

2006

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Partial oxidation of propane on ceria-and alumina-supported platinum catalysts

Vijaya Anil Bansode

**Thesis submitted to the College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemical Engineering**

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Mr. David Berry**

Department of Chemical Engineering

**Morgantown, West Virginia
2006**

Keywords: Propane, autothermal reforming, partial oxidation, reaction scheme, ceria supported platinum catalyst, alumina supported platinum catalyst

Abstract

Partial Oxidation of Propane on Ceria-and-Alumina Supported Platinum Catalysts

Vijaya Anil Bansode

Three Pt/CeO₂ catalysts and Pt/Al₂O₃ catalyst were studied for partial oxidation of propane. The 1 % Pt/CeO₂ (C) catalyst which was prepared using CeO₂ prepared by the decomposition technique showed the highest propane conversion and hydrogen selectivity. The 1 % Pt/Al₂O₃ showed better performance than 1 % Pt/CeO₂ (C).

The effect of flow rate was studied for 0.01 g and 0.02 g of 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃. Oxygen is totally consumed at all flow rates, even at 0.01 g catalyst loading for both catalysts. The total oxidation of propane is taking place first followed by steam reforming along with water gas shift and reverse Boudouard reactions. Water gas shift dominates over reverse Boudouard and is very close to equilibrium on 1 % Pt/CeO₂ (C). This indicates that ceria promotes water gas shift, whereas reverse Boudouard dominates over water gas shift on 1 % Pt/Al₂O₃.

Dedicated to my grandfather, late Mr. Shivaji R. Bansode

Acknowledgements

I am extremely grateful to my advisors Dr. Dady Dadyburjor and Dr. Edwin Kugler, for the invaluable guidance, help, time and encouragement they gave me during my graduate studies at West Virginia University. I am thankful to Mr. David Berry of National Energy Technology Laboratory, my research committee member, for his valuable suggestions and comments. The financial support from US Department of Energy is gratefully acknowledged.

I sincerely thank Dr. Tapan Das for all his help throughout this research work. I would like to express my appreciation to James Wright for carrying out BET surface area measurements. I thank my colleagues at reaction engineering laboratory, Dr. Wenping Ma and Huifang Shao for their input in my research.

I would like to thank Bonita Helmick and Linda Rogers for patiently helping me out in all important non-academic issues. I am thankful to every faculty and graduate student at West Virginia University who made my stay in Morgantown a memorable and valuable experience.

I am grateful to my parents, my grandmother, my aunt Dr. Aruna Mane and all my relatives for their motivation and support in good and in trying times. Finally I would like to thank all my friends Ajay Joshi, Aditi, Archana, Kedhar and Sandy who made these two years a wonderful experience to cherish forever.

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Chapter 1: Introduction

There has been increasing demand for hydrogen as a clean fuel for fuel cells. Hydrogen can be manufactured from solar cells or hydropower by means of electrolysis of water, but these processes do not supply enough hydrogen for potential hydrogen demand. This problem can be solved by multi-step processing of hydrocarbon-based fuels to derive hydrogen efficiently (Ayabe *et al.*, 2003).

Fuel cells can be used for transportation and also for stationary and portable power generation. The advantages of fuel cells are their high efficiency and lower emissions of pollutants. Fuel cells will lower emission of pollutants such as carbon monoxide, nitrogen oxides (NO_x) and sulfur oxides (SO_x). Fuel cells can operate on hydrogen, but the constraint on using hydrogen-fueled vehicles is hydrogen refueling and hence storage of hydrogen.

The alternative to storage of hydrogen in a vehicle is to carry fuels and convert them to hydrogen via an on-board fuel processor. All these fuels are hydrocarbons or oxygenates that need to be reformed. Reforming processes such as steam reforming, partial oxidation or autothermal reforming can carry out the reforming of a hydrocarbon to syngas. The carbon dioxide and carbon monoxide are removed from the product gases by variety of scrubbing techniques and reactions such as CO₂ absorption in amine solution, water gas shift reaction and preferential oxidation. (Ahmed and Krumpelt, 2001).

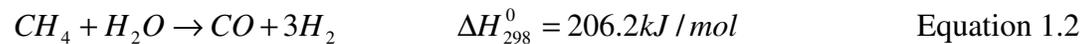
1.1 Reforming

Hydrocarbon fuels (C_nH_m) can be converted to syngas by a process known as reforming. Reforming can be carried out in three different ways (Ahmed and Krumpelt, 2001):

- The first way is Steam Reforming. It can be shown as follows:



For example:

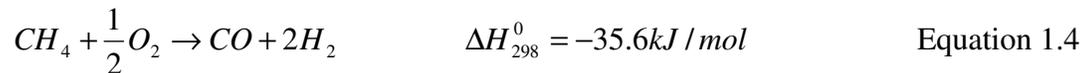


Steam reforming is catalyzed by nickel or a noble metal catalyst.

- The second way is Partial Oxidation which can be shown as follows:



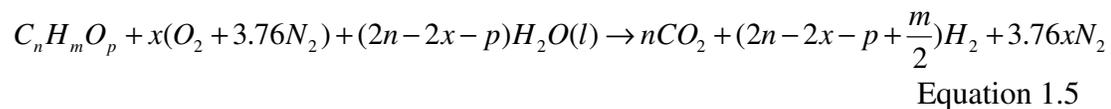
For example:



- The third way is Autothermal Reforming

Autothermal reforming can be defined as the combination of total oxidation and hydrogen production where both steam and oxygen are added. Here complete oxidation furnishes the thermal energy required for H_2 production.

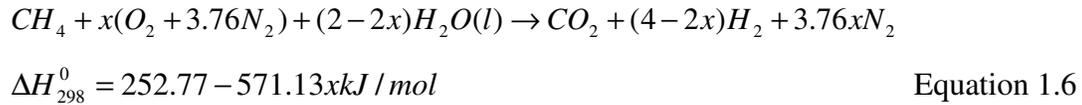
A nominal reaction can be written as:



where x is the oxygen-to-fuel molar ratio.

Equation 1.5 assumes that autothermal reforming consists of steam reforming and total oxidation, that no net carbon monoxide is formed and that there is a net loss of water.

For example:



1.2 Significance of Steam Reforming and Partial Oxidation

Hydrogen is manufactured commercially using steam and hydrocarbons over a nickel catalyst by steam reforming. The temperatures required for steam reforming are very high. The reaction is highly endothermic. Reactor designs are limited by heat transfer rather than reaction kinetics due to the endothermic nature of the reaction. The reactors which facilitate heat transfer tend to be large and heavy. Endothermicity of the reaction and the reactor size are the constraints for using fuel cells in automobiles (Ahmed and Krumpelt, 2001).

An alternative to steam reforming is direct catalytic partial oxidation of hydrocarbons which is an exothermic reaction. Hydrocarbons can be oxidized to syngas in presence of substoichiometric amount of oxygen. The oxygen is used in substoichiometric amount, hence the name partial oxidation. Partial oxidation reaction is faster than steam reforming. Partial oxidation can be carried out in smaller reactors, unlike steam reforming where reactor size increases due to heat transfer limitations (Pena *et al.*, 1996).

The direct-oxidation reaction is difficult to study because it involves feeding of hydrocarbon and oxygen (or air) mixtures. These mixtures are explosive and proper care should be taken so that the inlet composition does not fall into explosive limits. Partial oxidation is carried out under reducing conditions. This can lead to carbon deposition

over the catalyst surface. One solution to this problem is co-feeding of small quantities of water along with hydrocarbon and oxygen (or air) (Pena *et al.*, 1996).

1.3 Significance of Autothermal Reforming

Autothermal reforming is a combination of oxidation and steam reforming reactions. Autothermal reforming was developed by Haldor Topsoe in the late 1950s so that both the reactions can be carried out in a single reactor. If an endothermic reaction of steam reforming could be combined with an exothermic reaction in the same reaction vessel, the exothermic reaction that produces heat could be used to drive the endothermic reaction that requires heat. This can be achieved by combining the oxidation of hydrocarbon with steam reforming (Pena *et al.*, 1996). Because both reactions (steam reforming and partial oxidation) take place simultaneously, the reactor design is much simpler than that of a conventional steam reformer. Exothermic, endothermic and thermoneutral conditions can be selected by choosing an appropriate ratio of hydrocarbon: oxygen: steam. The thermoneutral point can be defined as a point where heat of reaction is zero. Referring to Equation 1.6, it can be seen that at $x = 0$, the reaction is endothermic. The reaction becomes less endothermic with increase in oxygen. It becomes thermoneutral at $x = 252.77/571.13 = 0.44$. Above this point, the reaction is exothermic. Addition of steam is also effective in suppressing deposition of carbon.

1.4 Statement of Problem and Objectives

The basic purpose of this research is to investigate platinum metal catalysts for partial oxidation of propane to produce hydrogen. Propane is used as a model compound for gasoline. The results obtained over propane feed can be extended to develop an on-board gasoline fuel processor.

Some of the initial objectives of this project were to test commercial catalyst Pt/Al₂O₃ obtained from Pressure Chemicals for partial oxidation of propane. Studies also included preparation of Pt/CeO₂ catalyst in-house and testing of its activity in the testing unit.

