtracting a smooth background representative of an isolated atom spectrum. Plotting the \( k^2 \)-weighted data improves the visibility of high-energy (high-k) features that would otherwise become difficult to observe. Decrease in the amplitude of the EXAFS oscillations as compared to the bulk (more clearly visible for sample S2) is caused by decreased particle size and/or increased atomic disorder (less crystallinity) possibly related to strain effects for Pt atoms in contact with the \( \gamma \)-Al\(_2\)O\(_3\) support. Applying a Fourier transform to the k-space data in the 2-16 Å\(^{-1}\) range results in the r-space plot shown in Figure 18(b). In this case, the peak observed at approximately 2.6 Å represents the average distance between a Pt atom in the sample and its nearest Pt neighbor while the peak appearing at

![Figure 18. \( k^2 \)-weighted EXAFS data in k-space (a) and r-space (b) for all reduced samples in H\(_2\) at room temperature. The inset in (b) shows data from the as-prepared samples measured in He at RT. Fourier transform was applied in the k-range from 2 to 16 Å\(^{-1}\).](image-url)
approximately 1.6 Å in the “as prepared” samples [shown in the inset of Figure 18(b)] indicates the length of the Pt-O bonds. It can be observed that this latter peak does not appear on the reference foil spectrum (metallic Pt) nor in any of the H₂-reduced samples.

The relative intensity of these peaks is related to the amount of Pt-Pt and Pt-O bonds in our samples. The lower intensity of the Pt-Pt peak, in the reduced samples, compared to the bulk is partially attributed to a particle size effect, although the shape of the NPs can also affect the measured intensity. From a multiple scattering analysis of the data in Figure 18(b) the coordination numbers (up to the 4th nearest neighbor) of each sample were extracted [128]. In all cases, such numbers were also smaller than those corresponding to bulk Pt. Furthermore, Ref. [128] also describes a procedure established by our research group that allows for the most likely NP shapes present in our samples to be estimated based on the EXAFS and TEM data. To achieve this, a large database of possible particle geometries (> 3000 different shapes) was generated and the resulting model shapes were compared to experimentally obtained values from EXAFS (coordination numbers) and TEM (NP diameter). The shapes displaying the best agreement between model and experimental values for each of the studied samples are displayed in Figure 19 along with the conversion data described below.

4.2.2 Catalytic Activity

Figure 19 shows the results from the packed-bed reactor experiments. Each curve represents the conversion of 2-propanol during oxidation reactions with regards to temperature for all samples studied following a short H₂ anneal preceding the experiment. In some cases, the conversion would increase upon heating to a new temperature but stabilize at some lower conversion level. Thus, Figure 19 contains two curves for each sample: one describing the
maximum conversion obtained at each temperature (dashed lines) and one for the conversion observed after all levels (partial pressures of species monitored by QMS) become stable (solid lines). For some samples, particularly around the reaction onset temperature, the conversion is seen to increase to above 80% after heating and then decrease to the point where no conversion is detected at the same temperature. This peak in activity followed by its decrease and stabilization usually occurs within a two-hour timeframe.

For all samples, the activity seems to increase rather suddenly from one temperature to the next (over a 10°C interval), and continue to increase with temperature until reaching a maximum at ~ 90°C. Since the maximum conversion is similar for all samples, the most critical parameter indicating catalyst performance seems to be the reaction onset temperature, considered hereon as the temperature following the greatest increase in conversion. As such, S2 would be considered to have the best performance as it displays the lowest onset temperature (~ 50°C). This is followed by S3, and finally S1. Whether the maximum or the more stable, long-term conversion is considered, the same trends were observed. However, further discussion will be based on the more stable conversion values as they seem to be representative of steady state, rather than transient conditions within our system.
Figure 19. 2-propanol conversion over Pt NPs on γ-Al₂O₃ with respect to temperature: Steady state conversion (solid lines) and at maximum conversion (dotted lines) at each temperature, following H₂ pretreatment. Also, the model of the NP shapes that resulted in the best agreement with the coordination numbers obtained from the fits to the EXAFS data [128] are shown next to the corresponding curve.

