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Catalytic Oxidation of Methane using Single Crystal Silicon Carbide

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CATALYTIC OXIDATION OF METHANE USING SINGLE CRYSTAL SILICON CARBIDE

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Chemical Engineering
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Keywords: Pd and PdO catalysts, Oxidation of streams with lean methane concentration, Semiconductor catalyst supports, SiC catalyst support, Single crystal SiC.

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SiC is a hard man-made material and has emerged as an excellent material for a wide range of applications which are exposed to extreme conditions such as high temperatures and harsh chemical environments. These applications range from SiC being used as an abrasive, to a refractory material, to a semiconductor material for high power and high frequency electronic devices. The properties of the material for each application is different, with the semiconductor grade material for electronic devices being the most refined. SiC, with its excellent thermal properties and high resistance to harsh chemical environments, lends itself to being an ideal support for catalyst systems. Various characterisation & analysis techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography (GC) are used in this thesis to investigate the suitability of single crystal SiC for high temperature catalytic systems. Low temperature oxidation of methane was used to investigate the catalytic activity of:

- Porous and standard 4H-SiC with and without Pd
- Porous and Standard 6H-SiC with and without Pd.
- Nanocrystalline Beta-SiC powder with and without Pd.
Part of the samples were impregnated with Pd using Palladium Nitrate (Pd (NO$_3$)$_2$) which is a common precursor for Pd. Activation treatments which were investigated were oxidation and reduction. Oxidation was generally better in activating the catalyst, as was expected, since the PdO phase is known to be more active in oxidising methane. A mixed set of Pd and PdO were observed by SEM and EDS which were the main characterisation techniques used to analyze the structure of the catalysts before and after the reaction. The Beta-SiC showed by far the best activity which could be attributed to the micro-crystalline powder format in which it was used, where as all other catalysts studied here were derived from crushed wafer pieces. Type II porous 4H-SiC was another of the samples which registered impressive results, vis-à-vis catalytic activity.
CHAPTER 1: INTRODUCTION

1.1 Introduction to Catalysis

Catalysis as a phenomenon has been under investigation since Berzelius described it in 1836 [1]. However, to date the phenomenon is not quantitatively well understood; there are many current hypotheses on various aspects of catalysis that are generally accepted. Through the decades, many assumptions and theories have been rejected as improvements in analytical characterization and computer aided simulation technologies usher in newer and more refined views of the older hypotheses.

This thesis attempts to apply some of the currently accepted hypotheses on various aspects of catalysis in literature in order to explore the possibilities of using silicon carbide (SiC) along with promoters as an effective catalytic system.

Catalysts by general definition are materials that increase the rate of the desired reaction by lowering the activation energy required for the reaction to take place without themselves being used up in the process. Catalysis has been widely used in the industry for varying purposes from increasing selectivity or yield of the desired product to increasing the rate of reaction.

Catalysts can be broadly classified either as homogenous catalysts or as heterogeneous catalysts. Of the two, the latter is more significant and favoured industrially. Homogenous catalysts generally dissolve in the reactant solution and enhance the rate of
reaction by acting uniformly throughout the reactant mixture. Due to the path of action taken by homogeneous catalysts, they have to be either separated from the product stream in order to be recovered or lost with the product, thus increasing the cost of the process. Heterogeneous catalysts on the other hand do not dissolve into the reacting solution; instead they facilitate the reaction on its surface by providing an advantageous electronic and/or structural environment for the desired reaction to occur.

The catalytic system under investigation in this thesis belongs to the heterogeneous class of catalysts. SiC was the first man-made abrasive substance. Invented by Dr. Edward Goodrich Acheson more than 100 years ago [2]; it was given the trade name Carborundum and was hard enough to cut glass. An extremely rare, naturally occurring mineral form of SiC is found in meteorites and is called Moissanite, named after the scientist who first classified SiC as a crystal, Henri Moissan. Researchers have mainly considered catalyst systems with polycrystalline forms of SiC as opposed to single crystal [3-9]. In this thesis we will investigate the catalytic activity of crushed single crystal SiC.

1.2 Silicon Carbide Material Properties

SiC has a tetragonal structure with a C/Si atom at the centre connected to 4 Si/C atoms. The distance between the C atom and the neighbouring Si atoms is found to be the same for all polytypes [10] and is approximately 3.08 Å.

The exact physical properties of SiC depend on the crystal structure realized. SiC has been observed to form over 200 polytypes or families of crystals [11]. Polytypes in SiC differ in the arrangement of the layers of Si and C atoms. The polytypes are named according to the periodicity of these layers, for example one of the most common polytypes is called 6H, and this means a hexagonal type lattice with an arrangement of 6 different Si + C layers.
needed before the pattern repeats itself. Some of the most common structures used are 6H, 4H and 3C where the, ‘C’ stands for cubic lattice structure.

![Figure 1.1 Stacking sequence in 4H, 3C and 6H polytypes of SiC](image1)

SiC has excellent material properties, which is a primary motivation for using this material for applications exposed to extreme conditions i.e.

- high melting point (Sublimes at temperatures greater than 1800 °C),
- exhibits excellent thermal conductivity (above 3 W/cm K at room temperature) and low thermal expansion, thus displays good thermal shock resistance. In addition,
- demonstrates high hardness, corrosion resistance and stiffness

SiC also possesses interesting electrical properties due to its semiconductor characteristics:

- The high bond strength in SiC leads to a wide energy bandgap (4H-SiC: 3.26 eV; 6H-SiC: 3.03 eV) allowing it to operate at extremely high temperatures without suffering from intrinsic conduction effects and also allows it to emit and detect short wavelength light.
- It has a high breakdown electric field (4H-SiC: $2.2 \times 10^6$ V/cm; 6H-SiC: 2.4
x $10^6$ V/cm (for 1000 V operation) which is an important parameter for high voltage, high power devices.

- It has a high, saturated electron drift velocity ($4H$-SiC: $2.0 \times 10^7$ cm/sec; $6H$-SiC: $2.0 \times 10^7$ cm/sec (at $E = 2 \times 10^5$ V/cm)) enabling operation at high frequencies.

As the properties of SiC began to be investigated, one of the initial results was the first light emitting diode (LED) made as early as 1907 [13], although far more efficient material systems have been fabricated for making LED’s instead of SiC. Currently the semiconductor industry has been in the process of utilising these robust material properties of SiC for high-temperature, high-frequency and high-power applications. However no commercial use of single crystal SiC has been reported for catalytic applications.