The main objectives include:

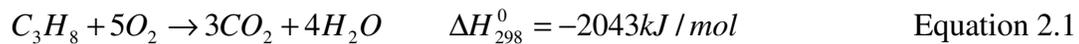
1. To study effect of support on partial oxidation of propane. Three Pt/CeO₂ catalysts having different surface area ceria supports are investigated for partial oxidation. The results obtained are also compared with Pt/Al₂O₃ catalyst.
2. In order to study support effects, catalyst activity is studied for different feed ratios (O₂/C₃H₈) and temperatures. Characterization studies such as BET surface area and hydrogen chemisorption are also performed to understand properties of the catalysts.
3. Effect of space velocity is studied to explain the reaction scheme.

Chapter 2: Literature Review

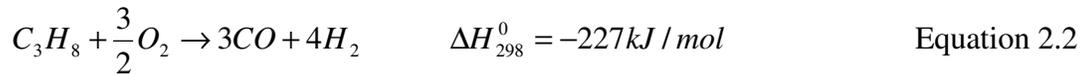
2.1. Thermodynamics of Propane Oxidation

There are several different reactions of propane with oxygen (Huff *et al.*, 1994). They are as follows:

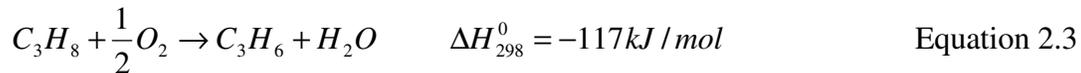
- Propane can react with O₂ to form total oxidation products.



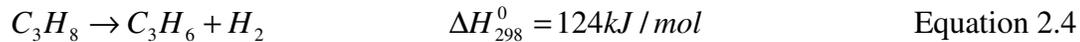
- Propane can react with substoichiometric amount of oxygen to form syngas.



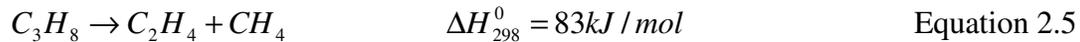
- Propane may dehydrogenate oxidatively to form propene.



- Propane can dehydrogenate thermally to form propene.

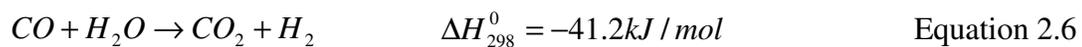


- Cracking of propane can take place to form ethylene and methane.



Some of the propane can react with water (formed from total oxidation) by steam reforming, Equation 1.1. The product mixture from combining steam reforming with propane oxidation will be affected by the water-gas-shift reaction, which occurs over many catalysts. This reaction increases the hydrogen concentration in the products at the expense of CO.

Water gas shift:



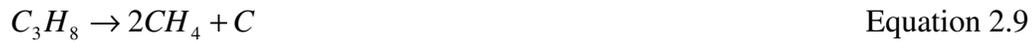
Some of the unreacted propane can also react with carbon dioxide formed from total oxidation through dry reforming to form syngas.



Carbon dioxide formed from total oxidation can undergo reverse Boudouard reaction to form carbon monoxide.



Huff *et al.* (1994) studied partial oxidation of propane on Pt/Al₂O₃ foam monolith. The results indicate that, below 4 % propane in air, the primary products are CO₂ and H₂O. Between 4 and 12 % propane in air, CO and H₂ are produced. At high temperatures (above 1250 K) propane can produce methane, which can be shown as follows:



A selective catalytic material must be used to favor oxidation of propane to carbon monoxide and hydrogen.

2.2. Study of Catalyst Activity

This section deals with effect of catalyst preparation methods on catalyst performance and studies of various catalysts for partial oxidation of propane. The importance of ceria support is also discussed.

2.2.1. Preparation

The incipient wetness impregnation technique is commonly used for preparation of metal supported catalysts. Jovanovic and Stankovic (1987) investigated an improved impregnation technology in which catalysts were prepared using single and multiple immersions of supports in different concentrations of Ni(NO₃)₂ solutions. After the impregnation, catalyst samples were dried, calcined and then reduced. The catalyst prepared from the most concentrated solution exhibited the largest surface area. The highest selectivity for the reaction was obtained when the catalyst was prepared by 6-fold immersion in the least concentrated solution of Ni(NO₃)₂. Stankovic and Jovanovic

(1997) studied the performance of magnesia-supported nickel catalyst prepared under different impregnation conditions. It was observed that selectivity towards syngas formation decreases in the order $\text{Al}_2\text{O}_3 > \text{MgO} > \text{CaO}$, where Al_2O_3 , MgO and CaO are used as promoters.

Pantu and Gavalas (2002) prepared the ceria support using the citrate complexation technique for studying partial oxidation of methane on Pt/CeO_2 . The ceria supported Pt catalyst was prepared using homogeneous precipitation method. The BET surface area of the catalyst obtained was $40 \text{ m}^2/\text{g}$ and the Pt dispersion was 69 %.

Pino *et al.* (2002) prepared the Pt/CeO_2 catalysts by novel solution-combustion method to study partial oxidation of methane. The hydrogen selectivity obtained was as high as 99 % at 800-900 ° C. The 2 % Pt/CeO_2 catalyst does not show any carbon deposition even after extended reaction of methane with air.

Pino *et al.* (2003) prepared the Pt/CeO_2 catalysts using coprecipitation, impregnation and combustion method. The methane conversion was between 80 % and 96 % with hydrogen selectivity between 90 % and 98 %. The catalyst prepared using combustion method showed the best performance for the reaction among all the ceria-supported Pt catalysts.

2.2.2. Activity

Pena *et al.* (1996) have shown that the Group VIII metals (Rh, Ni, Pt, Pd,) are active for partial oxidation of methane. Various metal-supported catalysts have been studied for autothermal reforming of methane (Ayabe *et al.*, 2003). The sequence of the activity is: $\text{Rh} > \text{Pd} > \text{Ni} > \text{Pt} > \text{Co}$. However, for propane oxidation (Maillet *et al.*, 1996), the sequence of the activity is: $\text{Pt} > \text{Pd} > \text{Rh}$, which is reverse of that observed by Ayabe *et al.*, (2003) for autothermal reforming of methane. The sequence of the activity of metals for steam reforming (corresponding to the reaction of water with unreacted propane after the oxygen is completely consumed) for propane is: $\text{Rh} > \text{Pd} > \text{Pt}$. Huff *et*

al. (1994) observed that the reaction over Pd behaves similarly to that over Pt; however, Pd catalyst is deactivated due to carbon deposition.

2.2.3. Effect of Catalyst System

Liu *et al.* (2001) observed that the nature of the oxide support for the catalyst has a significant effect on its activity due to the varying active surface area. Table 2.1 gives an idea about the effect of supports on catalytic activity. The values of parameters (temperature, O_2/C_3H_8 , $X_{C_3H_8}$), where maximum selectivity for hydrogen is obtained are listed in the table.

For Rh/Fecralloy reactor (Fecralloy contains 72.6 % Fe, 22 % Cr and 4.8 % Al), where Rh is deposited on Fecralloy, addition of steam increases the hydrogen production and hydrogen selectivity of more than 70 % is obtained (Gjervan *et al.*, 2003). Studies done by Barbier *et al.* (1992) show that there is a higher production of hydrogen with Rh and PtRh catalysts than with pure Pt.

The partial oxidation of propane to syngas over NiO/Al₂O₃, NiO/MgO and NiO/SiO₂ has been compared (Liu *et al.*, 2001). The propane conversion and hydrogen selectivity is much lower in the presence of NiO/MgO and NiO/SiO₂ catalysts than with NiO/Al₂O₃ catalyst.

Also, a large difference in the activities of the catalysts is seen when Fe or Co displaces the Ni component in LiNiLaO/Al₂O₃ catalyst. Propane conversion and hydrogen selectivity of the Fe-or-Co containing catalysts are much lower than those of

Table 2.1 Compilation of various catalyst systems investigated for partial oxidation and autothermal reforming (S/C-Steam to carbon ratio; $X_{C_3H_8}$ - Conversion of Propane)

Catalyst System	Metal Loading	Temperature (°C)	O ₂ /C ₃ H ₈	S/C	X _{C₃H₈} (%)	Reference
Ni/Al ₂ O ₃	10	800	0.5	1.5	100	Ayabe <i>et al.</i> (2003)
Rh/Fecralloy reactor**	-	900-1000	1.9	0	100	Gjervan <i>et al.</i> (2003)
Rh/Fecralloy reactor**	-	960	1.9	0.7	100	Gjervan <i>et al.</i> (2003)
Pt/Rh/CeO ₂ /Al ₂ O ₃	1 % Pt and 0.2 % Rh	500	2	0	100	Barbier and Duprez (1992)
Pt/ CeO ₂ /Al ₂ O ₃	1	500	2	0	70	Barbier and Duprez (1992)
Rh/CeO ₂ /Al ₂ O ₃	0.2	500	2	0	90	Barbier and Duprez (1992)
Pd/Al ₂ O ₃	1	600	2	0	100	Maillet <i>et al.</i> (1996)
Pd/Al ₂ O ₃	1	400	5	*	96	Maillet <i>et al.</i> (1996)
Pd/Al ₂ O ₃	1	500	2	*	96	Maillet <i>et al.</i> (1996)
Pt/Al ₂ O ₃	-	650	2.1	0	87.3	Ma <i>et al.</i> (1996)
LiNiLaO/Al ₂ O ₃	-	600	1.65	0	100	Liu <i>et al.</i> (2001)
NiO/ Al ₂ O ₃	-	600	1.65	0	100	Liu <i>et al.</i> (2001)
NiO/ MgO	-	600	1.65	0	41.3	Liu <i>et al.</i> (2001)
NiO/ SiO ₂	-	600	1.65	0	5.8	Liu <i>et al.</i> (2001)
LiCoLaO/Al ₂ O ₃	-	600	1.65	0	57.1	Liu <i>et al.</i> (2001)
LiFeLaO/Al ₂ O ₃	-	600	1.65	0	35.4	Liu <i>et al.</i> (2001)
NaNiLaO/Al ₂ O ₃	-	600	1.65	0	100	Liu <i>et al.</i> (2001)
KNiLaO/Al ₂ O ₃	-	600	1.65	0	100	Liu <i>et al.</i> (2001)
LiNiCeO/Al ₂ O ₃	-	600	1.65	0	100	Liu <i>et al.</i> (2001)
LiNiYO/Al ₂ O ₃	-	600	1.65	0	100	Liu <i>et al.</i> (2001)
LiNiSmO/Al ₂ O ₃	-	600	1.65	0	100	Liu <i>et al.</i> (2001)
Pt/Al ₂ O ₃ foam monolith	4.3	800-1200	2.1	0	100	Huff <i>et al.</i> (1994)
Pd/Al ₂ O ₃	1	600	2.5	0	70	Guimaraes <i>et al.</i> (2003)
Pd/CeO ₂ /Al ₂ O ₃	1	600	2.5	0	90	Guimaraes <i>et al.</i> (2003)