All the samples and conditions studied led to the formation of acetone, CO₂, and water. Such products are expected to derive from partial and complete oxidation of 2-propanol as such,

\[
C_3H_7OH + \frac{1}{2} O_2 \rightarrow C_3H_6O + H_2O \quad (19)
\]
\[
C_3H_7OH + \frac{9}{2} O_2 \rightarrow 3CO_2 + 4H_2O \quad (20).
\]
Both of these reactions appear to be taking place simultaneously in our reactor and further analysis is needed to get insight into possible correlations between the NP shape and their selectivity. No other byproducts were detected during the reactivity studies.

Further analysis of the most likely NP shapes present in our samples allows for the estimation of the number of atoms present at the surface (with low coordination) as compared to those completely surrounded (fully coordinated atoms which are termed “bulk-like” for the purpose of this study) or to the total number of atoms in a given NP. A bulk atom has 12 bonds in an fcc arrangement, while this number decreases for those atoms at the surface and corners of our NPs. Thus, another parameter that can be extracted from the NP shape model is the number of missing bonds in a particle as compared to the number of surface atoms. Calculations were carried out by group member Farzad Behafarid to estimate the following two ratios: the number of surface atoms/total atoms within a NP, and the number of missing bonds at the surface/surface atoms. Figure 20(a) shows the reaction onset temperature for each of the catalyst samples studied as a function of surface atoms/total atoms, while Figure 20(b) shows the onset temperature as a function of missing bonds (surface)/surface atoms. The latter shows a nearly linear correlation, indicating that a greater number of missing bonds may have a positive impact upon a material’s catalytic performance (onset reaction temperature, in this case). This is not surprising considering that uncoordinated atoms are regarded to be among the most active sites in NP catalysts.
4.3 Discussion

Detailed sample characterization involving materials in the ~ 1 nm range remains a challenging task. This size range appears to be at the resolution limit of various measurement techniques, including some of those used in this study, e.g., AFM. However, the use of multiple complimentary techniques can provide sufficient information with regards to a sample’s morphology and chemistry to investigate how certain properties may affect its performance as a catalyst. For instance, XPS measurements are useful in ensuring that all the possible synthesis residues have been removed. This is important as the presence of either C or Cl on the catalyst may have a detrimental effect upon its performance [35]. The annealing treatment used here appears to be effective in achieving this goal without causing particle sintering as demonstrated.
by the narrow size distribution in the $\gamma$-Al$_2$O$_3$-supported and annealed samples seen in HAADF microscopy images. Treatments conducted at higher temperatures would result in particle sintering and thus an increase in particle size and loss of surface. This may lead to lower catalytic activity as a result of decreasing the number of potentially active surface sites. The degree of particle mobility will depend on a series of factors including particle composition, size, support, environment, etc. Therefore, it is important to optimize treatment conditions for a particular system to ensure the removal of undesired species while preventing particle agglomeration.

The samples studied here were all prepared using the same method and subject to very similar pretreatment conditions. Furthermore, their characterization in terms of composition (XPS) and particle diameter (HAADF) showed virtually no differences among them. However, it is clear from the reactivity experiments that distinct catalytic properties are displayed by the different samples. Different polymers and metal-salt/polymer-head ratios were used during the particle synthesis which may have an impact upon the final sample characteristics. As mentioned above, HAADF measurements are limited with respect to evaluating particle shape or height. According to our EXAFS data combined with TEM and modeling results (as will be further explained), it is precisely this parameter which seems to vary among the samples studied here giving rise to the results obtained. Different metal loadings may have an impact upon the NP shape formed either inside the micelle or after deposition/annealing. Lower loadings and the use of a polymer with smaller polar head molecular weight, such as those used for samples S2 and S3, may result in smaller number of Pt atoms enclosed within the micellar nanocage. The presence of fewer atoms forming these clusters in a similar-sized area (same TEM diameter) may be indicative of a different structure, namely, of flatter particle shapes. On the other hand, sample
S1 was prepared using a polymer with a larger polar head (higher molecular weight), thus potentially developing different particle geometries (e.g., more 3D/round shapes).