### 1.3 Silicon Carbide in Catalysis

To date catalysis, researchers [4-6, 8, 9, 14] have mainly explored the viability of using ceramic grade polycrystalline SiC as a catalyst/catalytic support, work that has been on-going since the mid nineteen sixties[15, 16]. Newer and more improved methods of manufacturing ceramic grade SiC have been found and quite a few of them have been patented [17, 18]. The two main conclusions researchers have established regarding the attractiveness of SiC as a catalytic support for high temperature combustion reactions are:

- SiC has a thermal conductivity close to that of metals such as Ag or Cu[19], thereby reducing thermal shocks which can lead to sintering of the support and the active phase.

- It has been found to be physically and chemically stable in inert gases up to temperatures of $1650^\circ$C [8]. The chemical stability allows easy recovery of the
active phase and inhibits the reaction of the support with the active phase or other chemical reagents.

Lianos, et al [20] have tested the catalytic activity of Pd on a single crystal 6H-SiC(0001) for 1,3-butadiene hydrogenation reaction. Pd is the most common catalyst for this reaction. Pd was deposited on a single crystal 6H-SiC by an atomic deposition technique under ultra high vacuum (UHV) conditions. The catalytic activity of the Pd/ SiC system was found to be higher than that of Pd surface atoms on pure Pd (111) and Pd(110) crystals. This suggests a synergistic affect between the support (SiC), and transition metal (Pd) of known catalytic activity. There are many possible reasons for this observed increased activity including:

- Some amount of catalytic activity shown by the support.
- Optimum surface structure of the transition metal after depositing onto the support.
- Extended surface area provided by the support.
- Electronic interactions between Pd atoms and the support to lower the activation energy.
- Dispersion of the transitional metal on the support.
- Better heat dissipation over the extended surface area of the support.

Methivier, et al [19] have conducted tests with methane oxidation using Pd on polycrystalline SiC and found that different activation methods generally lead to different sizes of active Pd particles on the support. The sizes of active Pd particles were determined by H₂ thermal desorption and Transmission Electron Microscopy (TEM). Activities of the relatively smaller particles (d~ 5 nm) were much greater than the larger particles (d~ 25 nm). However, the larger particles showed a much improved resistance to deactivation at
temperatures greater than 800 °C over the smaller particles. Clearly the optimum catalytic geometry is application specific.

### 1.4 Thesis Outline

This thesis research involved the investigation of catalytic activity of Pd supported on single crystal substrates of porous and non-porous 4H, 6H and polycrystalline 3C forms of SiC. In addition, a newly developed Type II porous 4H material developed by M. Mynbaeva was also explored.

Investigations featured

- Different combinations of material systems.
- Different activation techniques of the Pd catalysts via:
  - Reduction.
  - Oxidation.
- Characterisation of catalysts using techniques such as:
  - Secondary Electron Microscopy (SEM)
  - Energy Dispersive Spectroscopy (EDS)
- Exhaust gas analysis techniques using:
  - Fourier Transform Infrared Spectroscopy.
  - Gas Chromatography.

Now that the motivation for the research has been presented, in the second chapter more details of the current accepted hypotheses of catalysis are presented. A strong
correlation between catalytic activity & surface structure exists and this is discussed in detail, vis-à-vis adsorption mechanisms, role of activation barriers and mechanisms of catalytic action. Current accepted models of catalytic kinetics are also discussed in this chapter.

The third chapter discusses current hypotheses found in literature for the mechanisms of methane oxidation on supported Pd and PdO catalysts including the mechanisms for their activation treatments, namely oxidation and reduction.

Chapter four discusses the features of the catalytic reactor test bed built for analysing catalytic material systems. The fifth chapter summarizes the results and concludes with ideas for future research work that could be adopted.
CHAPTER 2: HETEROGENEOUS CATALYSIS AND METHANE OXIDATION
- A LITERATURE REVIEW

The most common example of a heterogeneous catalyst is the catalytic converter on the exhaust pipe of automobiles. Heterogeneous catalysts are preferred over their homogeneous counterparts in most industrial processes despite the fact that homogeneous catalysts increase the rate of the reaction, to a greater extent than their heterogeneous counterparts. But the phase difference in heterogeneous catalysis makes the recovery of catalyst easier, than in homogeneous catalysis where the catalyst is lost with the products as they dissolve in the reactant matrix. Heterogeneous catalysis is a purely surface phenomena, hence the nature of the surface plays an important role as will be discussed later in this chapter. Most heterogeneous catalysts are solids and include:

- Supported metals.
- Transition metal oxides and sulphides.
- Solid acids and bases.
- Immobilized enzymes and other polymer bound species.

The scope of this thesis will be confined to the activity shown by supported transition metal catalysts. Supports tend to spread the active promoter uniformly, provide a larger surface area for catalytic activity and act as efficient means for energy transfer.
Work has been done using various transition metals as active promoters along with polycrystalline ceramic grade SiC as a support. We intend to use single crystal electronic grade SiC as a support. Crystalline structure plays a major role in catalysis as will be shown later in this chapter. Investigations of porous as well non-porous samples of different crystal structures of SiC, namely 4H-SiC and 6H-SiC, are presented.

2.1 Catalysis Involving Metals

The main pathways of catalytic action via metals are

- Initiating reactions
- Stabilising intermediates
- Holding the reactants in the right configuration

2.1.1 Initiating Reactions

Most gas phase reactions follow the initiation-propagation mechanism, where the formation of a free radical is essential to trigger the reaction. The ability of metals to dissociate the molecules rapidly allows a fast initiation reaction thus increasing the overall rate of reaction. Gases like oxygen and hydrogen will readily dissociate to form radicals so as to trigger the reaction.

2.1.2 Stabilising the Reaction Intermediates

The rate of the reaction is proportional to the concentration of the intermediates in a reaction. Thus, if one increases the concentration of the available intermediates in some way one can enhance the rate effectively.

Metals generally have a good cache of electrons in the bulk of the material system; these electrons are confined within the metal itself. But on the surface the story is different;
the free electrons can escape the metal and go into the gas phase. Thus any radical in the vicinity of the surface of the metal can be stabilised by these free electrons. This leads to an increase in concentration of the radicals or the so-called stabilised radicals on the surface of the metal catalyst, thus increasing the rate of the reaction. The d-bands play a major role in this process, by reducing the activation barrier for the reaction thus favouring the formation of bonds.

2.1.3 **Holding the Reactants in the Right Configuration**

Reactants have to come together to react. This is sometimes very well facilitated by the catalyst which provides the reactants, ‘active sites’ for the reactants to get adsorbed to and thus facilitates the transformation to the product state.

