

# **Optimization of Palladium Promoted Transition Metal Catalysts for Lean Methane Oxidation**

Undergraduate Thesis

Presented in Partial Fulfillment of the Requirements for Graduation with  
Honors Research Distinction in the College of Engineering

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November 19, 2020

# Abstract

The substantial increase in greenhouse gases in the atmosphere has been linked to global warming. Although carbon dioxide ( $\text{CO}_2$ ) has the largest contribution to the increase in the Earth's temperature, methane ( $\text{CH}_4$ ) has a global warming potential (GWP) that is 25 times that of  $\text{CO}_2$  and must be regulated as well due to this significant impact. This issue is exemplified by fugitive methane emissions from coal mining, which have a considerable contribution to anthropogenic methane emissions in the United States. In this study, a stable and economical system was investigated for catalytic  $\text{CH}_4$  mitigation with a state-of-the-art catalyst for the complete combustion of methane. Palladium (Pd)-based supported catalysts show high activity for the methane oxidation reaction but are very sensitive to the poisonous effect of water vapor. This sensitivity is problematic as water vapor is a product of the methane oxidation reaction and is present in the coal-mine ventilation air along with methane. A cobalt (Co)-based system was proposed as an alternative to the Pd-based catalysts, to avoid this water vapor sensitivity. The characterization technique of X-Ray diffraction (XRD) and temperature-programmed reduction (TPR) were utilized for determining the physical and chemical properties of the resulting Co-based catalysts. Methane oxidation activity tests were performed on the synthesized Pd-based and Co-based catalysts, both in the presence and absence of water vapor. These characterization and activity tests demonstrated that despite the higher light-off temperatures of Co-based catalysts compared to Pd-based catalysts, the Co-based catalysts were significantly more resistant to the poisonous effect of water vapor. This resistance was maintained for levels of water vapor present in a typical ventilation air methane (VAM) stream as well as that produced during the oxidation reaction. Comparatively, Pd-based catalysts suffered from lower activity in the presence of water vapor due to the formation of the non-active Pd-OH phase. Therefore, the Co-based catalysts are a well-founded alternative as they did not display deactivation due to the presence of  $\text{H}_2\text{O}$  in the reaction medium, and still allowed for methane combustion.

## Acknowledgements

I would like to thank all those in the Heterogeneous Catalysis Research Group for enabling me to pursue this research for the last two years. This opportunity was very sentimental to me. Not only has it opened my eyes to the importance of taking pride in what you are working on, but also in finding pleasure in the people you are working with, which helps shape your overall learning experience.

A special thank you to Dr. Umit Ozkan for being an amazing advisor. Joining your group has been one of the best decisions of my undergraduate experience. Thank you for providing me with access to these opportunities, and for writing recommendation letters for research internships and now for graduate schools. Your endless efforts and resources have been greatly appreciated.

I want to thank Dr. Seval Gunduz and Dr. Deeksha Jain for working closely with me. I am very grateful for their guidance and support, and for the time you took to teach techniques to me and help me understand the project. Your mentorship has taught me invaluable lessons that will aid me throughout my career. Deekha, thank you for allowing me to work alongside you and for always being there with tips and safety guidance. Seval, thank you for being a helping guide the way through this research, demonstrating new methods, patiently working with me, and reviewing my paper and presentation drafts.

I express my gratitude for my family and friends who inspired me and supported me through all the ups and downs of life. Their belief in my abilities, and celebration of my achievements has been encouraging and motivating.

I would also like to thank the College of Engineering for supporting me financially with an Undergraduate Research Scholarship. Lastly, I would like to thank the William G. Lowrie Department of Chemical and Biomolecular Engineering for allowing me to learn, grow, and find academic success and opportunities.

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# 1 Introduction

## 1.1 Background and Motivation

Greenhouse gases pose a threat to our environment, and reducing these emissions is a key component of combating climate change. Carbon dioxide is widely regarded as a large contributor because it makes up the majority of emissions as seen in Figure 1, but the effect of methane must not be discounted. This is because methane has a global warming potential (GWP) 25 times that of carbon dioxide. Emissions from coal mines make up almost 10% of the US methane emissions, therefore this represents the great need of a methane mitigation technology in this sector. Methane emissions from coal mines were over 237 million metric tonnes CO<sub>2</sub> equivalents in 2000, and increased to 584 million metric tonnes CO<sub>2</sub> equivalents in 2010 [4]. In these mines, there is a large volumetric flow rate, and a low methane concentration making it challenging to combust. Another issue is that methane is a highly stable and inert molecule, and cannot be oxidized using simple oxidation processes at low temperatures [5]. Additionally, the catalytic oxidation of methane is particularly difficult when comparing hydrocarbons due to the strength of the C-H bonds [6].

The ventilation systems in coal mines require methane mitigation systems. While necessary for the safety of workers, these systems cause ventilation air methane to be released to the atmosphere at concentrations of around 1% methane. There are two main methods for mitigating these low levels of methane: The ancillary approach uses ventilation air methane as a supplemental fuel for combustion, and the principal method uses ventilation air methane as the primary fuel to oxidize methane to carbon dioxide. The principal approach is investigated here, as ancillary only utilizes a fraction of the methane, while principal can have complete combustion. This catalytic combustion method uses flameless combustion and is ideal for highly diluted air and methane streams. When considering

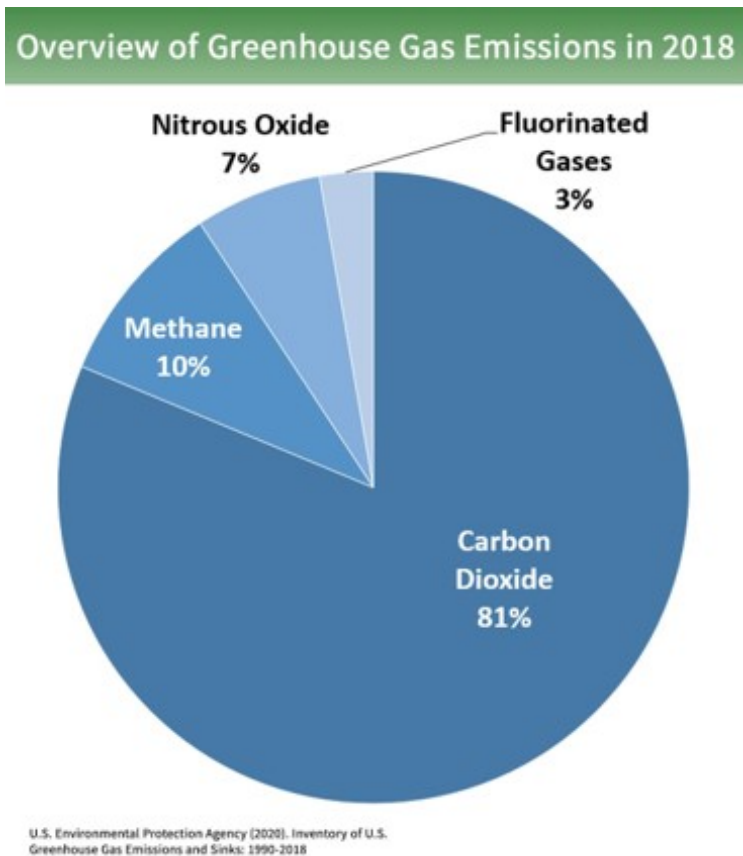


Figure 1: Major greenhouse gases [1]

methods of principal conversion, catalytic conversion is preferred to thermal conversion due to lower operating temperatures and nitrogen oxide emissions.

The catalysts were analyzed to gain information about their crystal structures using X-ray diffraction, by finding matches to peaks of known elements. Gas chromatography was used to examine and quantify the components of the reactant and product streams. The reactant stream had methane, air, and an inert gas in order to be able to test different oxygen to methane ratios while keeping the methane concentration the same in all the activity experiments. Carbon dioxide and water were found in the product stream. A 100% conversion of methane was targeted, but any incomplete reaction will also have methane in the product stream. Catalyst characterization was done using X-ray diffraction. Initial



activity tests were used to find the best catalyst candidates. Temperature programmed reduction investigated the reducibility of the active  $\text{Co}_3\text{O}_4$  phase. And lastly methane conversion tests were completed to compare the effect of a promoter and to test water stability.

Without catalysts for controlled combustion of methane, the coal mine emissions will continue to have a negative effect on the environment. Ventilation air shafts are naturally humid and will cause PdO catalysts to deactivate if methods are not used to prevent this. The metal oxide based catalysts will provide a solution to the problem of water deactivation and will be beneficial to the environment.

## 1.2 Literature Review

Studies have been completed on palladium-based catalysts and unsupported metal oxide catalysts. It was found that when reacted with sufficient oxygen, the only carbonaceous product of methane oxidation is carbon dioxide, but carbon monoxide is also formed with lower oxygen concentrations [7]. Noble metals, especially Pt and Pd, are used in combustion catalysts due to their high specific activity [8]. Other benefits are that Pt remains in its reduced state over the reaction conditions, but Pd is preferred because it has higher activity due to its formation of PdO [6]. It has been found that PdO is the active phase for this reaction, and forms via calcination between 300°C and 400°C [9]. Past experiments have been done with noble metals of palladium and platinum with alumina supports [10]. Despite positive results, this approach can be improved due to the scarcity and high cost of noble metals. Though catalytic combustion has typically been done using noble metals, these are downsides. Noble metals such as Pd and Pt are expensive, rare, and also can sinter: compacting into a solid mass [8]. This results in decreased activity as pores collapse causing reduced surface area. Another limitation is that palladium catalysts are can be sensitive to water, as the water in the feed stream will deactivate the PdO active sites to form the

less active PdOH [11]. Other studies have been complete on palladium-based catalysts and unsupported metal oxide catalysts.

Therefore, as an alternative to noble metals, transition metals can be used to prepare lean methane oxidation catalysts. Transition metal oxides are used because they offer technical and commercial advantages, and the transition metal oxide cobalt (II,III) oxide ( $\text{Co}_3\text{O}_4$ ) showed excellent promise when performing catalytic combustion of methane [12]. This is due to the  $\text{Co}^{2+}$  at tetrahedral sites and  $\text{Co}^{3+}$  at octahedral sites [8]. A unit cell ball-and-stick model of  $\text{Co}_3\text{O}_4$  is shown in Figure 2.