*Amount of steam added is not given

** See the text for composition of Fecralloy

the Ni-containing catalyst. The NiO/Al₂O₃ catalyst and catalysts with different alkali metal oxides ALaNiO/Al₂O₃ (A= Li, Na, K) and rare earth metal oxides LiBNiO/Al₂O₃ (B= La, Sm, Y, Ce) shows almost the same performance. Propane is converted completely. The selectivity of CO and hydrogen remain at about 45 % and 85 % respectively. Also it can be seen that modification of the NiO/Al₂O₃ catalyst with alkali and rare-earth metal oxides does not show a significant effect on the reaction performance of the partial oxidation of propane reaction (Liu *et al.*, 2001).

Studies done by Guimaraes *et al.* (2003) show that Pd/CeO₂/Al₂O₃ catalyst is less active than the Pd/Al₂O₃ catalyst at low temperatures but becomes more than Pd/Al₂O₃ catalyst at high temperatures.

2.2.4. Ceria Support

Cerium oxide has been used in three-way catalysts used for automotive emission control. In these catalysts, cerium oxide acts as oxygen-storage component. Cerium oxide shows an easy transition between Ce⁴⁺ and Ce³⁺ and so can store large amounts of O₂. This property is very useful in catalysis especially in oxidation reactions and also in promoting number of catalytic reactions on noble metal particles including water gas shift reaction. Ceria promotes stabilization of precious metals and prevents sintering of particles (Guimaraes *et al.*, 2003).

According to Pantu and Gavalas (2002), noble metals when supported on ceria show much higher rates for water gas shift, steam reforming and carbon dioxide reforming of methane than when supported on silica or alumina. These reactions exhibit a bifunctional mechanism, in which oxygen from cerium oxide reacts with carbon compounds adsorbed on the noble metal, while the partially reduced cerium oxide reacts with gaseous oxidant and gets reoxidized. Methane partial oxidation was studied over Pt/CeO₂ catalysts. Higher conversions and selectivities were obtained at lower temperatures. This is happening possibly because of the oxidation of adsorbed methane

by oxygen from cerium oxide and then reoxidation of partially reduced cerium oxide by CO_2 and H_2O .

Studies done by Diwell *et al.* (1991) to test the catalyst activity in a simulated exhaust environment show that ceria maintains the Pt metal in an oxidized state, thus stabilizing Pt dispersion. This effect is unfavourable for catalytic activity under oxidizing conditions, but under reducing conditions, ceria promotes the reduction of platinum oxide, thus improving activity of the catalyst for water gas shift, steam reforming and NO reduction. The presence of ceria support in the three way catalysts promotes stabilization of precious metals such as Pt and Rh. In case of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst, substantial sintering of Pt occurs at high temperature but addition of CeO_2 results in stabilization of Pt dispersion, as a result of strong Pt- CeO_2 interaction. Alumina supported Rh catalyst shows thermal deactivation as a result of detrimental Rh- Al_2O_3 interaction at grain boundaries. Addition of CeO_2 improves thermal stability of Rh significantly.

Steam reforming can be used to lower the hydrocarbon emissions under oxygen deficient conditions. The carbon monoxide in the products can be removed by water gas shift reaction. Addition of ceria in three way catalysts containing Pt-Rh promotes the steam reforming reaction.

Golunski *et al.* (1995) studied Temperature Programmed Reduction (TPR) of ceria supports and ceria supported Pt catalyst. Ceria shows two peaks at 450°C and 850°C . The first peak is due to surface reduction and the second peak is due to bulk reduction of ceria. After impregnating Pt on ceria, the first peak shifts to $120\text{-}250^\circ\text{C}$. This is due to interaction between Pt and ceria.

Otsuka *et al.* (1997) observed that cerium oxide could partially oxidize methane to syngas in absence of oxygen. Addition of platinum metal to cerium oxide increased the rate of oxidation to Syngas.

2.3. Effect of O₂/C₃H₈ Ratio

The O₂/C₃H₈ ratio has a significant effect on propane conversion and hydrogen selectivity. According to Huff *et al.* (1994), the stoichiometric O₂/C₃H₈ (O₂/C₃H₈ = 5) ratio gives carbon dioxide. Substoichiometric ratios give syngas. The O₂/C₃H₈ ratio is 1.89 for highest selectivity of hydrogen on Pt/ α -Al₂O₃ foam monolith. The ratio is 1.25 for LiLaNiO/ γ - Al₂O₃ (Liu *et al.*, 2001).

2.4. Effect of Steam Addition

Studies done by Ayabe *et al.* (2003) show that addition of steam has a significant effect on carbon deposition. Carbon deposition is more significant for higher hydrocarbons. Addition of steam lowers carbon deposition. Hydrogen concentration in the product gases increases with increase in steam/carbon (S/C) ratio. Addition of steam decreases the load on total oxidation of hydrocarbon and increases the amount of hydrocarbon made available for steam reforming. Table 2.2 and Table 2.3 show effect of S/C ratio. It is seen that as the S/C ratio increases, the amount of hydrogen produced increases.

Table 2.2 Effect of S/C ratio on autothermal reforming of propane

Catalyst system	Temperature (° C)	S/C	O ₂ /C ₃ H ₈	H ₂ (mol %)	Reference
Platinum coated honeycomb	700	0.55	2.1	24	Rampe <i>et al.</i> (2000)
Platinum coated honeycomb	700	1.4	2.1	27	Rampe <i>et al.</i> (2000)
Ni/Al ₂ O ₃	600	0	0.5	12	Ayabe <i>et al.</i> (2003)
Ni/Al ₂ O ₃	600	0.5	0.5	30	Ayabe <i>et al.</i> (2003)
Ni/Al ₂ O ₃	600	1.0	0.5	39	Ayabe <i>et al.</i> (2003)
Ni/Al ₂ O ₃	600	1.5	0.5	49	Ayabe <i>et al.</i> (2003)
Rh/Fecralloy reactor	1000	0	1.9	18	Gjervan <i>et al.</i> (2003)
Rh/Fecralloy reactor	1000	0.7	1.9	23	Gjervan <i>et al.</i> (2003)

Table 2.3 Effect of S/C ratio on autothermal reforming of propane (Guimaraes *et al.*, 2003)

Catalyst system	Temperature (° C)	S/C	O ₂ /C ₃ H ₈	H ₂ (mol %)
Pd/Al ₂ O ₃	600	0	2.5	1.25
Pd/Al ₂ O ₃	600	1	2.5	1.4
Pd/CeO ₂ / Al ₂ O ₃	600	0	2.5	0.9
Pd/CeO ₂ / Al ₂ O ₃	600	1	2.5	3.0

2.5. Mechanism and Kinetics

According to Maillet *et al.* (1996), there are two discrete zones for partial oxidation of propane. In the first zone (below 400 ° C), the complete oxidation of propane (Equation 2.1) takes place, producing CO₂ and H₂O. In the second zone (above 400 ° C), the remaining propane reacts with water by steam reforming (Equations 2.10 and 2.11).



Passos *et al.* (2003) has studied partial oxidation of methane on Pt/Y₂O₃, Pt/Al₂O₃ and Pt/CeO₂ catalysts. Pt/Al₂O₃ and Pt/CeO₂ catalysts showed indirect mechanism consisting two steps: In the first step methane undergoes total oxidation and in the second step unreacted methane undergoes steam and dry reforming, while Pt/Y₂O₃ showed direct partial oxidation. No steam reforming was observed for Pt/Y₂O₃ catalyst while dry reforming was observed at high temperatures.

Ma *et al.* (1996) has studied the reaction kinetics for propane oxidation on Pt/δ-Al₂O₃. The rate expressions were approximated by the power law equation:

$$r = k [C_3H_8]^a [O_2]^b \quad \text{Equation 2.12}$$

The parameters of the power law Equation 2.12 are given in Table 2.4.