The EXAFS results display a similar phenomenon where seemingly same-sized particles display differences in the coordination numbers, oxide content, etc. Once again, different particle shapes could explain these observations. While the bulk Pt displays a first neighbor coordination number, N1, of approximately 12 (meaning each Pt atom has 12 surrounding atoms as expected in an fcc arrangement), our NPs have lower values for N1, i.e., 9.1±0.5 for S1, 7.3±0.5 for S2, and 8.7±0.6 for S3 [128]. This is due the presence of a much greater number of atoms at the surface as compared to the bulk material. Thus, when considering the number of neighbors that each atom in the particle will have, the average coordination number is expected to drop considerably with decreasing particle size. Furthermore, for any given particle size, the maximum N will be obtained by a particle that is as spherical as possible. However, if a particle displays the same diameter but is flatter, N will be lower due to an increased number of atoms at the surface and the resulting decrease in the average number of nearest neighbors. A minimum N value would be obtained for a single-layer “disk” of atoms of a certain diameter. In this case, all the atoms in the particle would be at the surface and will only have in-plane neighboring atoms.

As mentioned above, a decrease in the coordination number would result in a lower intensity of the Pt-Pt peak in the r-space plot [Figure 18(b)]. A greater decrease in the number of Pt-Pt bonds with respect to the bulk correlates with the lower metal loadings used during particle synthesis for sample S2 and, to a lesser degree, S3. This illustrates an example of same-diameter particles (all ~ 1 nm) displaying different structures, e.g., flatter particles in S2 as demonstrated by the model NP shapes shown in Figure 19. The differences in the catalytic performance can
then be attributed to the structure effect and the increased number of surface (uncoordinated) atoms which constitute active sites during reactions.

Furthermore, flatter geometries result not only in an increased number of atoms at the surface but a relatively greater contact area with the support. This may be the origin of the greater degree of oxidation [illustrated by a greater Pt-O peak intensity in the inset of Figure 18(b)] observed for sample S2 due to a more intimate contact with the oxide support. Since the support itself might also be involved in the catalytic reaction (by means of charge transfer to the NPs or by providing additional active sites for the adsorption of reactants), the larger NP/support contact area might be beneficial for the catalytic reaction. In addition, the decrease in the amplitude of the k-space curve may be indicative of a smaller particle size and/or a greater degree of atomic disorder. The former would correspond with the above discussion, and the latter may be caused by strain created due to the mismatch between the lattice in the Pt NPs and the metal oxide support (the flatter particles may be particularly affected by this phenomenon due to enhanced support interactions). Such strain at the NP/support interface might induce shifts in the electronic d-band that have also been reported to enhance chemical reactivity. Thus, an increasingly greater number of uncoordinated atoms (lowering of the Pt-Pt peak intensity) and enhanced support interactions may play a role in the trend we observe for catalytic activity, where S2 shows the lowest onset temperature for 2-propanol oxidation.

Another important observation that can be derived from these data when comparing the “as prepared” samples to those in the reduced states is that there is not only a decrease in the Pt-O peak intensity but also an increase in the Pt-Pt bonds. These results point to the presence of an oxidized shell (i.e. mostly Pt-O) in our particles surrounding a metallic core of predominantly Pt-
Pt bonds. Upon reduction, the number of Pt-Pt bonds increases (while Pt-O bonds are eliminated) indicating that the oxidized shell has been removed and metallic Pt particles are formed. An increase in the particle size would also cause an increase in the number of Pt-Pt bonds in our particles, however this can be ruled out since the particle size remains unchanged through the process according to our TEM data. Nevertheless, despite the oxide shell, our “as-prepared” NPs display very good atomic ordering, as can be inferred from the resemblance of the 4-6 Å r-space EXAFS region to the bulk Pt reference sample.