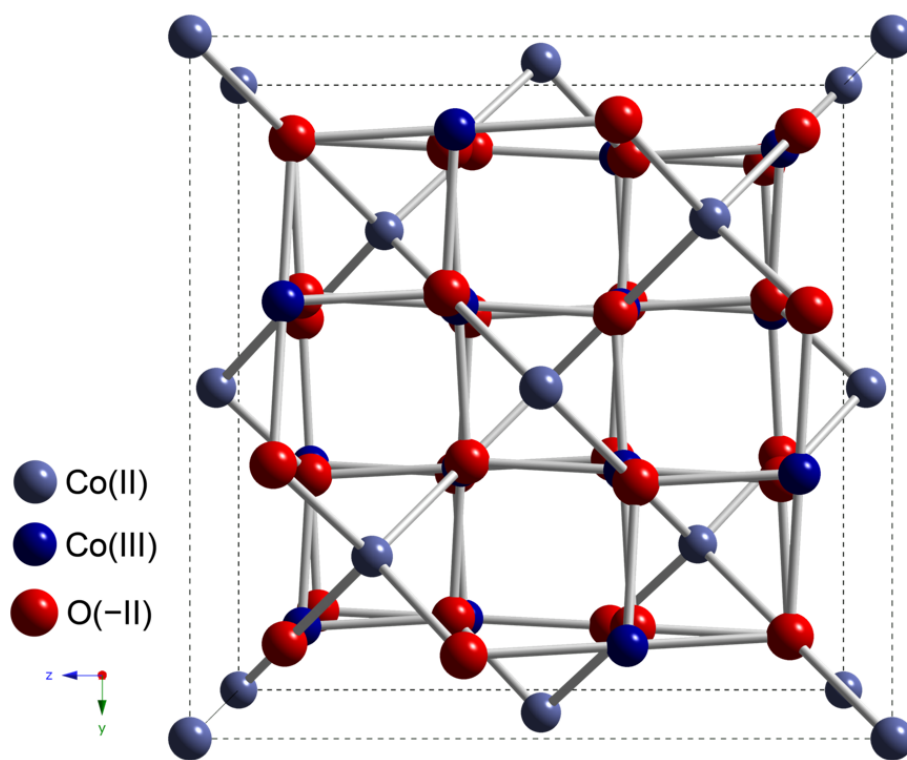


Figure 2: Unit Cell of  $\text{Co}_3\text{O}_4$  [2]

Oxygen mobility is a key component of catalysis methane oxidation with metal oxide

supports. Oxygen can be exchanged from the metal oxide and then bonded with the catalyst such as Pd, before being used in the reaction [13]. Oxidation over metal oxides involves the activation of gas-phase oxygen with the catalyst surface. This activation starts with dissociative adsorption on the catalysts, including coordination, electron transfer, incorporation into a lattice. At the end of this process, there are two states of oxygen: highly active absorbed oxygen and lattice oxygen [6], which can both play a role in oxidation.

## 2 Methodology

### 2.1 Catalyst Preparation

The beginning methods of the project started with the synthesis of catalysts, which was done using a wetness impregnation technique. This involves the filling of catalyst pores by suspending the catalytic support in a solution of aqueous metallic pre-cursor. In this experiment cobalt was used on metal oxide support materials of alumina, silica, zirconia, and ceria. A loading of 10 mol% Co was used in all cobalt catalysts.

The experimental synthesis procedure was as follows:

1) Weigh out 1g of support, and the 10% mol equivalent of cobalt, calculated according to Equation 1. The calculated masses for the synthesized catalysts are shown in Table 1.

$$1.0g \text{ support} \times \frac{1 \text{ mol support}}{MW \text{ support}} \times \frac{\% \text{ mol catalyst}}{\text{mol support}} \times MW \text{ catalyst} = \text{grams catalyst} \quad (1)$$

2) Dissolve support in 20mL DI water in a 50mL beaker.

3) Using stir plate, mix for 30 minutes with no heat.

4) Impregnate with cobalt nitrate solution:

- Dissolve cobalt nitrate in vial of water. With the catalysts involving Pd promotion, the order of mixing and addition is being varied at this step.

- Add dropwise to support solution slowly while stirring.

5) Cover beaker with Parafilm and stir for 3 hours.

6) Remove Parafilm and put beaker in a water bath for homogeneous heating.

7) After water has evaporated, dry in oven overnight at 110°C. If the resulting dried material is coarse, it is ground with a mortar and pestle.

8) Once the mixture was dried, the synthesis was finished with a 3 hour calcination in

Table 1: Calculated Masses for Catalyst Synthesis

<b>Alumina Calculations</b>	
	1.0 g Alumina
	0.2854 g Cobalt Nitrate Hexahydrate
	0.3494 g Cobalt Acetylacetonate
<b>Silica Calculations</b>	
	1.0 g Silica
	0.4844 g Cobalt Nitrate Hexahydrate
	0.5930 g Cobalt Acetylacetonate
<b>Ceria Calculations</b>	
	1.0 g Ceria (nanopowder <25nm)
	0.1691 g Cobalt Nitrate Hexahydrate
<b>Zirconia Calculations</b>	
	1.0 g Zirconia (monoclinic)
	0.2362 g Cobalt Nitrate Hexahydrate
<b>Palladium Calculations</b>	
	1.0 g Zirconia (monoclinic)
	0.2362 g Cobalt Nitrate Hexahydrate
	0.0202 g Palladium Nitrate Hydrate (1.0 mol% of zirconia support)

air at 400°C. The sample is prepared in a glass boat for calcination with air at 400°C flowing through a glass tube in a furnace. This process is to remove unwanted parts of the precursors such as the nitrate, as well as to oxidize cobalt.

The metal oxide solutions mixed before impregnation can be seen in Figure 3. The impregnated mixture stirring in the hot-water bath is shown in Figure 4. The catalysts at end of synthesis following calcination can be seen in Figure 5. As some of the catalysts such as silica were light in texture, they were pelletized to reduce its volume before analysis to be more consistent with more dense catalysts. Additionally, the sample are pelletized to compress the catalyst, so they will use a smaller bed to eliminate pressure drop in the reactor.

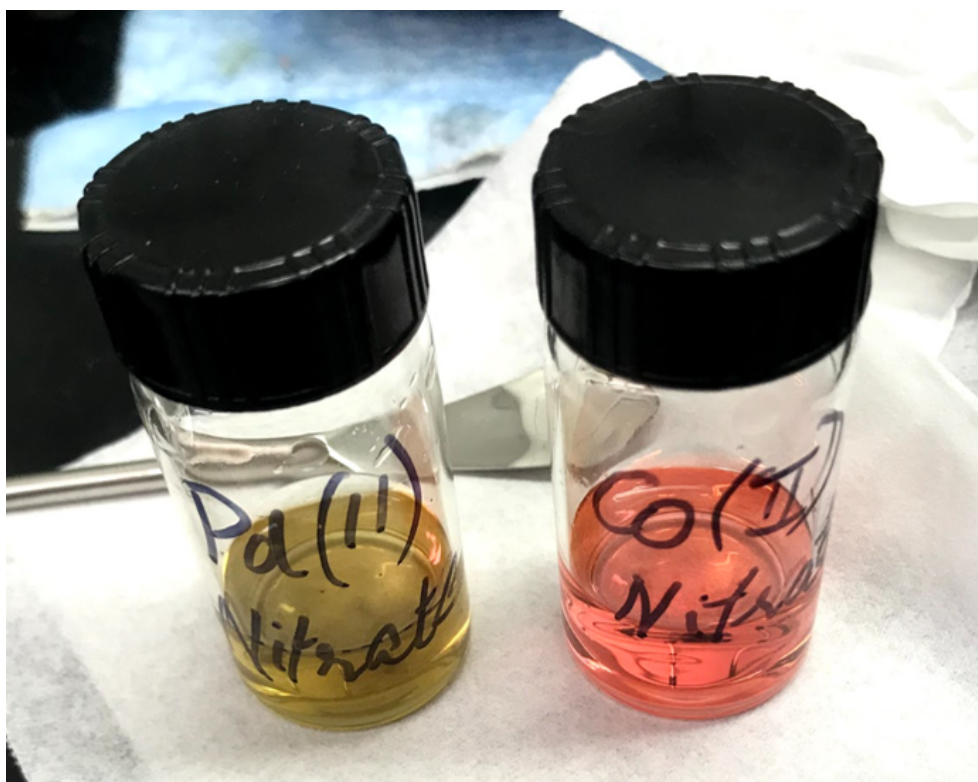


Figure 3: Metal Oxide Mixtures Before Impregnation Onto Support

## 2.2 Catalyst Characterization

Catalyst Characterization was done using X-ray diffraction (XRD) as seen in Figure 6. The cobalt samples were measured for their XRD diffraction pattern using a Bruker D8 Advance X-Ray Powder Diffractometer to study the bulk crystal structure. For the XRD, first one must clean the glass plate with ethanol, then load the catalyst on and press it flat. The first position on the device was used, and the device was set to the parameters shown in Table 2.

The catalyst was placed in the center and then illuminated with x-rays, from the source tube to the detector on the other side. The signal from the detector was recorded as an intensity, with the peaks related to atomic structure, which are unique to the components in the sample. The high energy x-rays were scattered at specific angles, which can be

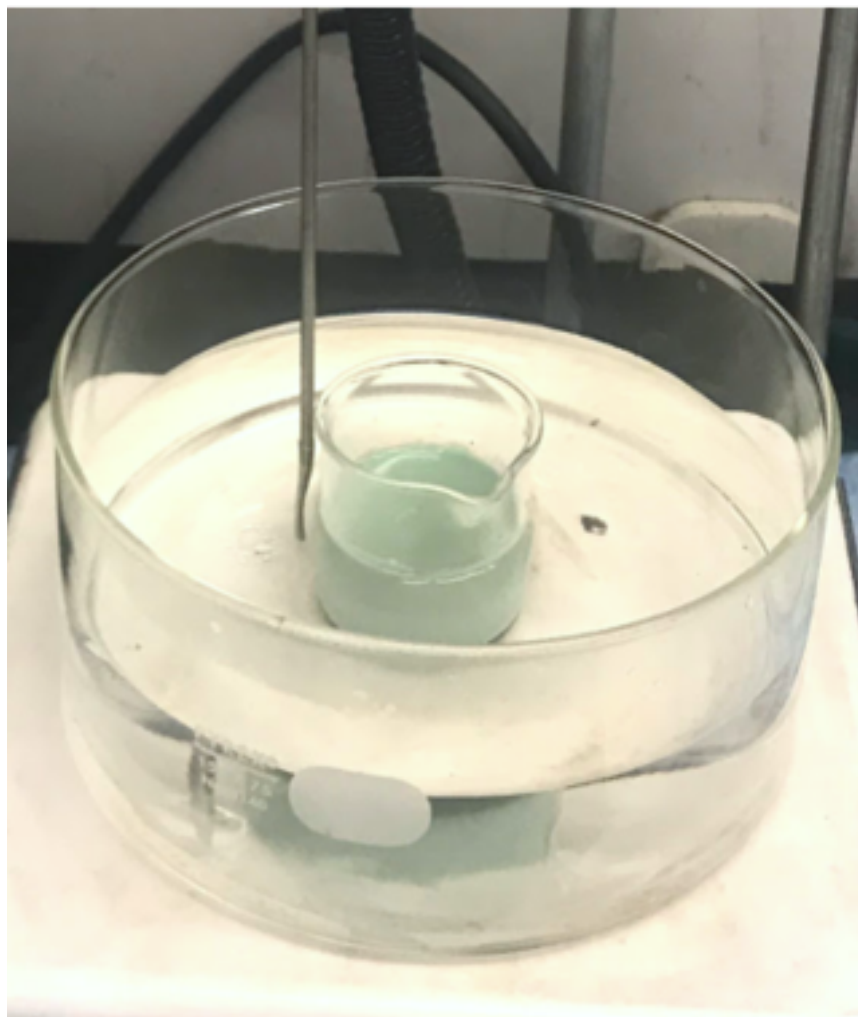


Figure 4: Wet Impregnation Mixture

related to the x-ray wavelength and distance between atomic planes. This relationship is demonstrated with Bragg's law in Equation 2, where  $d$  is the distance between atomic planes,  $\lambda$  is the x-ray wavelength, and  $\theta$  is half of the  $2\theta$  angle of the scattered x-ray.