Table 2.4 Parameters of the power law Equation 2.12

Catalyst	T (K)	k (mol/m ² h kPa ^(a+b))	E (kJ/mol)	a	b
Pt/ δ -Al ₂ O ₃	423-463	1.87 x 10 ⁹	104.7±1	1.1±0.05	-0.6±0.1

2.6 Dry reforming

Pantu and Gavalas (2002) studied partial oxidation and dry reforming of methane on 0.5 % Pt/CeO₂ and 0.5 % Pt/Al₂O₃ catalysts. The CO₂/CH₄ = 1 was used for dry reforming of methane. They observed that on Pt/CeO₂, steam reforming of methane is faster than reforming with CO₂. Also dry reforming on Pt/CeO₂ was two times faster than on Pt/Al₂O₃ at 600 ° C. Methane conversion was 56 % at 600 ° C over 0.5 % Pt/CeO₂. Both 0.5 % Pt/CeO₂ and 0.5 % Pt/Al₂O₃ are active for dry reforming of methane. Solymosi and Tolmacsov (2002) studied dry reforming of propane over alumina supported noble metals. The conversion of propane is 5.4 % over 1 % Pt/Al₂O₃ catalyst at 650 ° C. The activities of noble metals in dry reforming decrease in the sequence Ru > Rh > Pd > Pt = Ir. The results show that 1 % Pt/Al₂O₃ is a poor catalyst for dry reforming of propane.

2.7 Water gas shift reaction

According to Luengnaruemitchai *et al.* (2003), there are two types of commercial water gas shift catalysts. Oxides of iron and chromium are high temperature water gas shift catalysts and are used at 400-500 ° C. Low temperature shift catalysts consist of copper, zinc oxide and alumina and are used between 200 and 400 ° C. For water gas shift reaction, conversion is equilibrium limited at high temperatures and kinetically limited at low temperatures. Pt is much more active than Au when comparison is made between Pt/CeO₂ and Au/CeO₂ catalysts. Ceria promotes precious metal catalysts for water gas shift reaction. Hilare *et al.* (2001) discussed mechanism for water gas shift reaction on ceria-based catalysts.



CO adsorbs on transition metal site (σ) and reacts with oxygen from ceria to form CO_2 . Reduced cerium oxide is reoxidized by H_2O . Grenoble *et al.* (1981) studied water gas shift reaction over group VIII metals supported on alumina and found the order of activity at 300 °C to be $Ru > Pt > Pd > Rh > Ir$. The effect of support for Pt catalysts decrease in the sequence: $Pt/Al_2O_3 \gg Pt/SiO_2 > Pt/C$.

Chapter 3: Experimental Set Up and Procedure

3.1. Equipment Description

The flow sheet for the catalyst-testing unit is shown in Figure 3.1. The unit has three lines for gas feeds, each being independently controlled by a Brooks mass-flow controller (MFC). The gases first pass through 2 μm filters (F) and then pass through the MFC. The gases then pass through a mixing vessel before passing through either the reactor or a bypass line. The pressure in the reactor system is measured by a pressure gauge (P). The reactor consists of a stainless-steel tube (304L) of outer diameter of 12.7 mm (0.5 inch) and nominal length of 0.45 m (17.5 inch), placed in a 0.33 m (13.25 inch) long, single-zone furnace from Applied Test Systems. The effects of flow rate and dry reforming reactions were studied in a quartz reactor having the same dimensions as stainless-steel tube reactor. Typically 0.1g of catalyst is placed in the center of the reactor, with quartz chips placed upstream and downstream of the catalyst. The product gases pass through a cold trap for condensation of gases. For this research work, it was not filled with any material. The outlet of the reactor is connected to a Varian 3600 gas chromatograph (GC) and the product gases are analyzed on-line by GC using two columns and two detectors in parallel. The Chromperfect Software is used for data acquisition and analysis. In the GC, the flow is split between the two columns: a Haysep D packed column, 6 m x 3 mm, and an alumina capillary column, 30 m long. The oven temperature is ramped from 35 °C to 200 °C. The details of the GC operating conditions are given in Appendix A. The packed column is connected to a thermal-conductivity detector (TCD), which provides quantitative analysis for N_2 , H_2 , CO , CO_2 , CH_4 , C_3H_8 and H_2O . Nitrogen is the internal standard, while argon serves as the carrier gas. The capillary column is connected to a flame-ionization detector (FID), which is used to detect hydrocarbons such as CH_4 and C_3H_8 . The reactor system is placed in a hood.

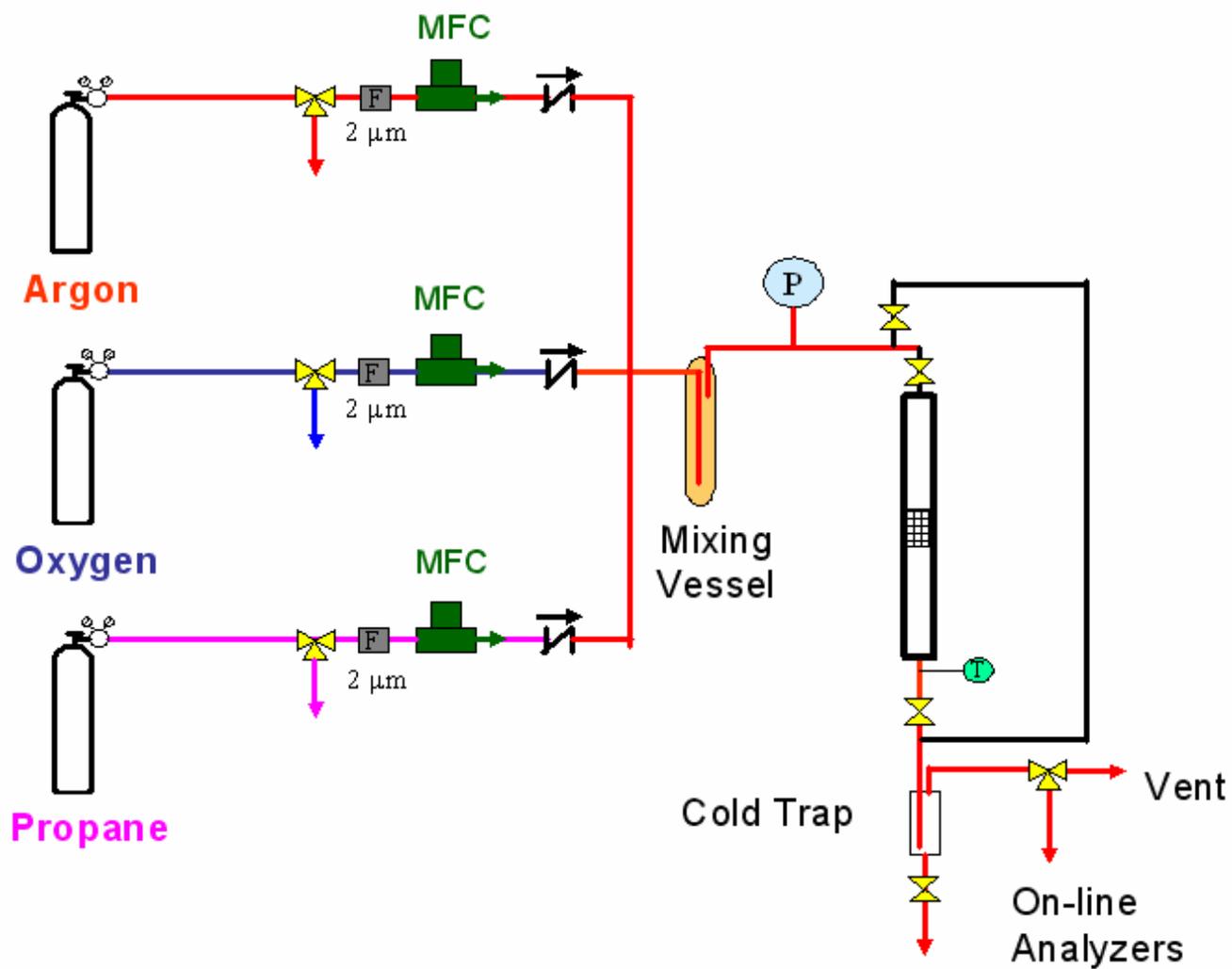


Figure 3.1 Flow sheet for Catalyst Testing Unit

3.2. Experimental Procedure

This section deals with catalyst preparation methods for ceria and alumina catalysts. The reactor loading and pretreatment procedure is also discussed.

3.2.1 Catalyst Preparation

The commercial ceria support that was obtained from Sigma-Aldrich has a very low surface area and that is 17.3 m²/g. Two high-surface-area ceria supports were prepared by homogeneous precipitation and by decomposition, as described in Sections 3.2.1.2 and 3.2.1.3. Platinum was loaded on these supports by incipient wetness method. Three types of Pt/CeO₂ catalysts, Pt/CeO₂ (A), Pt/CeO₂ (B) and Pt/CeO₂ (C) are tested for partial oxidation reaction where Pt/CeO₂ (A) corresponds to Pt catalyst prepared using commercial ceria, Pt/CeO₂ (B) corresponds to Pt catalyst prepared using ceria made by homogeneous method and Pt/CeO₂ (C) corresponds to Pt catalyst prepared using ceria made by decomposition method. The results obtained for the Pt/CeO₂ catalysts are also compared with Pt/Al₂O₃ catalyst prepared as described in Section 3.2.1.4.