2.2 **Cycles of Catalysis**

Catalysis in general can be shown to follow a cycle:

- Adsorption of one or all of the reactants.
- Reaction amongst the adsorbed species and or other unadsorbed reactant species.
- Desorption of the product species

2.2.1 **Adsorption**

Adsorption is solely a surface phenomenon. Masel in his book [1] defines the main types of adsorption as:

- Physisorption - where the adsorbate and the adsorbent do not undergo a significant change in their electronic structures.
Chemisorption - where the adsorbate and the adsorbent undergo a significant change in their electronic structures.

According to Masel [1] a molecule is first physisorbed and then converted into a chemisorbed state, hence adsorption is primarily discussed via the chemisorption process. Chemisorption of gases on surfaces can be either dissociative or molecular depending specific conditions of temperature, pressure so as to overcome the activation barrier for the reaction as will be discussed later in this chapter.

In dissociative adsorption the incoming molecule is first adsorbed and then undergoes dissociation depending on the magnitude of the activation barrier. Molecular chemisorption involves adsorption of a molecule without the dissociation.

The rate of dissociation is dependant on the crystal structure of the adsorbent. Having said that, there has been no quantitative method to show this but a number of qualitative methods/ experiments have shown that the nature of the crystal face, in terms of crystal orientation, the density of steps, terraces and kinks play a major role.

Adsorption may or may not change the structure of the adsorbent depending on the conditions of temperature, pressure and nature of the reacting species, namely the adsorbent and the adsorbate. Each crystal face has its own set of parameters vis-à-vis reactivity, active sites etc.

2.2.2 Surface Reaction

2.2.2.1 Activation Barrier Considerations

Activation barriers are crucial for any reaction to occur, but more so for catalysis. The whole idea of catalysis is based on lowering the activation barriers so that the reactants can be transformed into the products.
Consider a simple model put forward by Lennard-Jones to show the influence of the activation barrier over the nature of chemisorption that occurs. Consider an interaction between a flat surface and a molecule say B\textsubscript{2}. Assuming the interaction is a function of only a single dimension i.e. the distance of the molecule from the surface. The presence of a barrier influencing the nature of desorption can be quantitatively explained by the figure below.

In figure 2.1 (a) - the molecular state has a lower energy state than the dissociative state, hence molecular dissociation will dominate. In figure 2.1 (b) - the dissociated state has a lower energy than its counterpart. But there is a finite activation barrier which the molecule has to overcome, which in turn requires some energy. Hence in this case the molecular chemisorption will be dominant but dissociative chemisorption is also possible provided some energy is provided to the incoming molecule. This is the regime of operation for most catalytic reactions. In figure 2.1 (c) - the energy state of the dissociated state is far lower than the molecular state and the activation energy barrier is below the energy of the molecule, hence the incoming molecule will always dissociate.
For every reaction there is a certain barrier which has to be overcome by the reactants in order to be transformed into products. In other words specific amount of energy has to be supplied to the reactants so that the reaction can proceed. Masel in his book [1] has outlined the main causes for the activation barrier. They are:

- For a reaction to happen bonds have to be broken, thus requiring them to stretch and distort, which in turn requires energy.
- For molecules to react, they have to come close to each other. To do so they have to overcome Pauli repulsions and other steric effects. Thus requiring some form of activation energy.
- In a few cases quantum effects prevent a transition from the reactants to the products, hence requiring a certain amount of energy to overcome those effects.
- In certain cases reactants need to be in their excited state for the reaction to occur, which can be provided by the activation energy/barrier.

In catalysis the first two causes are the main reasons for the activation barrier as compared to the other reasons which are for specific cases.

2.2.2.2 Mechanisms of Surface Reactions

The adsorbed species has unique set of properties. It may be strongly or weakly bonded with the surface based on the electronic interactions between the surface and the adsorbate. Most catalytic surface reactions are said to follow either the three commonly accepted mechanisms of surface reactions, or some combination of these:

- Langmuir-Hinshelwood mechanism
- Rideal-Eley mechanism, and
• Pre-cursor mechanism.

Consider a reaction where

\[ A + B \rightarrow AB \]

In the Langmuir-Hinshelwood approach as shown in figure 2.2 (a) below both reactants are adsorbed, they react to form A-B adsorbed complex on the surface which then desorbs to form the product AB. Under the Rideal-Eley mechanism one of the reactants say A is adsorbed. The adsorbed species reacts with the other reactant B to give the A-B adsorbed complex which then desorbs.

![Figure 2.2 Mechanisms of surface reactions](image)

In the precursor mechanism A is adsorbed. B collides with the surface to form a mobile precursor state which rebounds on the surface until it collides with A to form the A-B adsorbed complex, which later desorbs.

### 2.2.3 Desorption

Masel [21] discerns 4 main types of desorption processes in metal catalysts:

- Simple molecular desorption
- Recombinative desorption
- Displacement desorption, and
- β scissions
In simple molecular desorption, the adsorbate complex formed from the surface reaction detaches itself from the surface to give the final product. In most of the cases the molecule leaves without significant rearrangement.

In recombinative desorption the adsorbed species react to form a stable molecular species which can leave the surface. This process is dominant in supported metal catalysts.

In displacement desorption a molecule from the solution that the surface is exposed to, comes in and displaces a ligand from the adsorbed species. This process is more dominant in metal clusters. β scissions are dominant in transition metal clusters wherein the desorbing species leaves a β-Hydrogen atom at the site.

2.3 Sites for Adsorption

It has also been seen that an adsorbate can be held onto a series of distinct sites on the surface, some of which are shown in the figure below, namely

- Directly above a surface atom called linear or on-top site.
- Between two adjacent surface atoms – bridge-bound site.
- Above a threefold hollow – triple coordinated site.
In a condition where the coverage of the adsorbate is low, random site filling is dominant where the sites fill up randomly as in case (a) in the figure below.

![Figure 2.4 Coverage of adsorption sites](image)

Under moderate coverages (case b) there is a presence of a weak order and under a strong coverage (case c) islands are formed. In some cases the adsorption of some species can occur only in certain fixed sites (case d) called random incommensurate adsorption.

2.4 **Mechanisms of Processes in Methane Oxidation - A Review**

Researchers have not delved deeply into the possibility of using single crystal SiC as a viable catalyst support apart from a handful of researchers like Lianos L.[20], Berthet A. [22] and Ledoux M.J. [3]. Research interest in the topic waned in the 1990’s until the latter half of the decade.
2.4.1 Methane Oxidation - Test Reaction

A test reaction was chosen to evaluate the below mentioned catalytic systems. Methane oxidation seemed an ideal candidate for this purpose for the following reasons:

- Methane is the least reactive of all the hydrocarbons and therefore the most difficult to oxidize.
- Complete oxidation of methane without any catalyst was found to occur at 950 °C in the test bed which is discussed in detail later in this chapter. Hence the reaction is an ideal candidate to lower the temperature of the reaction with the help of a catalyst.
- The methane molecule can trap energy twenty-one times more than a CO₂ molecule, thus making it a potent Greenhouse gas.
- Low temperature methane oxidation can significantly reduce NOₓ emissions which are formed as by-products from high temperature combustions.
- Sources of methane are mainly from production and transportation of coal, natural gas, and oil. Methane emissions also result from the decomposition of organic wastes in municipal solid waste landfills, and the raising of livestock.
- Possible applications based on this reaction could be low temperature Catalytic converters, Gas sensors, Exhaust scrubbers, H-reforming.
- The ease in modeling the C1 chemistry is also an additional bonus in choosing this test reaction system.