$$n \lambda = 2 d \sin(\theta) \quad (2)$$

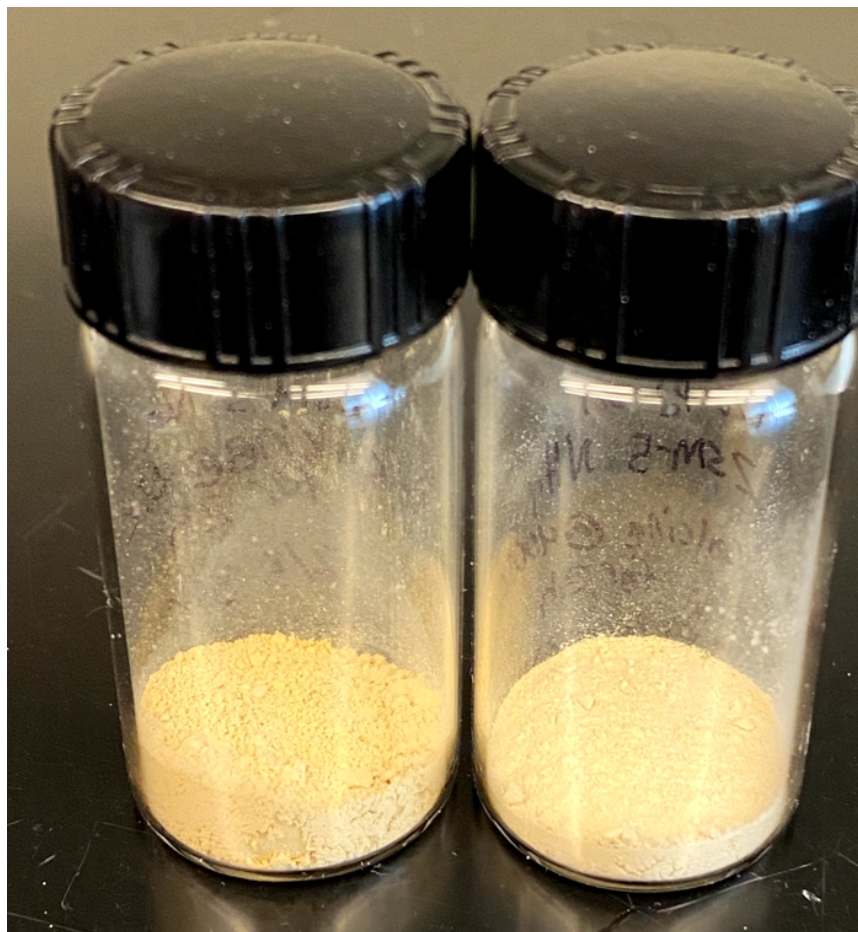


Figure 5: Catalysts at End of Synthesis

### 2.3 Activity Tests

Initial activity tests were used to find the best catalyst candidates. The reactor system uses a packed bed, with bench scale trials to replicated ventilation conditions seen in Figure 7. The methane oxidation tests were carried out using 50mg of catalyst with a bed height of 0.4cm. The reaction was in a packed bed in a 1/4 inch outside diameter quartz tube. The gas hourly space velocity (GHSV) was  $61000\text{h}^{-1}$  with a total volumetric flow rate of 50 sccm, 1% methane, varying oxygen from 2 to 21%, and with the balance of helium.



Table 2: XRD Operating Parameters

D8 ADVANCE XRD
Flat plate mode
0.6mm slit
0.5s dwell time
$2\theta$ increment of $0.014^\circ$
$2\theta$ range of $20-90^\circ$
Generator voltage of 40V
Current of 40mA



Figure 6: X-ray Diffraction Instrument

### 2.3.1 Initial Activity Screening Tests

The catalytic activity screening tests were performed in a temperature range of 450-850 °C on metal oxide supported catalysts: 10% Co/ZrO<sub>2</sub>, 10% Co/CeO<sub>2</sub>, 10% Co/SiO<sub>2</sub> and

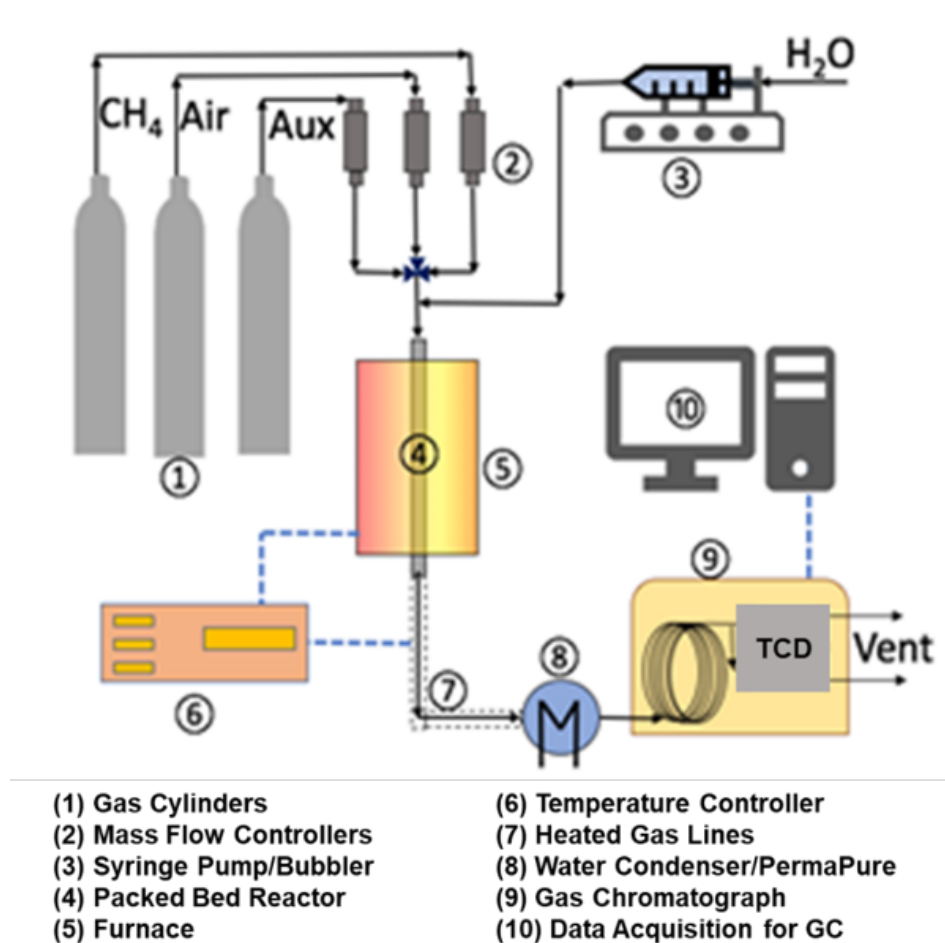


Figure 7: Activity Test System [3]

10% Co/Al<sub>2</sub>O<sub>3</sub>. These experiments used a bed height of 0.4cm with 35 mg of catalysts. The total gas flowrate was set to 50 sccm, with a composition of 0.4% CH<sub>4</sub>, 4.6% O<sub>2</sub> and balance of helium and nitrogen. For all catalysts except silica, the GHSV was 61000 h<sup>-1</sup>, which was made with a bed height of 0.7 cm due to its lower density, and therefore had a GHSV of 35000 h<sup>-1</sup>. The feed stream was analyzed using a micro gas chromatograph before each initial activity test.

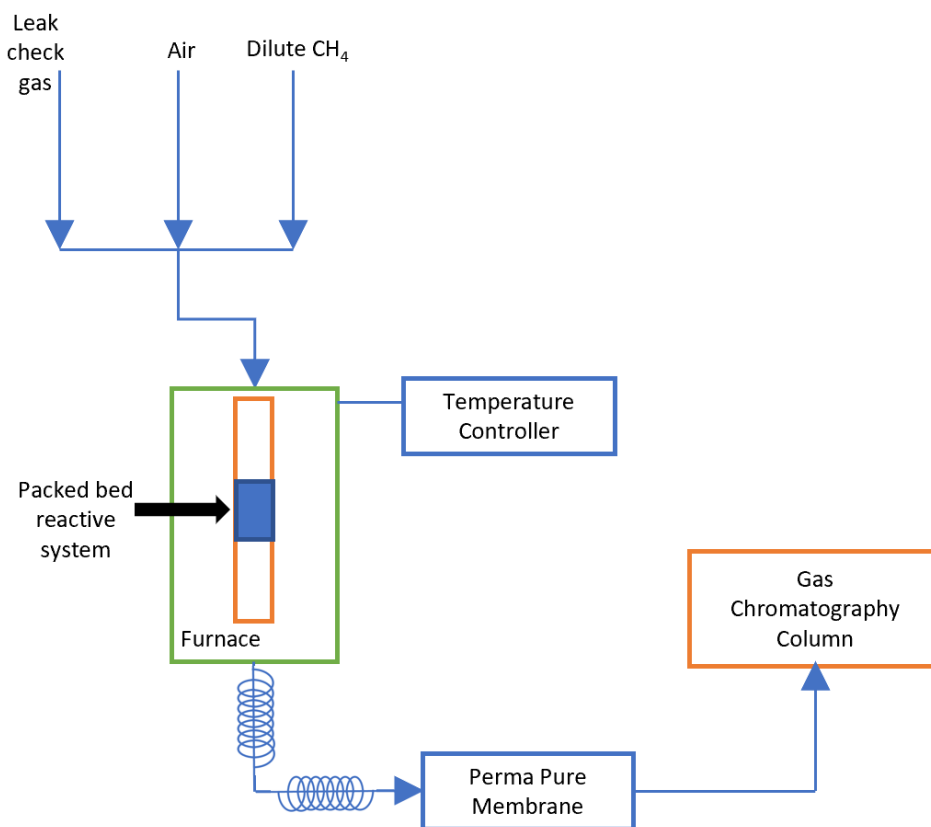


Figure 8: Test System

### 2.3.2 Promoter Activity Tests

The catalytic activity tests were then done on Co-based (10% Co/ZrO<sub>2</sub>), Pd-promoted Co-based (Co-Pd-ZrO<sub>2</sub>, Pd-Co-ZrO<sub>2</sub>, Pd+Co-ZrO<sub>2</sub>) and Pd-based (1% Pd/ZrO<sub>2</sub>) catalysts. For each experiment, the bed height was 0.4cm, with 50 mg of catalysts used. Mirroring the initial activity screening tests, the reactant gas composition was set to 0.4% CH<sub>4</sub>, 4.6% O<sub>2</sub> and balance helium and nitrogen with a total volumetric flowrate of 50 sccm.