3.2.1.1 Pt/CeO₂ (A)

Initially, cerium oxide (cerium (IV) oxide, powder, < 5 micron, 99.9 %) from Sigma-Aldrich was calcined at 400 °C for 3 hrs. As mentioned above, the Pt was added in-house by incipient wetness. The 1 % Pt/CeO₂ (A) catalyst was prepared by impregnating 20 g ceria with 0.9 g of 1.12 M H₂PtCl₆ solution to yield a catalyst containing 1 % Pt (wt %) metal. Then the impregnated support containing the catalyst was dried at 100 °C overnight. The dried catalyst was calcined at 400 °C for 3 hrs. The catalyst pellets were crushed and sieved into grains of 0.595-0.42 mm (30-40 mesh). The BET surface area of the catalyst was determined to be 9.9 m²/g. Another catalyst with 0.5 % metal loading was prepared using same method of preparation.

3.2.1.2 Pt/CeO₂ (B)

The Pt/CeO₂ (B) was prepared entirely in-house by Dr. Tapan Das of Department of Chemical Engineering, West Virginia University, with the cerium oxide prepared using precipitation. First, cerium nitrate was neutralized against ammonium hydroxide to form cerium hydroxide, which precipitated from aqueous solution. The slurry was dried, and then calcined at 400 ° C for 3 hrs to form cerium oxide. The platinum was added by incipient wetness. The 1 % Pt/CeO₂ (B) catalyst was prepared by impregnating 20 g ceria with 3.4 g of 0.31 M H₂PtCl₆ solution to yield a catalyst containing 1 % Pt (wt %) metal. Then the impregnated support containing the catalyst was dried at 100 ° C overnight. The dried catalyst was calcined at 400 ° C for 3 hrs. The catalyst pellets were crushed and sieved into grains of 0.841-0.595 mm (20-30 mesh). The BET surface area of the catalyst was 65.8 m²/g, which is about seven times larger than that of 1 % Pt/ CeO₂ (A).

3.2.1.3 Pt/CeO₂ (C)

The Pt/CeO₂ (C) was also prepared entirely in-house by Dr. Tapan Das. Now cerium oxide was prepared by decomposition of cerium nitrate through calcination under air at 500 ° C for 4 hrs. The platinum was added by incipient wetness. The 1 % Pt/CeO₂ (C) catalyst was prepared by impregnating 20 g ceria with 3.9 g of 0.26 M H₂PtCl₆ solution to yield a catalyst containing 1 % Pt (wt %) metal. Then the impregnated support containing the catalyst was dried at 100 ° C overnight. The dried catalyst was calcined at 400 ° C for 3 hrs. The catalyst pellets were crushed and sieved into grains of 0.841-0.595 mm (20-30 mesh). The BET surface area of the catalyst was determined to be 80.4 m²/g, which is about eight times larger than that of 1 % Pt/ CeO₂ (A).

3.2.1.4 Pt/Al₂O₃

The Pt/Al₂O₃ catalyst was prepared using γ - Al₂O₃ obtained from Sasol North America. The support γ - Al₂O₃ is used because it is a stable phase of alumina in the reaction temperature range. The γ - Al₂O₃ was calcined at 400 ° C for 3 hrs. The platinum

was added by incipient wetness. The 1 % Pt/Al₂O₃ catalyst was prepared by impregnating 20 g γ - Al₂O₃ with 10.3 g of 0.1 M H₂PtCl₆ solution to yield a catalyst containing 1 % Pt (wt %) metal. Then the impregnated support containing the catalyst was dried at 100 ° C overnight. The dried catalyst was calcined at 400 ° C for 3 hrs. The catalyst pellets were crushed and sieved into grains of 0.841-0.595 mm (20-30 mesh). The BET surface area of the fresh catalyst is 153 m²/g, which is sixteen times larger than that of 1 % Pt/ CeO₂ (A).

3.2.2 Reactor loading

For each run, the bottom of the reactor is first loaded with quartz chips. Then quartz wool is placed above the quartz chips. The catalyst bed consists of typically 0.1 g catalyst mixed with 0.5 g of quartz chips and it is loaded above the quartz wool. Then additional quartz wool is placed on the catalyst bed, followed by additional quartz chips. The loaded reactor is then sealed with quartz wool and mounted in a furnace. A thermocouple is adjusted so that the tip of it just touches the catalyst bed.

3.2.3 Pretreatment and Reaction

The catalyst pretreatment is carried out by reducing Pt catalyst with hydrogen at 400 ° C for 3 hours. Thus platinum oxides are reduced to platinum metal. The GC is started only after ensuring the flow of the carrier gas through the column and the detectors. After the pretreatment, the reaction is started by adjusting the required flows of the feed gases and setting the furnace temperatures using the temperature controller. The reaction is carried out at atmospheric pressure. The sample is injected to the GC by means of the 10 port sampling valve. The sample is injected 1 hr after the set point temperature is reached, and product analysis is carried out. The Chromperfect software is used to analyze the peaks for gases which are detected by TCD and FID. A typical analysis time is 45 minutes.

3.2.4 Materials and Methodology

This section deals with procedure and reaction conditions for the experiments for studying effect of various parameters such as temperature, O_2/C_3H_8 ratio and flow rate on partial oxidation of propane.

3.2.4.1 Materials

The catalyst pellets were made from the powdered form of a catalyst by applying 10 tons pressure on the catalyst powder. The catalyst pellets were crushed and sieved into grains of 0.841-0.595 mm (20-30 mesh). Typically 0.1 g of the catalyst was tested.

3.2.4.2 Effect of Temperature

Initially, the catalyst was reduced at 400 ° C for 3 hrs by passing hydrogen. The amount of catalyst used was 0.1 g. The feed ratio used was $C_3H_8:O_2:N_2:Ar = 10.8:19.2:10.8:259$ (molar ratios), with a total feed rate of 300 scc/min and 90 % inert. This feed ratio correspond to $O_2/C_3H_8 = 1.78$. This feed ratio was chosen so that the O_2/ C_3H_8 ratio does not fall in the explosive range (between $O_2/C_3H_8 = 2$ and 10). Also the minimum oxygen concentration is 11 % in the mixture of organic and inert gases. Hence 90 % of inert is used in the reactant mixture to avoid explosion. The reaction was carried out at atmospheric pressure. This reaction was carried out in the stainless steel reactor.

The catalyst was tested at temperatures ranging from 300 ° C to 800 ° C. The reaction temperature and reactant gases flow rates were kept constant for 1 hr at each temperature before the GC sample was taken.

3.2.4.3 Study of thermal stability of supports and catalysts

The thermal stability of the three ceria supports and the corresponding catalysts was studied under nitrogen atmosphere. The samples were placed in a tube furnace under N_2 flow. Temperature was increased at the rate of 10 ° C /min from room temperature to 900 °

C. Then the temperature was held constant at 900 ° C for 24 hrs. The BET surface areas of the fresh and heated samples were measured and compared.

3.2.4.4 Study of stability of catalyst for partial oxidation of propane

This experiment was carried out using 1 % Pt/ CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts. Initially, the catalyst was reduced at 400 ° C for 3 hrs in H₂ flow. The amount of catalyst used was 0.1 g. The total flow rate was 300 scc/min with 90 % inert. This reaction was carried out at 800 ° C for 1 % Pt/ CeO₂ (C) and at 600 ° C for 1 % Pt/Al₂O₃ catalyst. The ratio of O₂/C₃H₈ was 1.78. The stability of the catalyst was studied for 15 hours on stream.

3.2.4.5 Effect of O₂/C₃H₈ ratio

This experiment was carried out in the stainless steel reactor using 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalyst. Initially, the catalyst was reduced at 400 ° C for 3 hrs in H₂ flow. The amount of catalyst used was 0.1 g. The total flow rate was 300 scc/min with 90 % inert. This reaction was carried out at 675 ° C and atmospheric pressure. The ratio of O₂/C₃H₈ was varied from 0.5 to 8. It was increased in increments of 0.5 up to O₂/C₃H₈ = 5 and in increment of 1 thereafter. The ratio of O₂/C₃H₈ for total combustion is 5 and that for partial oxidation is 1.5.

3.2.4.6 Study of ceria and alumina support

Partial oxidation of propane was studied for CeO₂ (C) and γ -Al₂O₃ supports. The support was used in powder form. The amount of support used was 0.02 g. The support was diluted with 0.1 g of quartz chips. The support was initially activated at 350 ° C for 2 hrs in Ar flow. Then it was reduced at 400 ° C for 3 hrs in H₂ flow. The reaction was carried out at 600 ° C. It was studied at 50 scc/min and 300 scc/min total flow rates containing 90 % inert. The O₂/C₃H₈ ratio was 1.78.

3.2.4.7 Effect of flow rate

Effect of flow was studied for 0.01 g and 0.02 g amount of 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts. The reaction was carried out in the quartz reactor at 600 ° C and atmospheric pressure. This reaction temperature was chosen so that a low conversion of propane is obtained. This reaction temperature and small amount of catalysts (0.01 g and 0.02 g) were chosen so that the reactor can be studied as a differential reactor.

Initially, 0.01 g of 1 % Pt/CeO₂ (C) catalyst diluted with 0.05 g quartz chips was loaded in the reactor and reduced at 400 ° C for 3 hrs. The total inlet flow rate of gases was varied from 50 scc/min to 400 scc/min. The concentration of inert was 90 % and the O₂/C₃H₈ ratio was 1.78. The same reaction conditions were used for 0.02 g of catalyst. The same procedure was followed for studying effect of flow for 1 % Pt/Al₂O₃ catalyst.