Reactions involved:

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad \text{(?H}_r \text{ (STP) = -35.7 KJ/mol) (partial oxidation)}
\]

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \text{(?H}_r \text{ (STP) = -890 KJ/mol) (complete oxidation)}
\]
Both reactions are exothermic!

Methane oxidation has been well researched by many researchers but some of its aspects have not been fully understood. Most of the papers reviewed on CH$_4$ oxidation have either used Alumina or Zirconia as their choice of support, with the latter gaining the favour of most researchers. Many possible mechanisms have been reported in literature for the various processes we have used to test the samples, namely,

- Activation treatment - Reduction.
- Reaction on reduced Pd.
- Activation treatment - Oxidation.
- Reaction on PdO.

2.4.2 Activation Treatment - Reduction of PdO

Although a lean mixture of CH$_4$ along with an inert like N$_2$ can be used as a reducing mixture, Ciuparu et al in their review of CH$_4$ oxidation using Pd Based catalysts [23] observed that using H$_2$ at a high enough temperature reduced the uptake of O on the cooling cycle. Su et al.[24] found that reduction with H$_2$ as an activation treatment for a Pd/ZrO$_2$ at around 533 K, occurs so quickly that a layer of metallic Pd forms in a shell-wise manner. We used a 50/50 : H$_2$/N$_2$ mixture at 1073K for 2 hours as our reducing agent. Pd metal is formed on the surface screening the PdO layer. As the temperatures are increased so does the rate of reduction. The rate limiting step was found to be the removal of oxygen from the surface. Ciuparu et al [23] found that at low coverages, the PdO phase is known to spread over the support, while the metallic Pd phase forms larger, more segregated crystallites. This was evident in our samples as well.
According to them the encapsulation of metallic clusters into the oxide phase is likely because of their higher surface tension compared to the oxide phase, consistent with the "metal core growing in the PdO shell" model.

2.4.3 Reaction after Reduction of PdO

According to Ciuparu et al. [23] dissociative adsorption of O\textsubscript{2} is much faster than that of CH\textsubscript{4}. CH\textsubscript{4} dissociatively adsorbs onto metallic Pd as an adsorbed hydrogen species and an adsorbed methyl species. The Langmuir-Hinshelwood model of adsorption can be used to approximate the dissociative adsorption of CH\textsubscript{4}. Competitive adsorption patterns between O\textsubscript{2} and CH\textsubscript{4} make the adsorption of CH\textsubscript{4} the rate-controlling step for methane oxidation over metallic Pd. At higher temperatures the coverage extent of surface O has been found to decrease, thus allowing higher reactivity at higher temperatures. Ciuparu et al [23] in their review have noted that researchers have observed that at low coverages the PdO phase is well spread out, whereas the Pd phase segregates to form larger crystallites. This was also observed in our samples as well where clusters of Pd (size range: 1 - 5 microns) were detected by EDS (SEM images of the chunks are available in the Appendix A). They also observed that CH\textsubscript{4} oxidation over metallic Pd is structure sensitive as researchers have noticed that activity increased as the size of Pd increased.

![Figure 2.5 Optimized structures for critical points of the O - H bond formation reaction: (a) CH\textsubscript{3} + H on Pd fragment; b) intermediate activation; c) transition state; d) adsorbed CH\textsubscript{3} + OH (Bond distances are given in Å) [25]](image)
Broclawik et al. [25] suggest a mechanism for the reaction which follows the following path as shown in the figure above: a) Dissociative adsorption of CH$_4$ molecule at a bridge position, i.e., between two Pd atoms. b) An intermediate activated state. c) A transition state in which both adsorbed methyl and hydrogen species are weakly bound allowing the H species to move around the Pd-Pd dimer easily or to bind itself to a neighbouring surface O atom as well; and d) the final product is a surface hydroxyl. They found that the direct O-H interaction is apparently switched on. This activation costs 27 kcal/mol and the energy gain after forming a strong OH bond is -15 kcal/mol. The methyl species attains the position of the initially adsorbed methane and the next C-H bond becomes activated, thus the entire cycle may be repeated. The abstraction of next hydrogen atoms may be even easier than the first one and the adsorbed OH group may thus react to form water molecules.

### 2.4.4 Oxidation of Deposited Pd

Due to the disparity in the Pd-Pd distance in Pd (0.275 nm) and PdO (0.305 nm) the crystal structure has to undergo significant reconstructions during oxidation of Pd. The same holds true for reduction of PdO as well. According to Ciuparu et al. [23], the (001) and (110) bulk-terminated PdO surfaces expose only a single type of O species as no distinction can be made between surface, adsorbed or lattice O atoms. The O atoms are bridge bound to two Pd atoms.

Analysing the results from various researchers Ciuparu et al. [23] in their review of Pd based catalysts for methane oxidation, put forth a three-step mechanism for the oxidation of Pd (111). They are:

- Rapid adsorption that stops at 0.25 ML of atomic oxygen
• Oxygen penetration into the surface accompanied by island growth leading to the formation of two phases that are intermediate between Pd and PdO.

• Formation of bulk PdO.

0.25 ML saturation coverage of O is formed on the surface of the Pd atom at temperatures below and up to room temperatures and pressures on the order of $10^{-5}$ torr. They argue that oxygen growth on the surface has been found to take place via a nucleation mechanism due to the following reasons:

• Researchers have observed that the rate of oxidation increases with the temperature until a threshold value is reached after which it decreases considerably, which is a characteristic of the nucleation mechanism.

• TEM studies have shown that reoxidised Pd particles undergo considerable surface roughening which is another trait of the nucleation mechanism.