### 2.3.3 Activity Tests on the Effect of Water

The catalytic activity tests were done with Pd- and Co-incorporated catalysts: 1% Pd/ZrO<sub>2</sub> and 10% Co/ZrO<sub>2</sub>. For each experiment, the bed height was 0.4cm, with 50 mg

of catalysts used. Mirroring the initial activity screening tests, the reactant gas composition was set to 0.4% CH<sub>4</sub>, 4.6% O<sub>2</sub> and balance helium and nitrogen with a total volumetric flowrate of 50 sccm. The GSHV was 61000 h<sup>-1</sup> for both catalysts. The feed stream was analyzed using micro GC before each test. For the dry tests, not water was added to the feed stream. To test the effect of the presence of water, the feed gas mixture was sent to a water bubbler first to make a saturated feed with water. The amount of water sent to the reactor was 3% in all the activity experiments conducted in the presence of water.

## 2.4 Temperature Programmed Reduction Tests

Next, temperature programmed reduction using a thermal conductivity detector investigated the reducibility of the Co<sub>3</sub>O<sub>4</sub> active sites. This was to check for oxygen mobility as well, because if oxygen was more mobile, then it would react to form water at lower temperatures. The temperature programmed reduction was done with 5% hydrogen in nitrogen, analyzing the water output produced using a mass spectrometer.

A 50mg catalyst was packed in a quartz tube reactor. Quartz wool was used for packing, to plug the middle of the reactor tube. The catalyst was put in the long side of the tube, and the wool was added after that. First, before changing the reactor parameters, the valve to the mass spectrometer was closed, and the helium valve was turned off. The system was flushed with a 5% H<sub>2</sub>/N<sub>2</sub> stream of 30mL/minute at room temperature. Next, put the tube in with components and the O-ring. Then the gas flow was checked to be 30mL/min. Then the valve to send gas to the mass spectrometer was turned on, taking 10mL/min. The gas analyzer used was an MKS Cirrus bench top residual gas analyzer.

The reaction process starts out with just helium in the feed stream, then is switched over to 5% hydrogen with the balance of nitrogen. The heating begins at room temperature, then with a ramp rate of 10 degrees Celsius per minute up to 1000 degrees Celsius. The temperature is held at 1000 degrees Celsius for 1 hour, then the gas is switched to helium

and the temperature decreased back to room temperature. This reaction procedure is shown in Figure 9. The signal for water of 18 amu, was measured to investigate the reducibility of the catalyst.

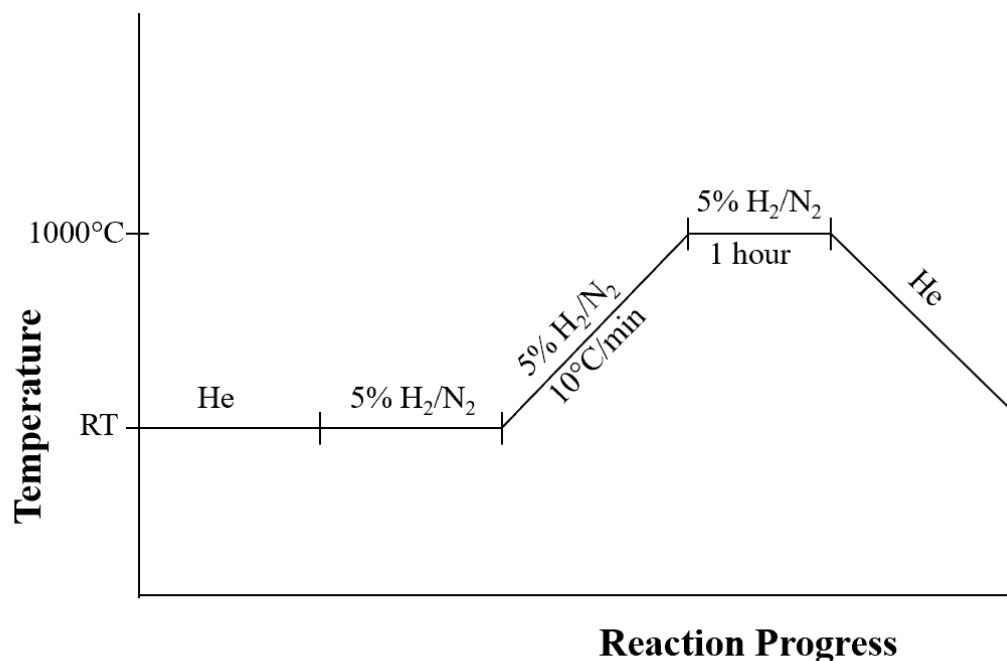


Figure 9: TPR Heating Scheme

## 2.5 Effect of Promoter

Based on the results from the screening activity and TPR tests, the cobalt zirconia catalyst was chosen as the best catalyst from those synthesized. Next, the effect of promoter addition on the cobalt zirconia catalyst was investigated. Palladium was selected as the promoter because Pd/PdO is the active phase for conventional catalytic methane combustion. The order of addition of this promoter was also investigated. 1%Pd-ZrO<sub>2</sub> is the 1% Pd catalyst which was included for comparison. Even though it shows the best activity, it is not reliable as it does not have resistance to water. Next are the three Pd-promoted catalysts, varied in synthesis order.

With Pd+Co-ZrO<sub>2</sub>, the Palladium and cobalt solutions were mixed and then added together on zirconia. For Pd-Co-ZrO<sub>2</sub>, it was cobalt first on zirconia, then palladium on that mixture. Then with Co-Pd-ZrO<sub>2</sub>, it was first palladium on zirconia, then cobalt onto the mixture. Lastly, 10%Co-ZrO<sub>2</sub> was the catalyst from previous tests, which has no palladium.

Methane conversion tests were done to compare the effect of a promoter and to test water stability.

## 2.6 Stability Tests

The long-term stability was investigated using a time-on-stream test. This activity test was conducted using 35 mg catalyst (catalyst bed height of 0.4 cm). The gas composition was 0.4% methane, 4.6% oxygen, with the balance helium and nitrogen. The GHSV was 61000 h<sup>-1</sup> and the total volumetric flow rate was 50 sccm. The Time-on-stream tests were for the long-term stability of the methane combustion catalysts, and a good result would be the catalysts maintaining the same initial conversion with no activity loss [8]. Next, methane conversion tests were completed to test the water stability of the catalysts, comparing the activity of the Pd and Co catalysts in the presence and absence of water.

### 3 Results and Discussion

#### 3.1 XRD Catalyst Characterization

The XRD characterization aimed to investigate crystalline structures, diffraction patterns, and crystal phase composition and morphology. The red bars in Figure 10 are the peak locations for the  $\text{Co}_3\text{O}_4$  diffraction pattern. This indicated that Cobalt has been oxidized during the calcination process to form  $\text{Co}_3\text{O}_4$  for these catalysts. Pd or PdO was not detected meaning it was highly dispersed in the support.

Later the XRD was done on the Pd based and Pd promoter Co catalysts, and the XRD results did not show any difference between the Pd-promoted catalysts.

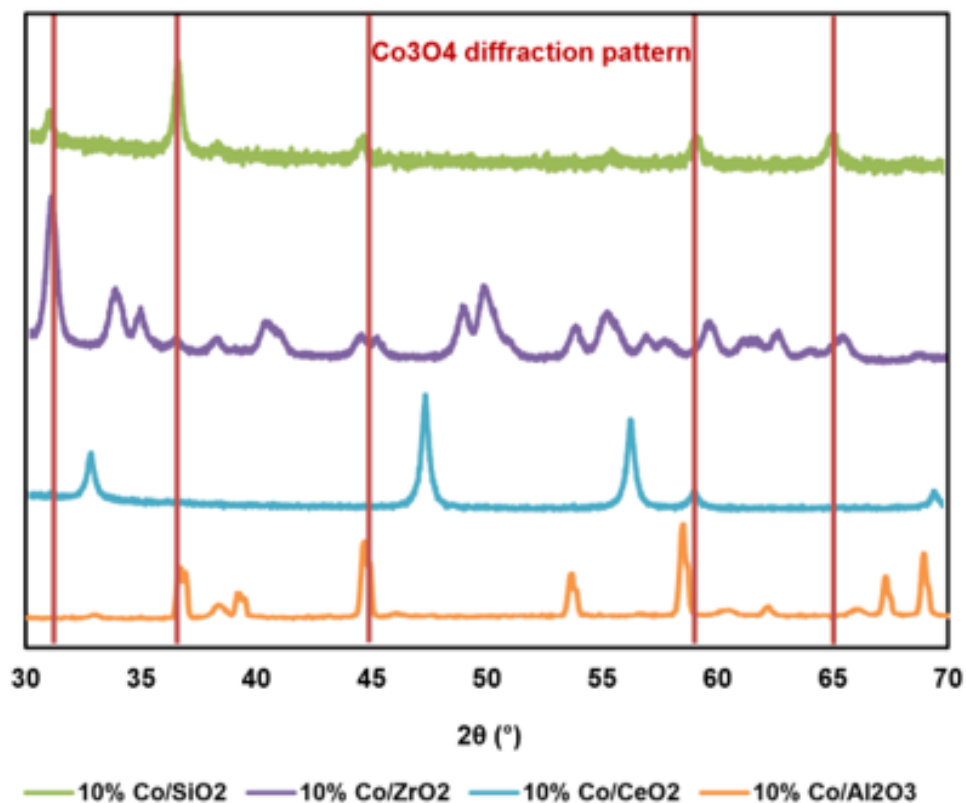


Figure 10: XRD Patterns for Cobalt Catalysts

### 3.2 Temperature Programmed Reduction Tests

The area under these curves in Figure 11 is useful for identifying the amount of active  $\text{Co}_3\text{O}_4$  phase reduced to  $\text{CoO}$  and  $\text{Co}$ . The greatest area for the silica catalyst indicated that the most  $\text{Co}_3\text{O}_4$  had been reduced, whereas the least area for the zirconia catalyst indicated that the least  $\text{Co}_3\text{O}_4$  had been reduced. This resistance to reduction is a preferred feature in the zirconia catalyst. The zirconia catalyst's behavior was attributed to zirconia's high redox abilities, as an oxygen donor to the  $\text{Co}_3\text{O}_4$  phase to protect it from extensive reduction.