3.2.4.8 Dry reforming of propane

Dry reforming of propane was carried out at 600 ° C to check if 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ are active for this reaction at 600 ° C. The reaction was carried out at atmospheric pressure. Partial oxidation was carried out on the catalyst first to make sure that the catalyst was active and behaving as expected before the dry reforming experiment was attempted. Initially, 0.02 g of catalyst was loaded in the reactor and reduced at 400 ° C for 3 hrs. Then, the partial oxidation reaction was carried out for the total flow rates 300 scc/min and 100 scc/min. The concentration of inert was 90 % and the O₂/C₃H₈ ratio was 1.78. The catalyst activity was measured. Then the oxygen flow was turned off and CO₂ was added to reaction mixture. The reaction mixture for dry reforming contained propane, nitrogen, argon and carbon dioxide. The concentration of inert was 86 % and CO₂/C₃H₈ ratio was 3 (stoichiometric ratio for dry reforming). The same flow rate of propane gas was maintained as was used for partial oxidation. The total inlet flow rate of gases was varied from 100 scc/min to 300 scc/min.

3.2.5 Characterization

The characterization of the Pt/CeO₂ and Pt/Al₂O₃ catalysts is done by measuring BET surface area and Pt dispersion.

3.2.5.1 BET surface area measurement

The Brunauer-Emmett-Teller (BET) surface area measurements were performed by James Wright of the Department of Chemical Engineering, West Virginia University, Morgantown.

3.2.5.2 Platinum dispersion measurement

Platinum dispersion measurements were carried out by Dr. Tapan Das. Platinum dispersion was measured by hydrogen chemisorption technique. Temperature programmed reduction (TPR) was carried out for 1 % Pt/Al₂O₃ catalyst from room temperature up to 400 °C. The catalyst was held at 400 °C for 2 hrs. Then it was cooled down to 100 °C. Then hydrogen flow was turned off and flow of argon gas was turned on. Temperature programmed desorption is carried out in argon flow up to 550 °C. Platinum dispersion measurement of ceria catalysts was carried out in similar way. Platinum dispersion was measured by measuring the difference between chemisorbed hydrogen of ceria supports alone and Pt/CeO₂ catalysts. Ceria supports and catalysts were reduced at 550 °C instead of 400 °C.

3.2.6 Safety Requirements

Safety is a concern since propane oxidation is an exothermic reaction. Major areas of concern are operation at high temperature, toxicity of chemicals, flammability of hydrogen, explosive range of operation with propane-oxygen mixtures, and mechanical and electrical connections.

All the experiments were carried out in the chemical hood. Safety goggles, gloves and laboratory coat are necessary all the time during experiment. Attention was paid during preparation of catalyst as platinum chloride, which is used for catalyst preparation, is toxic and can cause irritation to skin and eyes. As propane and oxygen can form explosive mixtures, care was taken to ensure that operating conditions are beyond explosive limits. The explosion was avoided by keeping high concentration of inert (about 90 %) in the feed gases.

The laboratory is equipped with chemical hoods, fire extinguishers, chemical safety showers, and eye wash stations. Other available equipments include gloves, masks, laboratory coats and safety goggles. Material safety data sheets (MSDS) have been obtained for the chemicals used. A list of people to contact in case of emergency is posted at the entrance of the laboratory.

Chapter 4: Effect of Temperature

4.1 Preliminary Results

Prior to catalytic testing, a blank reaction test was performed with a stainless-steel reactor, without any catalyst. Results for the blank run show that the light-off temperature (when the oxidation starts) is 600 °C and all the reacted propane is converted into CO₂. The conversion of propane is 13 % at 600 °C. The details of the calculation procedure for the conversions and selectivities are given in Appendix C. The results for blank reaction for stainless-steel reactor are given in Table 4.1.

Table 4.1 Effect of temperature on the activity of the stainless-steel reactor for partial oxidation of propane (total flow rate = 300 scc/min, O₂/C₃H₈ = 1.78)

Temperature (° C)	X _{C₃H₈} , %	X _{O₂} , %	S _{H₂} , %	S _{CO} , %	S _{CO₂} , %
300	0	0	0	0	0
400	0	0	0	0	0
500	3.4	2.3	0	0	0
600	12.8	16.8	0	0	29.1
700	31.1	52.5	0.5	0	50.9
800	63.0	100	5.7	6.1	50.1

The first part of preliminary experiments was to carry out partial oxidation reaction using commercial Pt/alumina catalyst. The second part was to prepare and test the catalytic activity of Pt/ceria catalyst. For this, 0.5 % Pt/CeO₂ (A) catalyst was used. The results for preliminary experiments are given in Section 4.1.1 and 4.1.2.

4.1.1 Commercial Pt/Al₂O₃ catalyst

The commercial 5 % Pt/Al₂O₃ (wt %) catalyst was obtained from Pressure Chemical Co. The materials are given in Section 3.2.4.1 and the methodology is given in Section 3.2.4.2.

Figure 4.1 shows the effect of temperature on partial oxidation of propane over 5 % Pt/Al₂O₃ catalyst. The outlet volumetric flow rates of reactants and products are plotted against temperature. Oxygen is the limiting reactant in the feed and thus is completely consumed at all the temperatures. As the temperature increases, the outlet volumetric flow rate of propane decreases which indicates that the conversion of propane increases. Below 500 ° C, propane is converted to CO₂ and H₂O exclusively. It can be seen from Figure 4.1 that the hydrogen production starts at around 400 ° C. Productions of hydrogen and carbon monoxide increase with temperature and reach maxima at 800 ° C. Propane conversion is almost constant until 500 ° C, but after that temperature, propane conversion increases. Propane is completely consumed at 800 ° C. As the temperature increases, carbon dioxide production decreases. The outlet flow rate of methane is very low and always below 1 scc/min.

From Figure 4.1 it can be concluded that the reaction shows two regimes. The regime below 500 ° C is a total combustion regime and the regime above 500 ° C is a reforming regime. These results are comparable to the results obtained by Maillet *et al.* (1996).

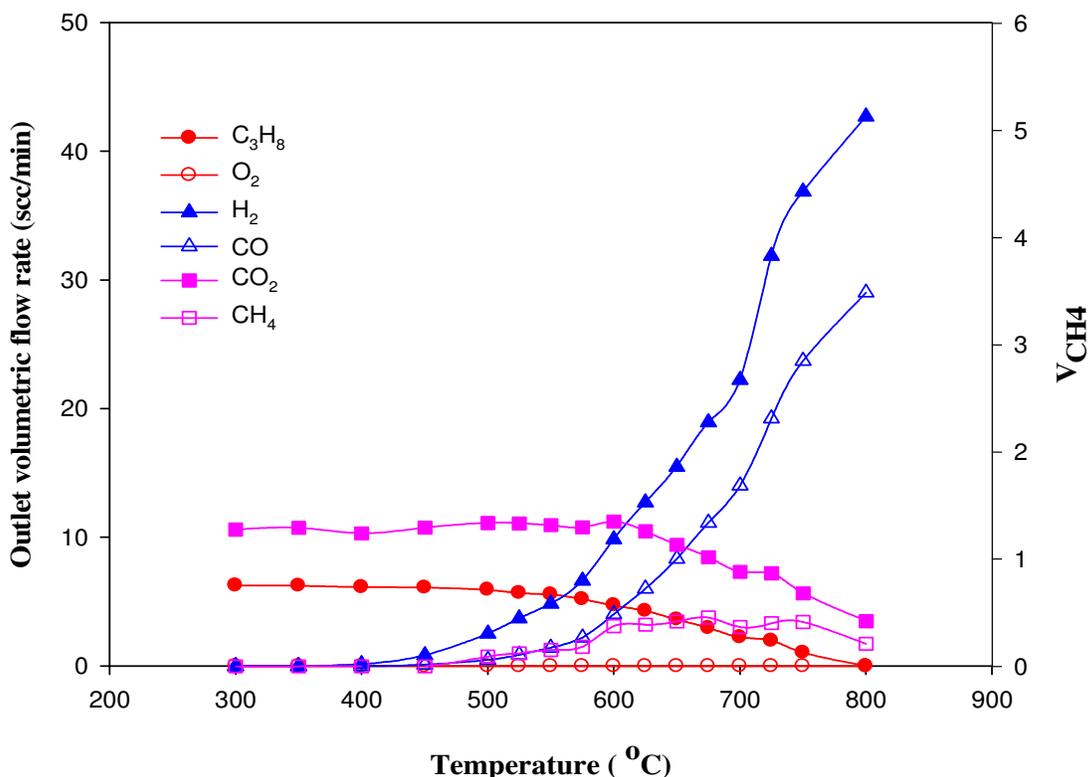


Figure 4.1 Effect of temperature on activities and product distribution over 5 % Pt/Al₂O₃ commercial catalyst (Feed ratio: O₂/C₃H₈ = 1.78, total feed rate: 300 scc/min)

4.1.2 Ceria supported Pt catalyst

The 0.5 % Pt/CeO₂ (A) catalyst was used for this study. The Brunauer –Emmett –Teller (BET) surface area of the catalyst was 16.83 m²/g. The total pore volume of the sample was 0.045 ml/g. The materials are given in Section 3.2.4.1 and the methodology is given in Section 3.2.4.2.

Figure 4.2 shows the effect of temperature on the partial oxidation of propane over 0.5 % Pt/CeO₂ (A) catalyst in the increasing-temperature mode. As expected, the volumetric flow rate of propane decreases with temperature indicating conversion of propane increases with temperature. It can be seen from Figure 4.2 that oxygen is completely consumed at all temperatures. Hydrogen and carbon monoxide production start taking place at 600°C and then increase with temperature. Hydrogen and carbon monoxide

production reach maxima at 800 ° C. Carbon dioxide production drops as temperature increases. Production of methane is very low and always below 1 scc/min.