The chemisorbed O atoms from the first monolayer tend to penetrate the surface forming Pd-O clusters along with other Pd atoms on the surface. These clusters grow to form islands until the whole surface is covered under favourable conditions. The PdO thus formed say, Carstens et al [26] is more amorphous than that formed under reactions conditions at the same temperature. They have examined the catalyst Pd/ $\text{ZrO}_2$ for methane combustion under reaction conditions and have found that a thin crystalline PdO film formed over metallic Pd of approximately 7 monolayers thick is required for achieving high activity. They also suggest that PdO along with small amounts of Pd increases the activity of the catalyst as CH$_4$ dissociates readily over metallic Pd rather than PdO.
Crystalline PdO has been found to be stable in temperatures under 1046 K. Researchers have found that crystalline PdO is more active than metallic Pd at lower temperatures. the activation energies of methane oxidation on crystalline PdO is lesser than metallic Pd. [23].

2.4.5 Reaction over Oxidised Pd

The mechanism for oxidation of methane over PdO is not entirely understood and many hypotheses have been put forward but the most recent published article on the subject was from Ciuparu and Pfefferle [27]. They propose that methane oxidation on PdO follows a redox mechanism where the CH$_4$ molecule first dissociates on a Pd–O lattice site as shown in the figure 2.6 suggested by Broclawik [28]. The dissociation products are an adsorbed methyl and surface hydroxyl species.

This mechanism suggests that any surface dimer site can participate in methane activation and the gas phase methane molecule is directly adsorbed on the surface. The methyl radical undergoes further H abstraction to produce more surface hydroxyls and CO$_2$. CO$_2$ is desorbed rapidly creating a vacant site which can be occupied either by O from the gas side or from the support based on the partial pressure of O over the catalyst and the O mobility in the support. Finally when the hydroxyl recombine with another adsorbed H species and desorb, further vacant sites are created. The hydroxyl desorption was found to be the rate controlling step for this mechanism. They also suggest that due the slow recombination of the surface hydroxyl and desorption of water prevents the reoxidation of the site. Ciuparu and Pfefferle in [29] propose 2 regimes of methane oxidation. The first regime occurs at lower temperatures where recombination of the surface hydroxyl is the rate
controlling step and the second regime is at higher temperatures where methane activation is the rate controlling step.

Figure 2.6 Optimized structures of; a) collinearly adsorbed methane, b) bridging adsorption, and c) the dissociated product (Bond distances given in Å) [28]
CHAPTER 3: CATALYTIC REACTOR DEVELOPMENT

The catalytic reactor test bed shown in figure 3.1, was setup which consisted of a bank of mass flow controllers connected to the tubular quartz reactor, which in turn is connected to the Fourier Transform Infrared Spectrometer (FTIR) for analysing the exhaust gases.

3.1 Experimental Test Bed

A gas delivery system was designed to setup a 2 % (vol) methane stream with the help of four mass flow controllers (MFC) bought from MKS Instruments Inc.; of type 1179A; of which two were rated for a flow of 20 sccm, another for 50 sccm and the final MFC was rated for 100 sccm. The MFC’s were calibrated by the manufacturer for nitrogen flow and the appropriate gas correction factor was applied via a MKS - 247D four channel flow controller readout, which was used to control the MFCs. The correction factors were made prior to running the various gases through the MFCs. The gases from the respective MFC’s were mixed in a static mixer of length 6 inches. A vent/purge line was also added to this delivery system for safety purposes. The 2% CH$_4$ mixture which emerges out of the static mixer is then passed through a final flow controller before entering the reactor.
Table 3.1 Details of the flow controllers connected for the respective gases

<table>
<thead>
<tr>
<th>Gases</th>
<th>Flow (sccm)</th>
<th>Correction factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>20</td>
<td>198</td>
</tr>
<tr>
<td>Methane</td>
<td>20</td>
<td>144</td>
</tr>
<tr>
<td>Final mixture</td>
<td>100</td>
<td>99</td>
</tr>
</tbody>
</table>

Figure 3.1 Block diagram of the catalytic reactor test bed

Figure 3.1 shows a block diagram of the test bed. The reactor is a ¼" quartz tube with a constriction in the centre so as to create a packed bed of 1 cm in length where the catalyst material is loaded. The ends of the tube are connected with Ultra-Torr™ tees to provide sample ports for inlet and outlet streams for analysis using with the Gas Chromatograph (GC) or the FTIR. The reactor is placed in a Lindberg/ Blue M tube furnace which is capable of heating till 1100 °C. The gases, on leaving the reactor go through a gas cell accessory of the FTIR for analysis from where they are properly vented.
A Bio-Rad Excalibur™ series FTIR was used for analysis of the exhaust gases from the reactor. It is fitted with a liquid nitrogen cooled, Mercury Cadmium Telluride (MCT) detector which can analyze effectively for wavenumbers between 4000 & 600 cm\(^{-1}\) a range that is relevant for most of the gases used and produced in the reactor. The gas cell provides an infra-red beam path length of 2.1 metres through multiple reflections from KBr coated optical mirrors. The gas cell is kept under a constant vacuum with the help of a roughing pump as well as to reduce the ambient CO\(_2\) and water vapour contaminations in the background infrared (IR) spectrum. A photograph of the FTIR system is shown in figure 3.2.

### 3.2 Catalyst Preparation

The catalyst compound to be evaluated in the catalytic test bed was prepared in the following manner:
• n-Dodecanol, being a non-polar solvent, was used as a solvent to dissolve the Pd(NO$_3$)$_2$ salt.
• Crushed pieces of wafer/powder are then introduced into this n-dodecanol/Pd(NO$_3$)$_2$ matrix.
• The alcohol is then slowly evaporated over a period of approximately 2 hours.
• The residue is then calcined under atmospheric conditions at 500 °C for 2 hours.
• As the calcined catalyst attains room temperature it is weighed and loaded into the reactor.
• (Activation step) Once loaded into the reactor it is oxidised under a 50/50:N$_2$/O$_2$ mixture at a flow rate of 10 sccm through the reactor at about 800 °C for about 2 hours.

Secondary Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were carried out on the samples before and after the reaction.