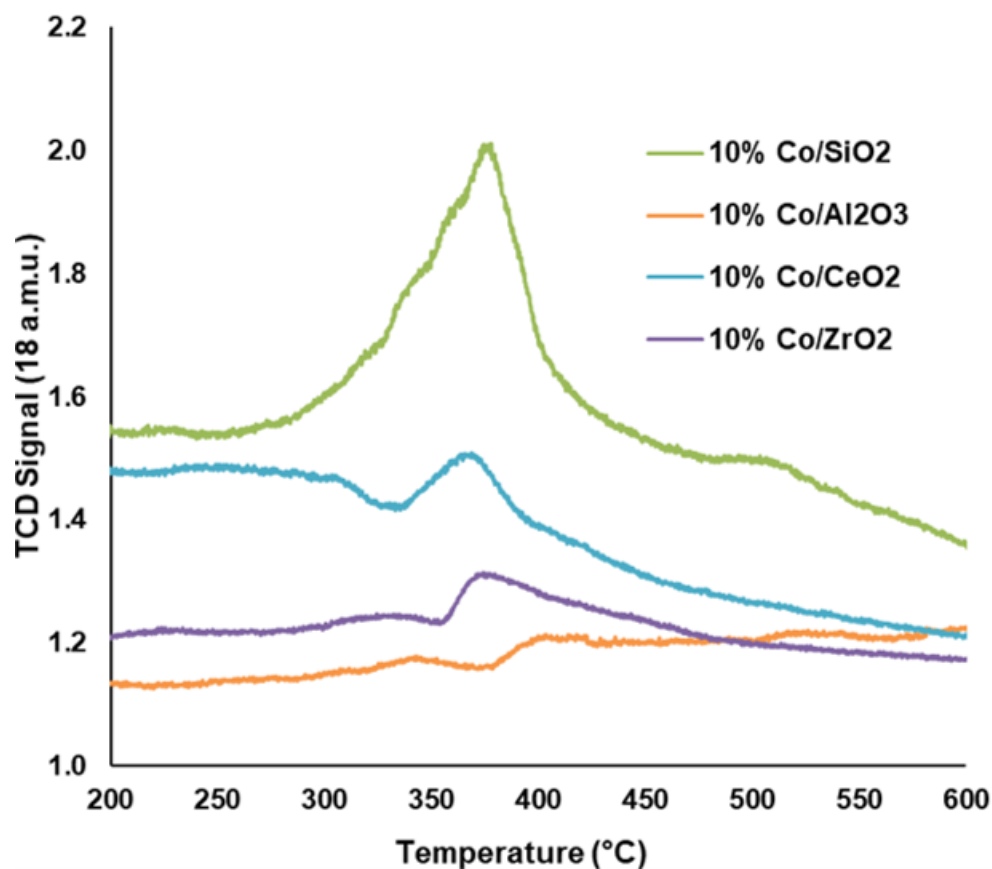


Figure 11: TPR Tests of 10%  $\text{Co/SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{ZrO}_2$

Therefore based on these TPR results showing resistance to further reduction of the active phase of methane combustion as well as the activity screening results, the cobalt



zirconia catalyst was chosen to as the best methane oxidization catalyst of those tested.

### 3.3 Activity Tests

The methane conversion was calculated in terms of the CH<sub>4</sub> inlet and outlet concentrations as shown in Equation 3.

$$\text{Methane Conversion, } x = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (3)$$

#### 3.3.1 Catalyst Activity Comparison

The activity tests in Figure 12 showed that the silica catalyst had higher conversion at lower temperatures, and at higher temperatures was similar to the zirconia catalyst. The silica activity was higher than expected, but this was due to it having higher surface area and lower gas hourly space velocity because of its lower density. These results showed there were still multiple possible candidates, further tests needed to be done.

#### 3.3.2 Effect of GHSV on Activity

Previous experiment showed that the higher activity of 10% Co/SiO<sub>2</sub> could be due to higher GHSV as it has a lower density, the effect of GHSV on activity was explored. This was demonstrated in Figure 13, which showed that the methane conversion activity was higher when the GHSV was lower. This can be explained by when the reaction system has a low GHSV, the reactants spend more time in the reaction bed on the active sites, giving a higher chance of reacting.

#### 3.3.3 Varying Methane Level for Activity

The effect of methane concentration was investigated by performing activity tests at 0.5, 1, 2, and 3 % CH<sub>4</sub> with excess oxygen, shown in Figure 14. This experiment used 50mg

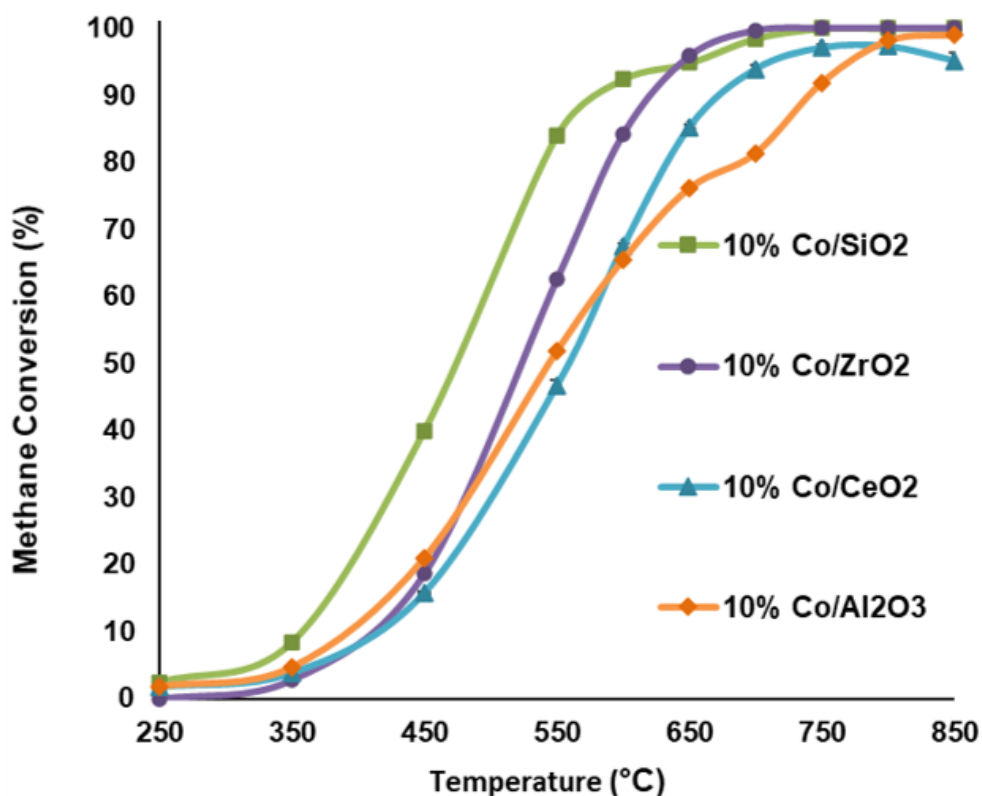


Figure 12: Lean Methane Oxidation Activity of Cobalt Catalysts

of catalyst (0.5%Pd+10%CoZrO<sub>2</sub>). The total flow rate was 50 sccm, and the GHSV was 61000h<sup>-1</sup>. The methane concentrations were diluted from a 10% CH<sub>4</sub>/He stream with air and He. This activity test resulted in very little difference between the four trials, meaning there was not a significant effect of methane concentration on the catalyst activity. This was likely because oxygen was provided in excess, so there was not competitive adsorption between methane and oxygen. This is a positive result, because oxygen levels in ventilation shafts are expected to have oxygen levels that would be considered excess. Additionally, as methane levels are expected to be around 1% or less, this shows that these catalysts would be effective at, and around, the anticipated methane concentrations.

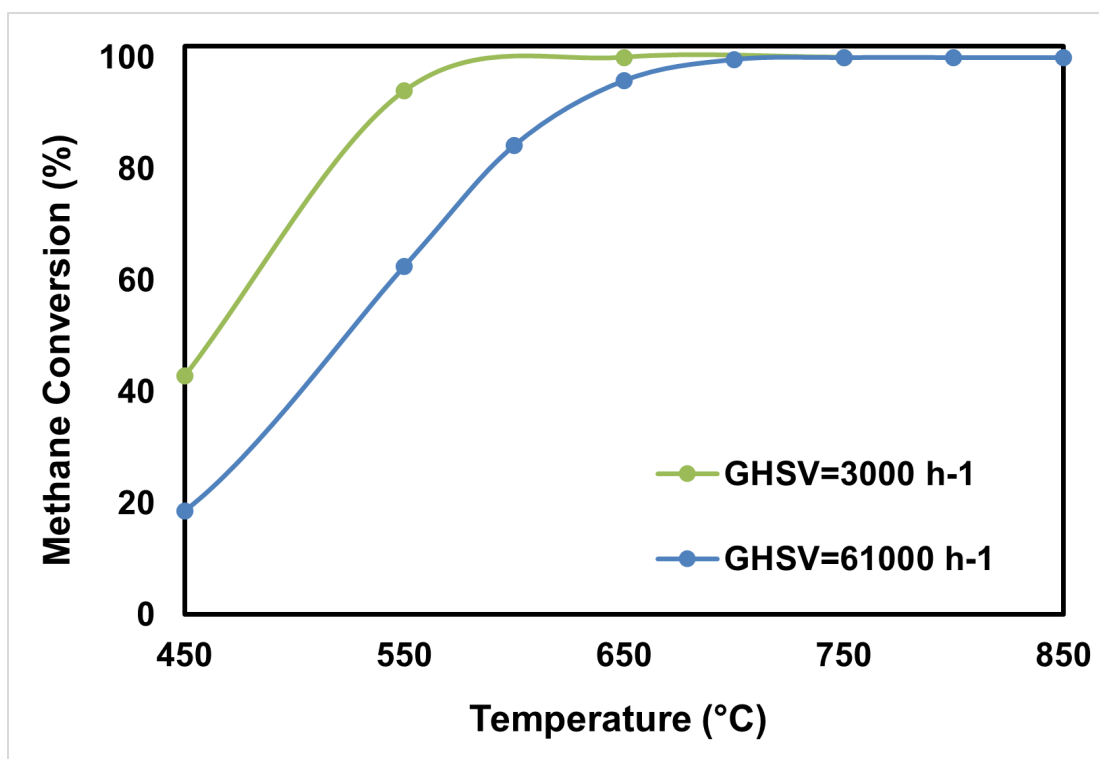


Figure 13: Activity of 10% Co/ZrO<sub>2</sub> at GHSV of 3000 h<sup>-1</sup> and 61000 h<sup>-1</sup>

### 3.3.4 Varying Oxygen Level for Activity

The effect of oxygen concentration on the activity of the 10% Co/ZrO<sub>2</sub> Catalyst was investigated next. This was completed with 50mg of the catalyst in a catalyst bed height of 0.4cm. The GHSV was 61000h<sup>-1</sup> with a total volumetric flow rate of 50 sccm, 1% methane, varying oxygen from 2 to 21%, and with the balance helium. Similar to the effect of methane concentration, all trials were relatively close in value. As seen in Figure 15, there was a slight positive effect of oxygen concentration on methane conversion. The lowest concentration of oxygen gave the lowest methane conversions, while the highest oxygen concentration in the feed gave the highest conversions. Again, this was a positive result as the highest methane conversion was with the 21% oxygen which is what the expected VAM stream condition will be.