Table 4.2 shows effect of time on stream on stability of the catalyst. The reactor temperature is brought down to 700 ° C to study the deactivation, if any is taking place. After the temperature is brought back to 700 ° C and is held for 3 hrs, the catalyst does not show any deactivation. It is interesting to note that the values for conversions and selectivities for these runs are greater than that of initial reading taken at 700 ° C, also shown in Table 4.2. This can be attributed to the stabilization of the catalyst by reaction at 800 ° C.

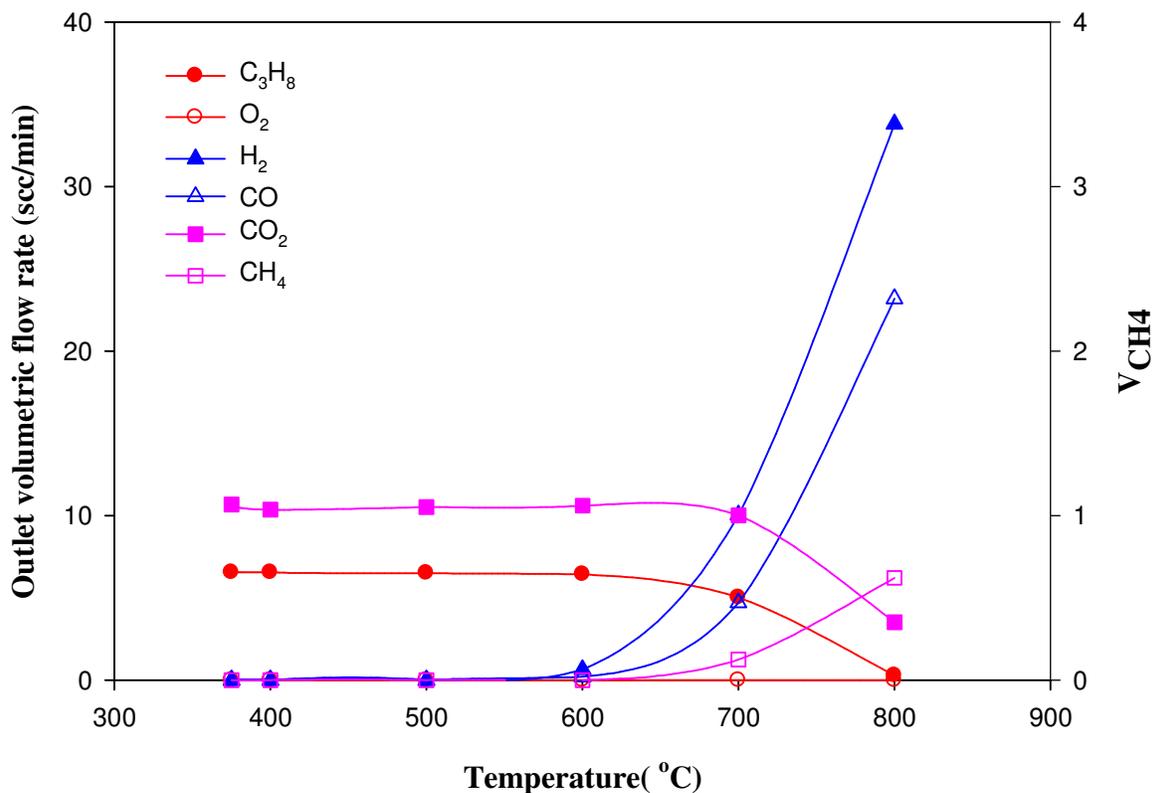


Figure 4.2 Effect of temperature on activities and product distribution over 0.5 % Pt/CeO₂ (A) catalyst (Feed ratio: O₂/C₃H₈ = 1.78, total feed rate: 300 scc/min)

Table 4.2 Effect of time on stream on stability of the 0.5 % Pt/CeO₂ (A) catalyst at 700 ° C (Feed ratio: O₂/C₃H₈ = 1.78, total feed rate: 300 scc/min)

Time (hrs)	X _{C₃H₈}	X _{O₂}	S _{H₂}	S _{CO}	S _{CO₂}	S _{CH₄}
*	54.11	100	42.40	26.51	56.36	0.70
1	58.91	100	47.86	34.64	48.76	0.64
2	57.05	100	48.68	32.46	51.54	0.67
3	57.50	100	45.09	30.40	56.85	0.66

* Increasing temperature mode

4.1.3 Summary

The activities of the commercial 5 % Pt/Al₂O₃ catalyst and of 0.5 % Pt/CeO₂ (A) were studied for partial oxidation of propane with O₂/C₃H₈ = 1.78. The preliminary studies show that both catalysts are active for this reaction. Hydrogen production starts taking place above 500 ° C.

The reaction follows two regimes. Below 500 ° C, it is a total combustion regime, where propane is converted exclusively to carbon dioxide and water. Above 500 ° C, is it a reforming regime, where propane is converted into carbon monoxide and hydrogen. For 0.5 % Pt/CeO₂ (A) catalyst, after bringing down the temperature back to 700 ° C and holding it for 3 hrs, catalyst does not show any deactivation. The values for conversions and selectivities for these runs are greater than that of initial reading taken at 700 ° C. This can be attributed to the stabilization of the catalyst by reaction at 800 ° C.

4.2 Effect of support on partial oxidation of propane

Partial oxidation of propane has been studied mainly for irreducible oxides such as Al_2O_3 , SiO_2 , MgO etc. The reducible oxides like CeO_2 can offer additional benefits for the reaction due to their oxygen storage capacity. There have been reports on the reaction regimes, total combustion being the first regime and reforming being the second regime (Pantu and Gavalas, 2002).

In this section, the effect of temperature is studied for the partial oxidation of propane using Pt/CeO_2 (B) and Pt/CeO_2 (C). Both the catalysts contain 1 % (wt %) Pt metal. The results are also compared with the 1 % $\text{Pt/Al}_2\text{O}_3$ catalyst. The effect of temperature on 0.5 % Pt/CeO_2 (A) was discussed in Section 4.1.2. The similar behavior is observed for 1 % Pt/CeO_2 (A) catalyst and hence it is not discussed in this chapter but the quantitative comparison is made between 1 % Pt/CeO_2 (A), 1 % Pt/CeO_2 (B), 1 % Pt/CeO_2 (C) and 1 % $\text{Pt/Al}_2\text{O}_3$ catalysts later in this chapter.

4.2.1 Pt/CeO_2 (B) catalyst

The 1 % Pt/CeO_2 (B) catalyst is tested for effect of temperature in increasing temperature mode. The materials are given in Section 3.2.4.1 and the methodology is given in Section 3.2.4.2.

Figure 4.3 shows the effect of temperature on partial oxidation of propane over 1 % Pt/CeO_2 (B) catalyst. The outlet flow rate of propane decreases with increase in temperature. This indicates that conversion of propane increases with temperature. Oxygen is completely consumed above 500 ° C. Productions of hydrogen and carbon monoxide are measurable above 500 ° C. The products increase with increase in temperature. Carbon dioxide production initially increases with temperature, but above 400 ° C, reforming reactions become important and production of carbon dioxide levels off. Carbon dioxide production starts decreasing around 650 ° C. Methane formation is low and always below 1.2 scc/min.

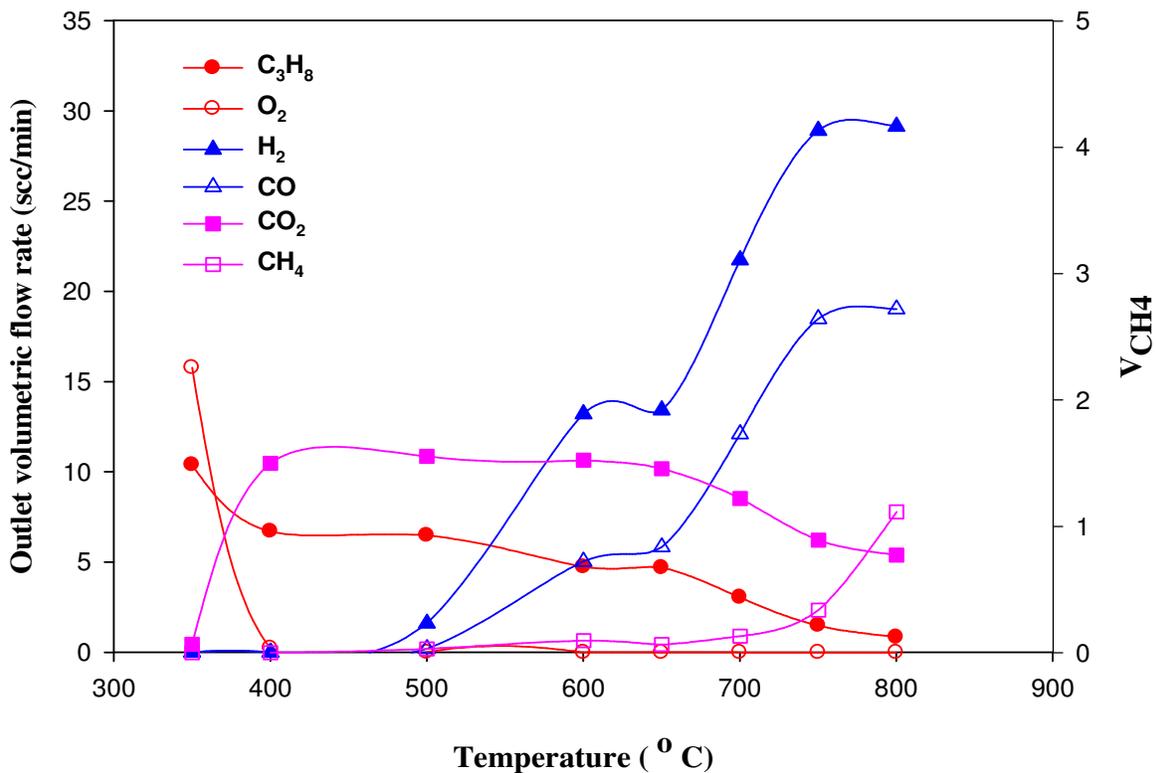


Figure 4.3 Effect of temperature on activities and product distribution over 1 % Pt/CeO₂ (B) catalyst (Feed ratio: O₂/C₃H₈ = 1.78, total feed rate: 300 scc/min)

4.2.2 Pt/CeO₂ (C) Catalyst

The 1 % Pt/CeO₂ (C) catalyst is tested for effect of temperature in increasing temperature mode. The materials are given in Section 3.2.4.1 and the methodology is given in Section 3.2.4.2.