3.3 Test Reaction Conditions

The Nitrogen flow through the reactor was 88 volume %; oxygen was 10 volume % and methane was at 2 volume %. The total flow through the reactor was 10 sccm. The products of the reaction were analysed using the FTIR spectra at every 50 °C increments ranging from room temperature till about 950 °C, or until all the methane was spent, whichever came first. From the FTIR spectra a conversion plot was created based on the concentrations of CH$_4$/CO$_2$ over the entire temperature range, to compare the abilities of the various catalyst systems tested. Before describing how the data was analysed, the analytical instrumentation is presented.
3.4 Instrumentation

The FTIR used for analysing the exhaust gases from the reactor was a Digilab (formerly Bio-Rad) Excalibur™ - FTS 3000 which was fitted with a liquid N\textsubscript{2} cooled Mercury Cadmium Telluride (MCT) detector which has a range of 4000 - 600 cm\textsuperscript{-1} wavenumbers, respectively. A gas cell accessory, bought from Pike Technologies Inc., was fitted into the sample compartment chamber of the FTIR. The gas cell is permanently aligned with an infrared beam path length of 2.4 m. It has a borosilicate glass body, with KBr coated windows and an approximate volume of 0.1 liters. The mirrors of the gas cell accessory were manually aligned with the infrared beam of the FTIR by adjusting the mirrors on the gas cell manually. At the start of every exhaust gas analysis run the MCT detector was cooled by filling the liquid N\textsubscript{2} reservoir which, once filled, lasts for 8 - 10 hours of continuous operation. There was a constant N\textsubscript{2} purge applied to the sample compartment chamber and the chamber, which housed the interferometer. Once the detector was cooled the gas cell was purged with N\textsubscript{2}, which flowed at 10 sccm through the reactor for 40 minutes to purge the gas cell of residual CO\textsubscript{2} and H\textsubscript{2}O contamination from the previous run. The voltage response from the detector was checked and was always adjusted between 5 and 7 volts as suggested by the manufacturer. Changing the aperture diameter or the sensitivity through the program supplied by Digilab to control the instrument did this adjustment. A reference scan was then taken with N\textsubscript{2} flowing at 10 sccm and also at the reaction configuration. The total flow at anytime through the reactor was kept constant at 10 sccm. The FTIR was run at the following scan settings:

Number of scans: 16
Scan resolution: 0.1 cm\textsuperscript{-1}

An inventory of the components used in the experimental test bed are given in Appendix B.
3.5 Sample Calculation for Conversion

The sample scans were ratioed with their appropriate backgrounds collected at the beginning of the sample run and the conversion of CH₄ into products were calculated as is explained in this section. Figure 3.3 is a sample spectrum at 300 °C for the type II porous 4H-SiC/Pd sample with 10 sccm flow of the reactant mixture. Figure 3.4 is a background spectrum collected at room temperature with 10sccm N₂ flow through the gas cell. The peaks were identified as follows:

![Sample Spectrum at 300 °C](image)

**Figure 3.3** Sample spectrum of type II 4H-SiC/Pd under reaction conditions at 300 °C

<table>
<thead>
<tr>
<th>Species</th>
<th>CH₄</th>
<th>CO₂</th>
<th>CO₂</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Limit</td>
<td>2650</td>
<td>2230</td>
<td>620</td>
<td>2060</td>
</tr>
<tr>
<td>Upper Limit</td>
<td>3200</td>
<td>2400</td>
<td>720</td>
<td>2230</td>
</tr>
</tbody>
</table>
An absorbance spectrum is obtained by the ratio of the sample spectrum and the background spectrum. The area under absorbance spectrum is a measure of the concentration of the species, at that time. The number within the brackets in figure 3.5 are the values for the area under the curve, which is obtained from the DigiLab (WINIR - PRO) software.

The area under the curve for all temperatures is tabulated for methane and carbon dioxide species as follows:

**Table 3.3 Analysis of FTIR data**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>CO₂ (Area under the curve)</th>
<th>CH₄ (Area under the curve)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>53.359</td>
<td>1.871</td>
<td>0.905923</td>
</tr>
<tr>
<td>300</td>
<td>3.732</td>
<td>19.807</td>
<td>0.063361</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>19.888</td>
<td>0</td>
</tr>
</tbody>
</table>
The conversion for any temp is calculated as follows:

Inlet concentration of methane at room temp (area under the curves are noted) = 19.888

Final concentration of methane at 950 °C = 1.871

Hence final conversion is:

\[
\frac{(19.888 - 1.871)}{19.888} = 0.9059
\]

Hence fraction of methane spent is 0.9059

Therefore,

If the area under the peak for CO\textsubscript{2} @ 950 °C which is 53.359 corresponds to conversion of 0.9059 of methane

Then the CO\textsubscript{2} area of 3.732 at 300 °C corresponds to a methane conversion of:

\[
3.732 \times 0.9059 / 53.359 = 0.063361
\]
CHAPTER 4: CATALYTIC REACTOR EXPERIMENTS

4.1 Substrates Used

Samples of porous and non-porous 4H and 6H - SiC wafers (obtained from the DURINT Program) and also 3C – Beta SiC powder (obtained from Marketech Intl.) were investigated as substrates for a catalyst system. Pd was chosen as the active phase in the catalyst on the basis of literature for the methane oxidation reaction system.

The substrates tried were

- 4H-SiC
  - porous
  - non-porous/standard
- 4H-SiC impregnated with Pd
  - porous
  - non-porous/standard
- 6H-SiC
  - porous
  - non-porous/standard
- 6H-SiC impregnated with Pd
  - porous
  - non-porous/standard
4.2 Beta-SiC vs. Polycrystalline 3C-SiC - an XRD Comparison

Most of the SiC samples were obtained from the DURINT - ONR program. The beta SiC powder was obtained from Marketech International. An XRD comparison was conducted between a standard 3C-SiC wafer obtained from the ONR program and the beta SiC. The beta SiC was of a lower crystalline quality than the 3C wafer as is evident from the graph below, when one compares the FWHM values for both.

Figure 4.1 XRD spectra of substrate
4.3 SEM Analyses Before the Reaction

The SEM images before the reaction did not show too many differences between the samples. (See Appendix A for images). On most of the SiC samples, Pd tended to aggregate as a bunch of spheres or lobes the size of which were not greater than 0.1 μ. A network of these lobes & bunches were formed. Pd was also deposited as whole chunks measuring upto 10μ in size in some cases. Pd was well dispersed over the supports. The 4H polytype showed a relatively greater affinity towards Pd than the rest of the samples. This is fairly evident from the figures in Table 4.1 below.

Table 4.1 Loading of Pd (in wt %) on the substrate from EDS

<table>
<thead>
<tr>
<th>Sample</th>
<th>6H-STD/Pd</th>
<th>6H-PSC/Pd</th>
<th>4H-STD/Pd</th>
<th>4H-PSC/Pd</th>
<th>Type II 4H-PSC/Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>1.85</td>
<td>1.89</td>
<td>4.30</td>
<td>3.41</td>
<td>1.78</td>
</tr>
</tbody>
</table>

The figures in the table were obtained from EDAX – EDS. They were averaged from the readings obtained at 10 different spots on each of the samples. The figures for Beta SiC powder could not be ascertained because the sample was lost at the time of unloading the sample after running the reaction.