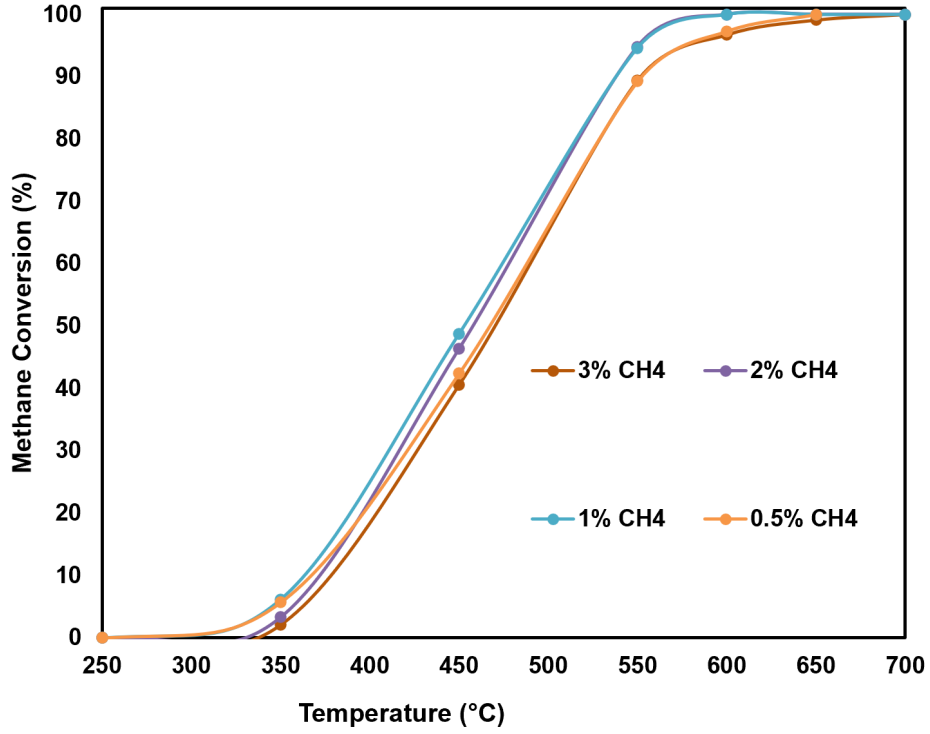


Figure 14: Methane Concentration Effect on 10% Co/ZrO<sub>2</sub> Catalyst Activity

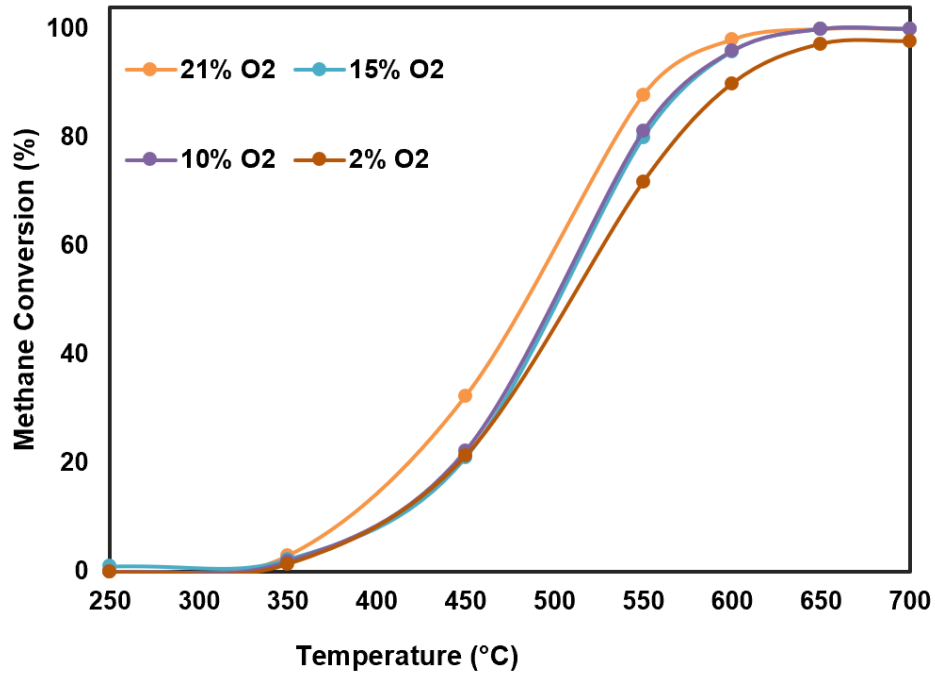


Figure 15: Oxygen Concentration Effect on the Activity of 10% Co/ZrO<sub>2</sub> Catalyst

### 3.4 Effect of Promoter

As expected, the palladium promotion caused an increase in activity. Figure 16 shows the differences between the three orders, especially in orange as it showed high activity at lower temperatures due to accessibility of Pd particles on the outer surface, but these could have been affected by water at higher temperatures and cause this apparent deactivation of the Pd sites.

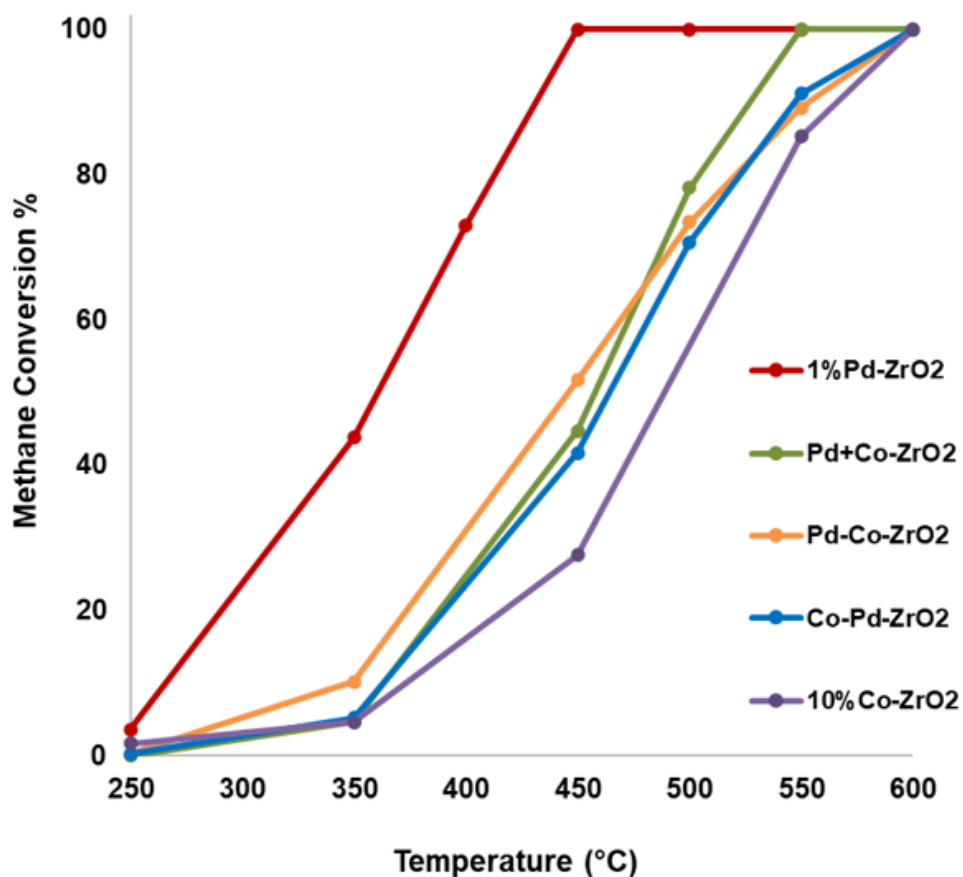


Figure 16: Lean methane oxidation activity of Pd Promoted Catalysts

## 3.5 Stability Tests

### 3.5.1 Effect of Water in Reactant Stream for Pd and Co Catalysts

The cobalt and palladium catalysts were compared using a catalytic activity test, with a temperature range of 250-600°C. The effect of water on activity was investigated by sending the feed gas mixture to a water bubbler, resulting in 3% water in the wet activity tests. 50 mg of the catalyst was used with the reactant gas of 0.4% methane and the balance He and air, a flow rate of 50 sccm and a GHSV of 61000 h<sup>-1</sup>. The activity in terms of methane conversion for the 10% Co/ZrO<sub>2</sub> catalyst is shown in Figure 17, for the presence and absence of water. The experiment was repeated with the 1% Pd/ZrO<sub>2</sub> in Figure 18.