The time-on-stream effects observed, i.e., increase in activity above the steady state conversion followed by stabilization at lower level, are not believed to be caused by catalyst poisoning, such as that caused by the deposition of carbonaceous species. If this were the case, irreversible loss in activity would be observed unless the catalyst was subject to a regeneration process, e.g. increased temperature in O₂ or H₂O flow. Instead, in our example, a similar overshoot in activity after increasing the temperature by only 10°C is observed to take place at each new temperature, indicating that the catalyst is still active. In addition, C deposition tends to be more prominent at higher temperatures as was shown in the previous chapter of this report. Therefore, if this mechanism (C poisoning) were responsible for the time-dependent decrease in activity, this effect would be more prominent at higher temperatures. This is not the case as it can be observed that the activity at the higher temperatures, e.g. 80°C-100°C, is less affected by this phenomenon even when exposed to reactants for longer periods, e.g. 6 hours. Furthermore, if the Pt catalyst was deactivated due to carbon poisoning, a change in the product distribution would be expected where those reactions potentially taking place over the γ-Al₂O₃ support, i.e. 2-propanol dehydration to propene and water, would become dominant [129, 130]. However, the
formation of propene is never observed under our reaction conditions. One possible explanation for this transient increase in activity is that as the temperature increases, so does the rate of conversion. However, greater conversion also increases the generation of water as a product of the 2-propanol oxidation reactions. This increase in the water formation may lead to its deposition over the catalyst surface, which has been shown to negatively affect catalytic activity due to the blocking of active sites [131]. While the reaction rate may present a fast response with respect to an increase in temperature, the water deposition over the surface may take place more slowly over time. Once equilibrium is reached between the water in the gas phase and that absorbed on the catalyst surface, the conversion rate reaches steady state conditions at a lower conversion than originally achieved. Another possibility is that the decrease in activity can be caused by the depletion of relevant species over the catalyst surface. For instance, the presence of oxygen and OH species over the metal catalyst have been shown to enhance 2-propanol conversion [89, 129]. However, the coverage of these species over the Pt surface may be reduced with increasing temperature. Thus, upon reaching a new temperature, those adsorbed species could play a role in enhancing the short term reactivity but become depleted over time. As equilibrium is reached at a lower surface coverage, the conversion becomes stabilized at a diminished rate.

The information extracted from Figure 20 is useful in understanding the different types of sites that may exist in a NP catalyst and the role they play in a chemical reaction. If the geometry of a nanocatalyst is known, the number of atoms at the surface and at corners as well as degree of faceting can be estimated. Thus, if clear trends emerge with respect to the presence of a particular site or arrangement, then valuable information with respect to structure sensitivity of a
reaction can be derived. In our case, two different approaches were taken in order to try to understand catalytic performance as it relates to NP structure. The first approach, shown in Figure 20(a), evaluates the reaction onset temperature as a function of the surface atoms/total atoms. In general, it could be expected that an increasing number of atoms in the bulk (at the expense of those at the surface) would decrease the activity observed over a catalyst. Such a decrease in performance corresponds to the increase in temperature required for significant reactant conversion to be observed. S2 shows the lowest onset temperature, but a trend is not clear when considering the fraction of surface atoms. On the other hand, an increase in the number of missing bonds does seem to correspond to a decrease in the onset temperature, indicating better catalytic performance. This trend can be explained by the fact that a greater number of missing bonds is indicative of the presence of more uncoordinated atoms, which are considered the most active sites for nanocatalysts. Thus, the number of missing bonds may be a better parameter when considering the effect of NP structure upon catalyst performance. This may derive from the fact that when considering the total number of surface atoms, no distinction is made between different types of surface sites (e.g. corners, steps, different facets, etc). On the other hand, in the assessment of missing bonds, corner atoms, for instance, would have a greater number of missing bonds (lower coordination) than a step, and the latter would have more missing bonds than a crystalline plane.

As mentioned above, the oxidation of 2-propanol over the Pt/γ-Al₂O₃ catalyst under our experimental conditions leads to the formation of both acetone and CO₂, along with water, indicating that both partial and complete oxidation may take place. These reactions are believed to take place sequentially rather than in parallel [89, 129]. Burgos et al. [129] reported similar
results over a Pt/γ-Al2O3 catalyst, particularly for the low temperature range used in our experiments, while the selectivity became dominated by CO2 formation above ~ 250°C. By studying this reaction under both continuous flow conditions and temperature programmed surface oxidation (TPSO) they concluded that acetone was an intermediate in the complete oxidation of 2-propanol. The reaction mechanism being proposed involves the adsorption of 2-propanol over the γ-Al2O3 surface due to this substrate’s acidic nature which has been reported to enhance the activation of organic compounds in oxidation reactions [132-134]. The adsorbed 2-propanol molecule may then interact with oxygen atoms chemisorbed on the Pt clusters following dissociative adsorption. This leads to the formation of acetone and water via oxidative dehydrogenation of 2-propanol. Further oxidation of acetone, involving C-C bond cleavage, leads to CO2 formation. However, this latter step (involving the complete oxidation of a ketone) is, in general, considered to be less favorable as compared, for instance, to alcohol oxidation over metal catalysts [135]. The notion that Pt is primarily responsible for providing sites for O2 dissociation rather than 2-propanol adsorption is consistent with studies indicating that O2 binds 200 more strongly than 2-propanol to Pt surfaces [136].