SEM and EDS were primarily used to characterize the catalyst. XPS and XRD were also tried out but the results from these analyses turned out to be vague because:

- The design of the XPS system we had access to did not facilitate analysis of powders.
- The amount of catalyst sample involved was too small to conduct a decent XRD analysis.
4.4 Reaction Data

4.4.1 Under Reduction Regime

The most common activation treatment for most metal/supported metal catalysts is a reduction process. Hence we used reduction using a 50/50 : N\textsubscript{2}/H\textsubscript{2} stream as the activation step. The initial reaction results were obtained using the Gas Chromatograph (GC) using a 6” silica gel column.

![Graph showing reaction results from the GC](image)

**Figure 4.2 Reaction results from the GC**

Of particular interest was the activity shown by bare porous substrates i.e. 4H-PSC and 6H-PSC 600 °C and 700 °C mark respectively, which indicated some limited amount of catalytic action albeit a small amount unlike other supports which were pretty much inert to the reaction. The porous 4H-SiC (4H-PSC) coated with Pd showed some activity around 450 °C, which had been observed in other catalyst systems.
The set of reactions from here on were monitored by the Bio-Rad FTIR which are relatively more accurate. Under the same reduction regime as the activation step the tests were carried on to give the following results as shown by the graph below:

![Graph showing conversions of various substrates under a reduction regime.](image)

**Figure 4.3 Conversions of various substrates under a reduction regime.**

Most samples follow a similar route wherein they have a range of temperature in which there is some minute activity i.e. conversion is less than 10% and then the gas reaction takes over after 875 °C.

- The beta-SiC powder starts to show some conversion (less than 10%) from 500 °C onwards till 900 °C when the gas reaction takes over at that temperature.
- The type-II porous 4H-SiC follows a similar line but the start of activity is delayed till 700 °C.
- The standard/ non-porous 4H-SiC shows its share of minute activity from around 750 °C or so.
This shifted our thinking from the viewpoint that SiC in itself could be a catalyst on its own to that SiC may facilitate catalysis in very controlled amounts unlike other inert supports.

After testing the substrates, the reaction data for the loaded substrates under the reduction regime is shown in the graph below. Most samples in this set follow similar suit, but the presence of Pd marks the difference between the graph below and the previous graph. For the initial range of temperatures till around 650 °C, the conversion is below 10% after which the catalytic action takes over.

Figure 4.4 Reaction results of porous SiC and beta SiC impregnated with Pd after reduction (activation treatment)

- Beta SiC coated with Pd showed a light-off at about 350 °C after which the activity steadily increases unlike the other samples. It does not have a region of very low activity (conversion < 10%) which is interesting.
• Type II porous 4H-SiC which has a Pd loading of about 1.7 % by weight shows the distinctive region of low activity from 300 °C onwards 600 °C after which the catalytic action takes over the reaction more definitively.

• The porous 6H-SiC has a Pd loading of around 1.8 % by weight, follows a similar route as the previous sample. The region between 350 and 750 °C is the region of low activity where conversions are less than 10%. After 750 °C the catalytic action takes over the reaction.

• The porous 4H-SiC has the highest Pd loading of about 3.4 % by weight. This sample does not show the region with consistently low activity. Instead activity starts from 600 °C and from thereon itself the catalytic action takes over.

4.4.2 Under Oxidation Regime

Instead of reducing we thought of oxidising the catalyst sample to see the changes that it may bring to the catalytic action. We found in literature [30] that PdO is a much more potent catalyst than Pd itself. Hayes et al say that palladium oxide (PdO) is readily formed when Pd supported on alumina is heated in an oxygen environment above 600 °C. Hence we switched the activation step from reduction to an oxidation step with a 50/50 : \textit{N}_2/\textit{O}_2 mixture. The results were much better across all samples in terms of the catalytic action:

Under the oxidation regime beta SiC powder coated with Pd had a much better result where it lit-off around

• 200 °C and showed the sustained catalytic activity till the end. This sample however did sinter forming aggregates & plugging the reactor tube.
- The standard 4H-SiC sample which had a Pd loading of about 4.3 % by weight starts to show catalytic action from around 225 °C.

![Graph showing reaction results after oxidation (activation treatment)](image)

**Figure 4.5 Reaction results after oxidation (activation treatment)**

- The standard 6H-SiC sample with a Pd loading of around 1.8 % by weight comparatively has a higher temperature from where it shows activity i.e. around 475 °C.
Figure 4.6 Reaction results from porous SiC substrates with Pd after oxidation (activation treatment)

- The porous type II 4H-SiC sample with a Pd loading of about 1.7 % by weight lights-off the earliest amongst all the samples i.e. 175 °C. But it rises gradually till 600 °C and only then takes off.

- The porous 4H-SiC with a relatively Pd loading of about 3.4 % by weight follows the route taken by the Type II. Catalytic activity rises gradually from 225 °C onwards till around 650 °C after which the reaction really takes off.

- The porous 6H-SiC with a Pd loading of around 1.8 % by weight shows some minute activity (conversion < 10%) from 375 °C till about 750 °C after which the reaction really starts.
4.5 Reaction Data For Beta-SiC

The switch from reduction to oxidation as the activation step affected beta SiC the most. It was by far the best sample in terms of activity shown. Having said that, the sample was the only one in which sintering effects could clearly be seen in the reactor. A possible reason for this sample doing so well as it did might be because of its fine powder format whereas the other samples were in the form of small wafer pieces. Unfortunately the Pd loading on this sample could not be found out as the sample was lost in the reactor while being removed.

4.6 Reaction Data for Type II Porous 4H-SiC

Type II porous 4H-SiC was by far one of the better samples showing activity from 150 °C onwards. Oxidation definitely seems to work a lot better as an activation treatment
when considering Pd. There was no evidence of sintering as well for this sample.

![Graph showing reaction results of type II porous 4H-SiC](image)

**Figure 4.8 Reaction results of type II porous 4H-SiC**

4.7 **Reaction Data for Standard and Porous 4H-SiC**

Both the 4H samples, porous and standard showed a greater affinity towards getting coated with Pd than any of the samples as shown in Figure 4.10. The loading for the porous 4H sample was around 3.8 % by weight and that of the standard sample was about 4.3 % by weight. They do show a lot of promise as materials for catalytic supports.
4.8 Reaction Data of Porous and Standard 6H-SiC

The porous 6H-SiC sample was one of the worst in the set that was tested. The standard 6H showed much more reliable catalytic activity from 500 °C than the Porous sample which showed similar activity from 750 °C onwards. There did not seem to be much of a change even when the activation step was altered.