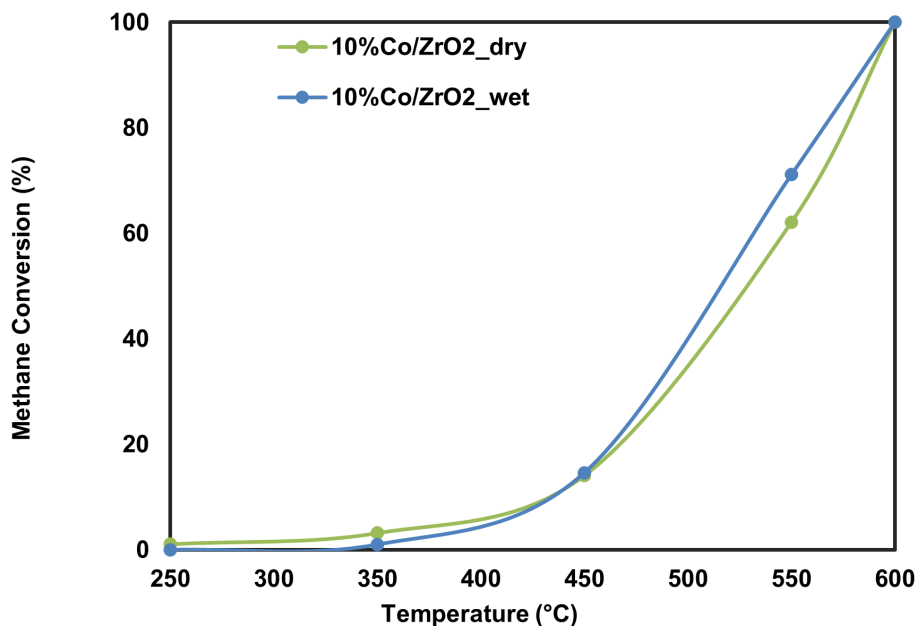


Figure 17: Dry and Wet Methane Oxidation Activity of 10% Co/ZrO<sub>2</sub>

The cobalt catalyst showed almost no effect of the presence of water, which was the desired result. Interestingly, the wet test result had slightly higher activity than the dry test at 550°C, which is ideal because the VAM is likely to have the presence of water. On the other hand, the palladium catalyst showed a negative effect on activity in the

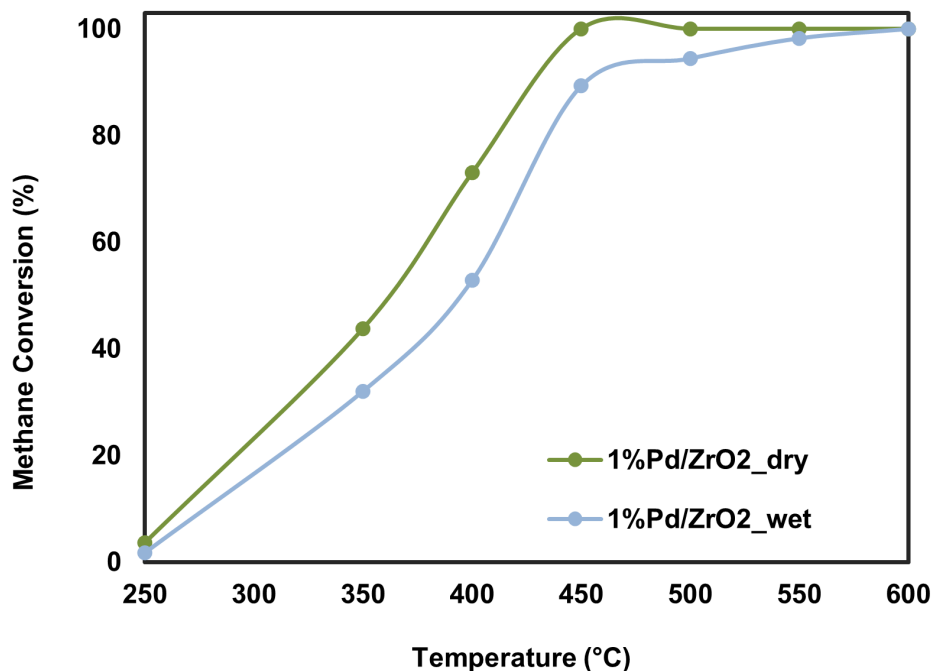


Figure 18: Dry and Wet Methane Oxidation Activity of 1% Pd/ZrO<sub>2</sub>

presence of water. At temperatures lower than 600°C, the activity of the wet test was lower than that of the dry test. This inhibition can be attributed to the conversion of active palladium oxide sites into less active palladium hydroxide sites at high temperatures. At temperatures higher than 550°C, this inhibition effect of H<sub>2</sub>O disappears, most likely due to the regeneration of the active sites, transformation of palladium hydroxide back to active PdO, in the presence of excess amount of O<sub>2</sub> in the reactant stream. Overall, although the palladium catalyst had higher activity at lower temperatures, the cobalt is preferred as it does not show deactivation. This is in addition to the known disadvantages of palladium being expensive, rare, and susceptible to sintering.

### 3.5.2 Long-Term Time-on-Stream Tests

The long-term stability was investigated using a time-on-stream test. This activity test was conducted using 35 mg catalyst (catalyst bed height of 0.4 cm). The gas composition

was 0.4% methane, 4.6% oxygen, with the balance helium and nitrogen. The temperature was held at 700°C for 24 hours, under dry conditions. As shown in Figure 19, there was not a significant decrease in methane conversion over the course of the test. Therefore, as the activity did not decrease the catalyst can be considered stable without deactivation over this time period.

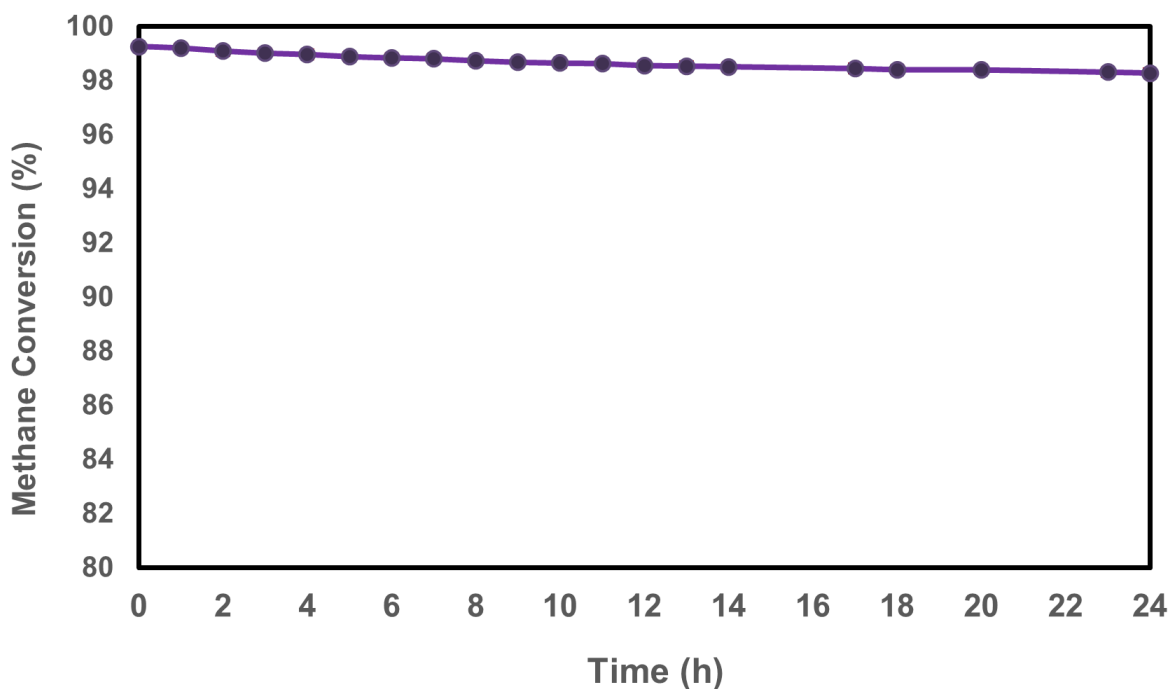


Figure 19: Dry Stability of 10% Co/ZrO<sub>2</sub>

The wet stability of 1%Pd-ZrO<sub>2</sub> in 0.5% CH<sub>4</sub> was examined next. An activity test was performed for 12 hours to test the long term stability with 3% water in the feed stream. The results of the stability test for the 1%Pd-ZrO<sub>2</sub> catalyst are shown in Figure 20. This shows the instability of the palladium catalyst over time in the presence of water.

Lastly, the effect of the 3% water in the reactant stream on the stability of the cobalt catalyst was examined. An activity test was performed at 550°C and 570°C for 12 hours to understand long term stability. The results of the stability test for the wet methane oxidation of 10% Co/ZrO<sub>2</sub> are shown in Figure 21.



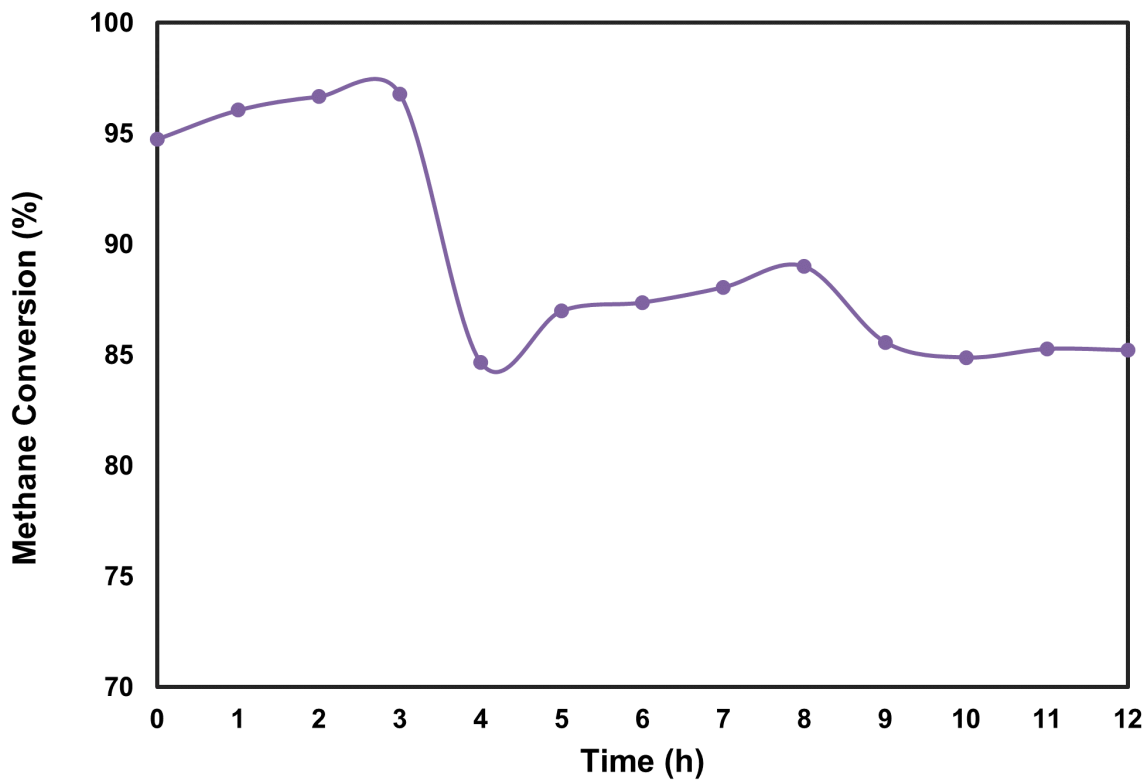


Figure 20: Wet Methane Oxidation of 1%Pd-ZrO<sub>2</sub>

As there was no significant activity decrease or catalyst deactivation, this showed that the cobalt zirconia catalyst is highly stable under reaction conditions and in the presence of water.