The fact that complete oxidation to CO2 is thermodynamically favorable does not seem to govern the selectivity observed under these conditions. Rather, it seems that the relative amounts of the different products are determined by the reaction kinetics [137]. Studies show that various factors may have an impact upon reaction rates and selectivities, including partial pressure of reactants, nature and state of catalyst, and contact time, among others [89, 136, 137]. Therefore, selection of the proper reaction conditions may improve selectivity for desired products, as well as improving reaction rates and minimizing catalyst poisoning [89, 137].
CHAPTER FIVE: CONCLUSIONS

Advances in the field of nanotechnology have brought about significant improvements in the way materials are synthesized, characterized, and used in numerous applications. This is particularly true as it relates to the field of catalysis. As processes occurring at the molecular level, chemical reactions may be affected by phenomena that can be easily ignored when considering macroscopic systems. However, in depth understanding of those processes occurring at spatial and time scales much smaller than those of most events we normally experience are critical in solving some of the most pressing issues of our time. Alternative sources of energy, improved pollution control and remediation processes, optimization of chemical synthesis processes, and decrease in energy consumption are only a few of the many areas upon which improved catalytic performance may have a significant positive impact. Therefore, it is imperative that efforts are extended to understand the fundamental mechanisms that dominate catalytic processes in order to maximize their performance without loosing focus on the ultimate goals of using this knowledge in real-world applications.

Our sample synthesis process (inverse micelle encapsulation) is ideal for producing model systems for catalysis studies composed of highly dispersed metallic NPs with very narrow size distributions in the range of ~ 1-15 nm. This is critical in improving our understanding of the properties that control the performance of different systems, particularly those in the nanoscale, whose properties may be greatly affected by small size differences. Our micellar encapsulation process can be applied to different metals, and even the synthesis of bimetallic particles [36]. Furthermore, the metal-loaded solution can be applied to virtually any support, allowing us to study a variety of metal/oxide support systems [37].

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The utilization of multiple techniques for the characterization of materials in the nanoscale is a requirement since it is difficult to obtain a deep understanding of these complex systems based on only one technique. It has been shown that powerful tools are available that enable us to gain understanding about our nanocatalyst’s size, including AFM, TEM, and HAADF-TEM. Even though there are still limitations associated with each of these techniques, their capacity and accuracy continue to improve. Spectroscopic techniques such as XPS and XAFS can provide information about a sample’s composition and oxidation state, as well as NP structure. Thus, combining the information collected from these various techniques provides information about a number of properties that may affect a sample’s performance as a catalyst. Furthermore, evaluation of the studied systems following reaction experiments allows us to assess the impact that reaction conditions may have upon the catalyst. This provides relevant information with regard to very practical concerns in the application of catalysts, including catalyst deactivation due to poisoning or sintering. In addition, our packed-bed reactor is a useful tool in evaluating some of the most important properties dictating the real-world applicability of a catalyst system, including its activity, selectivity, and stability.

After conducting a systematic study of the decomposition of C1-C4 alcohols over Pt/ZrO2 nanocatalyst in the temperature range of 100°C-400°C, the main results derived from the analysis of our data include: (i) the onset temperature for alcohol decomposition (and H₂ generation) increases from propanol ≤ butanol < methanol ≤ ethanol, ranging from 125°C to 200°C; (ii) the maximum alcohol conversion was found to increase from ethanol < 2-butanol ≤ 2-propanol < methanol, ranging from ~ 47% to 100% in a temperature range of 100-300°C; (iii) the maximum H₂ production rates followed the same trend as the conversion rates, with a
maximum of \(\sim 12 \, \mu\text{mol}(\text{H}_2)/\text{s} \cdot \text{g catalyst}\) during methanol decomposition, down to \(\sim 3 \, \mu\text{mol}(\text{H}_2)/\text{s} \cdot \text{g catalyst}\) for the ethanol reaction.