Figure 4.9 Reaction results of standard and porous 4H-SiC
Figure 4.10 Reactions results of 6H-SiC
5.1 Summary

In this study porous and non-porous samples of semiconductor grade single crystal SiC and nanocrystalline β-SiC powder were investigated as substrates in catalytic systems. Methane oxidation was chosen as the test reaction for which Pd and PdO supported on alumina or zirconia are the current catalytic systems of choice. Two forms of activation pre-treatments were explored, viz., reduction and oxidation. The oxidation pre-treatment proved to be far more effective in activating the catalyst system as compared to reduction. This was well supported by researchers that PdO along with a Pd phase together is more effective for methane oxidation. As EDS showed for the samples used in this work, Pd segregated and the PdO phase spread out well around the Pd phase and also over the support.

Nanocrystalline beta SiC powder obtained from Marketech international initially showed the most promise vis-à-vis the lower light-off temperature and the sustained high level of conversion after light-off. These results could be attributed to the fact that the beta-SiC/Pd was the only sample in a powder form thus increasing the surface area of contact with the reactant gases. The other samples were derived from crushed wafer pieces. However, the β-SiC/Pd system did sinter easily and did show considerable amount of CO as compared to the other wafer derived samples. Therefore, this material can prove to be the most expensive and environmentally hazardous. The 4H-SiC polytype sample shows
tremendous promise, the type II porous in particular. This may be due to an efficient handling of the adsorbed OH species which is the rate controlling step for methane oxidation over PdO based catalysts. Researchers have ascribed to the fact that, supports in catalyst systems which showed greater ability to move oxygen showed better results. The standard 4H polytype also showed results which were almost at par with its porous counterpart. The 6H polytype porous and standard showed less activity than the 4H samples – this may be due to the lower electron mobility of 6H-SiC vs. 4H-SiC; further investigation is needed. Small amounts of CO were observed as one of the reaction products. For most samples CO was observed at temperatures between 700 – 900 °C. The research work conducted on these catalyst systems, being of preliminary nature, more work needs to be done for commercial applications, in particular, for MEMS, micro-reactors and portable fuel cells to be produced based on this material system.

5.2 Future Work

These were some of the thoughts or directions in which further research work could be conducted:

- Most of the catalyst systems used were crushed wafer pieces except for Beta SiC. To provide level playing field catalyst systems need to be finely powdered before reaction takes place.

- Characterisation data from either/ or XPS & XRD needs to be collected and investigated. This would definitely aid us in finding out the dominant surface phase at each step of the process. XRD would give us the nature of the active phase and it’s crystalline quality along with the crystal face. We could not use either of these techniques as the XPS system we have is not really
suited to analysing powders and the amount of catalyst material was less than required for a proper XRD analysis.

- Catalyst aging studies need to be carried out along with temperature programmed desorption and adsorption studies. The life of the catalyst is an important aspect which can increase or decrease the cost of the process.

- Different deposition/impregnation techniques to deposit the Pd/PdO phase onto the SiC support need to be looked into as well. Electron-beam implantation could be one of the possible alternatives for a better uniform deposition.

- Since SiC is a semiconductor, it could be used as a catalyst in itself by biasing it, to promote the exchange of electrons with the adsorbed species, thus aiding in catalysis so as to open a vista for a plethora of microelectronic devices.

- SiC could be well suited as part of a photocatalytic system, where on exposure to UV radiation, activated oxygen is formed, which could trigger most gas phase reactions at lower temperatures thus also decomposing organic systems.

- Although Pd has emerged as the transition metal of choice for catalytic oxidation of methane, combinations of different transition elements could be tried out to enhance the quality of the result, vis-à-vis the selectivity. Ni and Rh could be used specifically for partial oxidation.

- Different stoichiometric ratios of reactants could also be experimented to see if there are any effects, positive or negative from it, as CH₄ in O₂ lean mixtures can act as a reducing agent.
REFERENCES


Appendix: A

Before reaction:  After reaction:

EDS map after reaction:

Figure A.1 SEM and EDS images of 6H-SiC
Appendix A (Continued)

Before reaction:

After reaction:

EDS map after reaction:

Figure A.2 SEM and EDS images of 6H - PSC
Appendix A (Continued)

Figure A.2 continued

Before reaction:     After reaction:

EDS map after reaction:

SEM image       Pd

Figure A.3 SEM and EDS images of type II 4H -PSC
Figure A.3 continued

Before reaction:     After reaction:

Figure A.4 SEM and EDS images of 4H-PSC
Appendix A (Continued)

EDS map after reaction:

SEM image

Pd

Si

O

C

Figure A.4 continued
Figure A.5 SEM and EDS images of 4H-SiC
Appendix A (Continued)

Figure A.5 continued
## Table B.1 Components used in the catalytic reactor test bed

<table>
<thead>
<tr>
<th>COMPONENT DESCRIPTION</th>
<th>COMPONENT NUMBER</th>
<th>QUANTITY</th>
<th>VENDOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digital Pressure Gauge</td>
<td>EW-68111-20</td>
<td>1</td>
<td>Cole Parmer</td>
</tr>
<tr>
<td>316 SS Tube Mixer</td>
<td>EW-04669-56</td>
<td>1</td>
<td>Cole Parmer</td>
</tr>
<tr>
<td>Gas Flow Meter</td>
<td>EW-32915-15</td>
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<td>Cylinder Regulators, 2-stage</td>
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<td>Air Products &amp; Chemicals</td>
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<td>500gm 1-Dodecanol</td>
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<td>Lancaster Synthesis Inc</td>
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<td>1/4&quot; .035&quot; SS pipe</td>
<td>SS-T4-S-035-20</td>
<td>60 ft</td>
<td>Swagelok</td>
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<tr>
<td>Tube fitting plug</td>
<td>SS-400-P</td>
<td>20</td>
<td>Swagelok</td>
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<td>Tube cap</td>
<td>SS-400-C</td>
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<td>Swagelok</td>
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<td>Set ferrule set</td>
<td>SS-400</td>
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<td>Ball valve</td>
<td>SS-33-VS4</td>
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<td>Swagelok</td>
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<td>Nut</td>
<td>SS-402-1</td>
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<td>S-Series fine meter</td>
<td>SS-SS4-VH</td>
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<td>3-way ball valve</td>
<td>SS-42-XS4</td>
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Table B.1 continued

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<th>COMPONENT DESCRIPTION</th>
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<th>QUANTITY</th>
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<td>1/4&quot; tube fitting</td>
<td>SS-4-UT-6-400</td>
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<td>Quartz tubing 4mm-id</td>
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<td>Quartz tubing 10mm-id</td>
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<td>4ft.</td>
<td>National Scientific Co.</td>
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<td>Palladium Nitrate</td>
<td>11035</td>
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<td>Alfa Aesar</td>
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<td>Pike Technologies</td>
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<td>Cut septa</td>
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<td>Shimadzu septa</td>
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