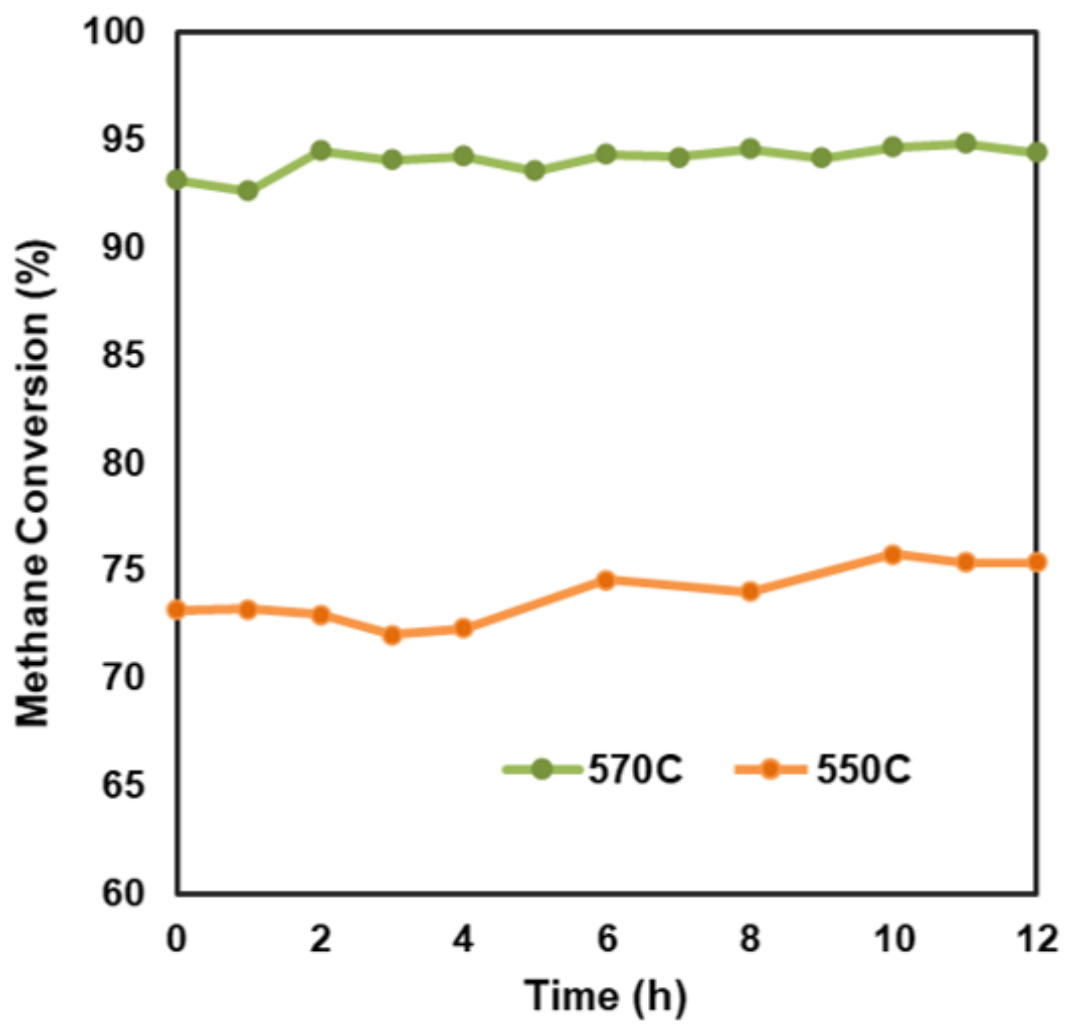


Figure 21: Wet Methane Oxidation of 10% Co/ZrO<sub>2</sub>

## 4 Conclusions

### 4.1 Summary

In conclusion, this effort aimed for the catalytic mitigation of coal mine ventilation air methane. This was achieved by synthesizing cobalt catalysts with different metal oxide support materials. Palladium promoted cobalt catalysts were shown to be similar to the palladium-based catalysts. The cobalt based catalyst, despite having lower activity, showed significant resistance to water vapor. These experiments demonstrated the potential of the cobalt zirconia catalyst, due to its resistance to the active  $\text{Co}_3\text{O}_4$  phase as well as its long-term stability. The cobalt based catalysts are the preferred solution as they are more economically feasible than palladium catalysts.

### 4.2 Future Work

Further experiments could include the investigation of the activation energy of the methane oxidation reaction. This could be informative as the reaction is very sensitive to changes in temperature: there is a large difference in activity with only small changes in temperature. For example, as seen previously in the long term stability tests in Figure 21, a difference of  $20^\circ\text{C}$  caused the methane conversion to increase from 75 to 95%. Investigating the activation energy could give insight into the specific requirements of the reaction.

The future work of this experiment involves the commercialization of these technologies. A potential design can be seen in Figure 22 for the catalytic oxidation of ventilation air methane.

This method is recommended as it reduces the required reactor temperature, because the auto-ignition temperature is lower, which also reduces nitrogen oxide emissions. Mass and energy balances on this system showed the possibility and cost-saving benefit of using the exhaust stream to pre-heat the ventilation air stream. As this project was conducted

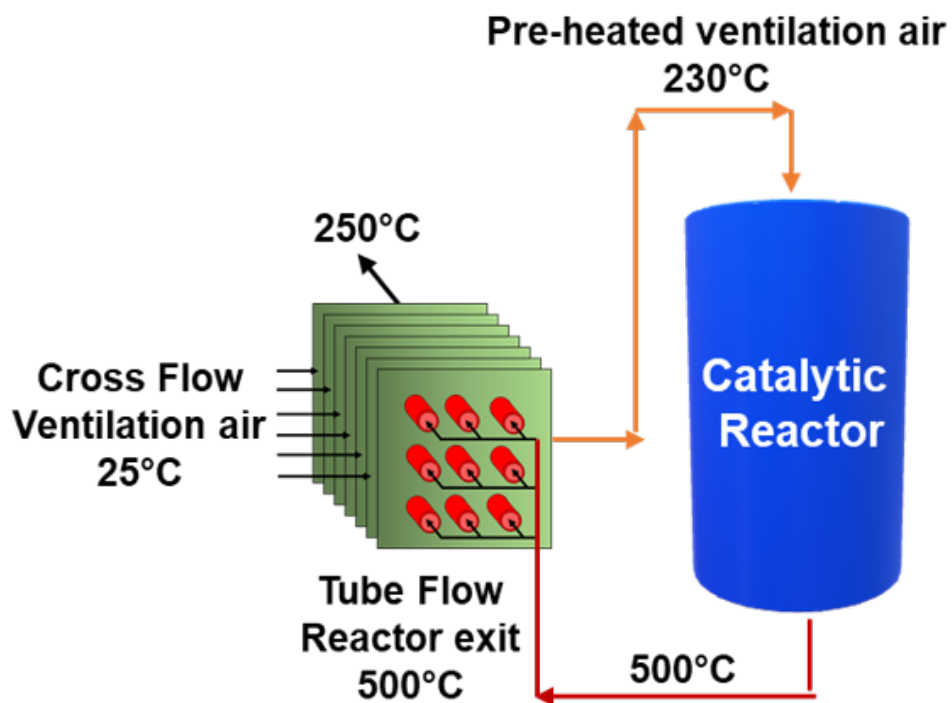


Figure 22: Commercial Design for Catalytic Oxidation of VAM [3]

at the bench-scale, additional work is needed at the pilot scale. At this larger scale, initial temperatures and pressures can be more difficult to regulate and these fluctuations would need to be tested to prevent any safety issues or potential downtime. Also the feasibility of the process would need to be verified using scaled up parameters. Lastly, extra precautions should be taken when investigating the operating parameters that lead to nitrogen oxide production, to ensure that these conditions are avoided.

## References

- [1] United States Environmental Protection Agency Greenhouse Gas Emissions. <http://www.epa.gov/ghgemissions/overview-greenhouse-gases>, Sep 2020. Overview of Greenhouse Gases.
- [2] Ben Mills. Ball-and-stick model of the unit cell of cobalt(ii,iii) oxide,  $\text{Co}_3\text{O}_4$ . *Colour code: Cobalt(II), CoII: lighter blue Cobalt(III), CoIII: darker blue Oxygen, O: red Crystal structure from J. Magn. Magn. Mater.*, pages 300–305, 2006.
- [3] Umit Ozkan, Seval Gunduz, Deeksha Jain, and Brian Wynne. Catalytic combustion of methane emitted from coal mine ventilation air systems. *OCRC Agreement Number: R-17-14*, 2020.
- [4] Yagang Zhang, Zhangfeng Qin, Guofu Wang, Huaqing Zhu, Mei Dong, Shuna Li, Zhiwei Wu, Zhikai Li, Zhonghua Wu, Jing Zhang, and et al. Catalytic performance of  $\text{mno}_x\text{-nio}$  composite oxide in lean methane combustion at low temperature. *Applied Catalysis B: Environmental*, 129:172–181, 2013.
- [5] Xiu-Hui Gao, Sheng Wang, Dian-Nan Gao, Wei-Gang Liu, Zhi-Ping Chen, Ming-Zhe Wang, and Shu-Dong Wang. Catalytic combustion of methane over  $\text{pd/mwcnts}$  under lean fuel conditions. *Journal of Fuel Chemistry and Technology*, 44(8):928–936, 2016.
- [6] Naoufal Bahlawane. Kinetics of methane combustion over cvd-made cobalt oxide catalysts. *Applied Catalysis B: Environmental*, 67(3-4):168–176, 2006.
- [7] Adi Setiawan, Eric M Kennedy, and Michael Stockenhuber. Development of combustion technology for methane emitted from coal-mine ventilation air systems. *Energy Technology*, 5(4):521–538, 2017.

- [8] Zhiying Pu, Yan Liu, Huan Zhou, Wanzhen Huang, Yifan Zheng, and Xiaonian Li. Catalytic combustion of lean methane at low temperature over zro<sub>2</sub>-modified co<sub>3</sub>o<sub>4</sub> catalysts. *Applied Surface Science*, 422:85–93, 2017.
- [9] Patrick Gélin and Michel Primet. Complete oxidation of methane at low temperature over noble metal based catalysts: a review. *Applied Catalysis B: Environmental*, 39(1):1–37, 2002.
- [10] TR Baldwin and R Burch. Catalytic combustion of methane over supported palladium catalysts: Ii. support and possible morphological effects. *Applied catalysis*, 66(1):359–381, 1990.
- [11] RFFJ Burch, FJ Urbano, and PK Loader. Methane combustion over palladium catalysts: The effect of carbon dioxide and water on activity. *Applied Catalysis A: General*, 123(1):173–184, 1995.
- [12] Christian A Müller, Marek Maciejewski, René A Koepfel, and Alfons Baiker. Combustion of methane over palladium/zirconia: effect of pd-particle size and role of lattice oxygen. *Catalysis today*, 47(1-4):245–252, 1999.
- [13] Qifu Huang, Wenzhi Li, Qizhao Lin, Xusheng Zheng, Haibin Pan, Dong Pi, Chunyu Shao, Chao Hu, and Haitao Zhang. Catalytic performance of pd–nico<sub>2</sub>o<sub>4</sub>/sio<sub>2</sub> in lean methane combustion at low temperature. *Journal of the Energy Institute*, 91(5):733–742, 2018.