High selectivity toward hydrogen production was observed for all the alcohols being decomposed over the Pt/ZrO\(_2\) catalyst. With the exception of methanol, all the studied alcohols caused the catalyst to become deactivated at high temperatures (T \(>325^\circ\text{C}\) for ethanol and T \(>250^\circ\text{C}\) for 2-propanol and 2-butanol) due to the deposition of carbonaceous species over the Pt particles and their ZrO\(_2\) support. The onset of dehydration reactions, possibly over the ZrO\(_2\) support, was observed following indications of catalyst deactivation during 2-propanol and 2-butanol reactions. Optimum temperatures with the highest alcohol-to-H\(_2\) conversions are 300°C for methanol and ethanol, and 250°C for 2-propanol and 2-butanol. Under these conditions, the Pt/ZrO\(_2\) catalyst is expected to perform well for an extended period of time. It should also be noted that the oxidized Pt species originally present in the as-prepared samples were found to become significantly reduced in the course of the decomposition reactions of the different alcohols.

On the other hand, the oxidation of 2-propanol has been studied over three similarly synthesized catalysts (Pt/\(\gamma\)-Al\(_2\)O\(_3\)) consisting of NP having \(\sim 1\, \text{nm}\) diameter. In general, this catalyst holds potential for oxidation reactions as demonstrated by the high conversions observed at relatively low temperatures (50°C-100°C). Within this temperature range all the samples displayed conversions of up to \(\sim 90\%\), and the formation of acetone, CO\(_2\), and water. This indicates that both partial and complete oxidation are taking place, which shows the potential that this catalyst holds in chemical synthesis as well as VOC abatement applications if reaction conditions are optimized to improve selectivity towards the desired products. Furthermore, no
catalyst deactivation was detected after exposure to reactants under reaction conditions (up to 100°C) for over 20 hours.

Clear differences in the catalytic performance of the different samples were observed and are attributed to differences in NP morphology (shape). EXAFS measurements provide an indication that samples containing similar size distributions with respect to particle diameter, present different coordination numbers. This may be explained by some particles being flatter while others being more spherical or hemispherical. Flatter particles tend to display higher activity as they possess a greater number of uncoordinated atoms which are considered to be catalytically active sites. They also show a greater degree of oxidation following the annealing treatment in O₂ as well as a higher degree of atomic disorder. Both of these effects could be attributed to a more intimate contact with the oxide support.

These studies demonstrate the value of utilizing multiple methods to assess the characteristics and performance of systems that are relevant in the field of heterogeneous catalysis. This information provides insight into the key parameters that should be considered in the synthesis, characterization, and evaluation of metal nanocatalysts. However, despite the significant advances in science, technology, and engineering, many fundamental questions remain unanswered and may still be subject to debate. One of such questions involves the role played by oxygen and other adsorbates as well as the oxidation state of a catalyst under reaction conditions. Further structural characterization and a better understanding of particle-support interactions are also fundamental in identifying the most relevant mechanisms involved in heterogeneous catalysis. In addition, catalyst activity under gas mixtures, halogenated
compounds, and over extended periods of time should be assessed carefully when considering potential applications of model catalyst on large-scale industrial systems.

Significant contributions to the fields of catalysis and nanotechnology will most likely be made in the coming years. The advancement of knowledge and applications requires the efforts from experts of many fields and it is expected that such developments will have a great impact upon improving quality of life in our society. The advances that have been made in the past with regards to the way products and energy are generated and the way pollutants are controlled, are proof of the great benefits derived from a better understanding of catalysis and nanomaterials. However, it is the great potential that these fields hold what makes their research instrumental to solving some of the most pressing issues of our day and striving to create a more prosperous and sustainable future.
LIST OF PUBLICATIONS


Solving the structure of size-selected Pt nanocatalysts synthesized by inverse micelle encapsulation. B. Roldan Cuenya, J. R. Croy, S. Mostafa, F. Behafarid, L. Li, Z. Zhang, J.C. Yang, Q. Wang, A.I. Frenkel (*Submitted*).
LIST OF REFERENCES


[103] Introduction to atomic force microscopy (AFM), Department of Chemistry, Johns Hopkins University, http://www.jhu.edu/chem/fairbr/teach/AFM/AFwebpage.html