Figure 4.4 shows the effect of temperature on partial oxidation over 1 % Pt/CeO₂ (C) catalyst. The volumetric flow rate of propane decreases with increase in temperature indicating an increase in conversion with temperature. Oxygen is not completely consumed at all temperatures. Below 500 °C, some oxygen is observed and it is completely consumed above 500 °C. More oxygen and propane is observed below 500 °C as compared to 1 % Pt/CeO₂ (B) which indicate that conversion of propane and oxygen is higher for 1 %

Pt/CeO₂ (B) than 1 % Pt/CeO₂ (C) below 500 ° C. Production of hydrogen starts at 450 ° C. Productions of hydrogen and carbon monoxide increase with increase in temperature and reaches maxima at 750 ° C. Carbon dioxide production levels off at 550 ° C and then decreases with temperature.

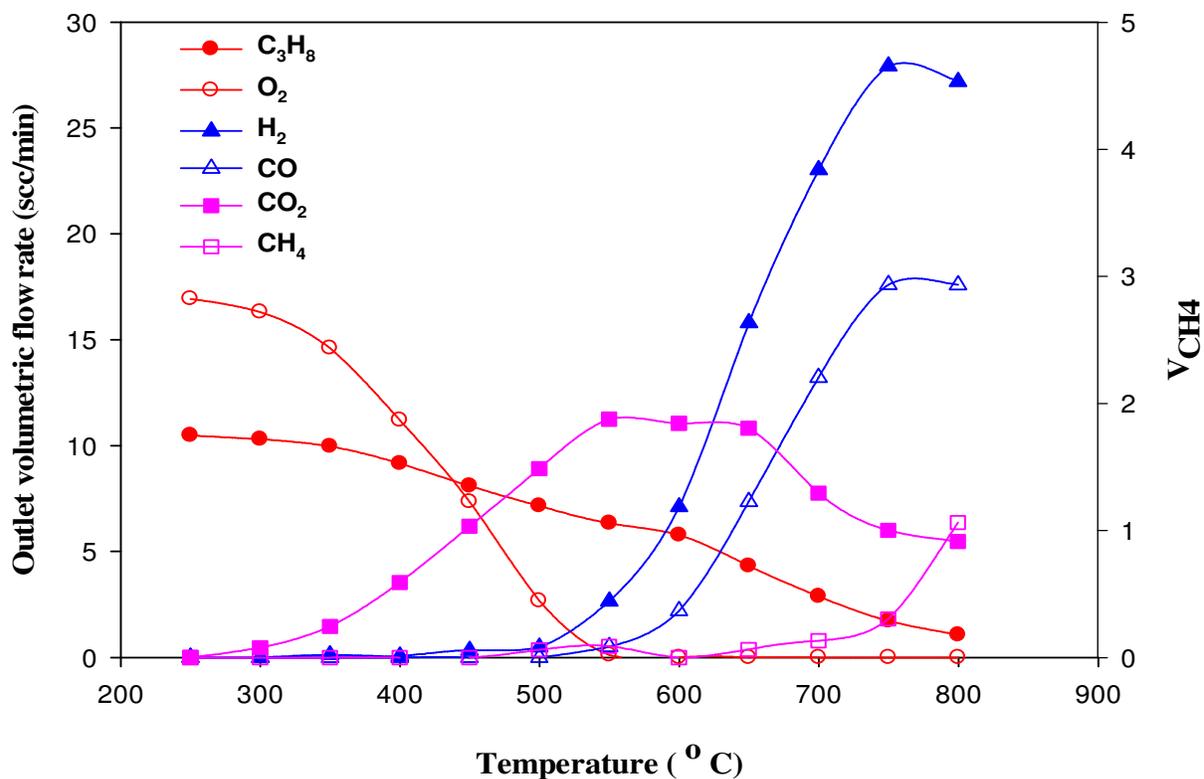


Figure 4.4 Effect of temperature on activities and product distribution over 1 % Pt/CeO₂ (C) catalyst (Feed ratio: O₂/C₃H₈ = 1.78, total feed rate: 300 scc/min)

4.2.3 Pt/Al₂O₃ Catalyst

The 1 % Pt/Al₂O₃ catalyst is used for comparison with results obtained for Pt/CeO₂ catalysts. The materials are given in Section 3.2.4.1 and the methodology is given in Section 3.2.4.2.

Figure 4.5 shows the effect of temperature on partial oxidation of propane over 1 % Pt/Al₂O₃ catalyst. The outlet flow rate of propane decreases with increasing temperature indicating the conversion is increasing. Oxygen is consumed completely at all temperatures. Productions of hydrogen and carbon monoxide start taking place at 500 °C and increase with increasing temperature. The outlet flow rate of carbon dioxide is almost constant up to 600 °C and then decreases with temperature. The trends observed for all the products are same as observed with Pt/CeO₂ catalysts. The conversions and selectivities over different catalysts are quantitatively analyzed in Section 4.2.6.

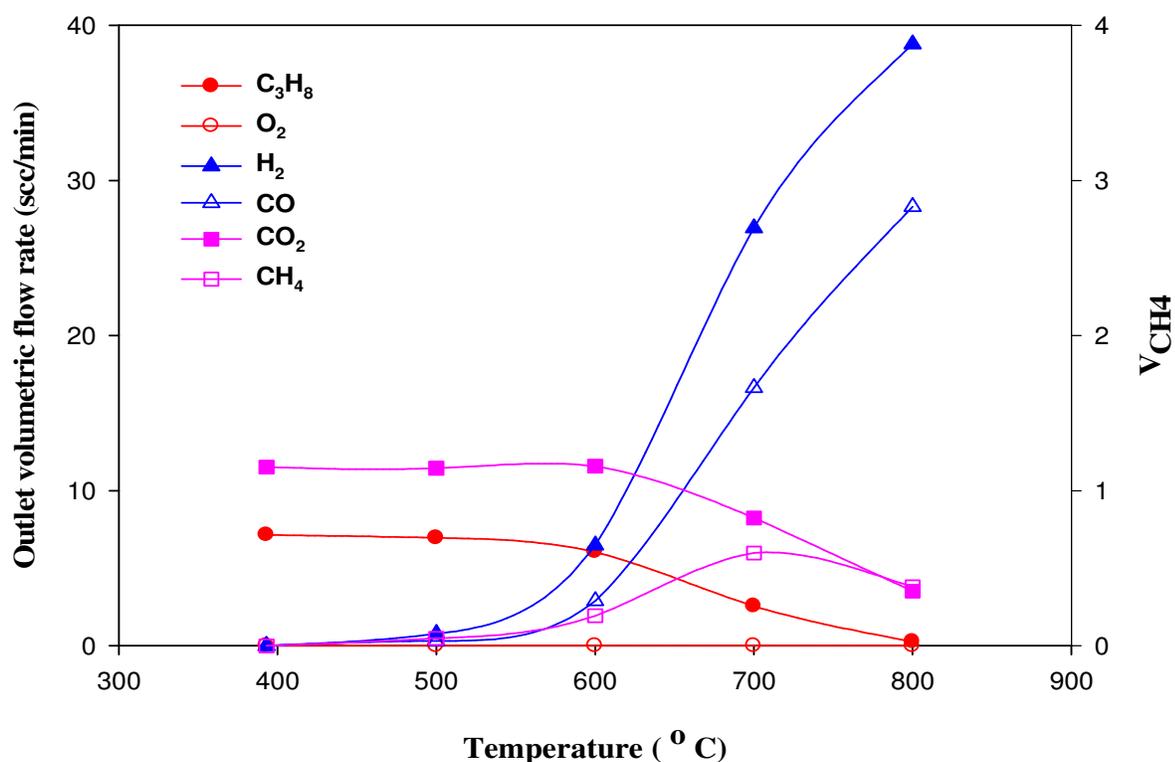


Figure 4.5 Effect of temperature on activities and product distribution over 1 % Pt/Al₂O₃ catalyst (Feed ratio: O₂/C₃H₈ = 1.78, total feed rate: 300 scc/min)

4.2.4 Study of Thermal Stability

The thermal stability of ceria supports and catalysts were studied under N₂ atmosphere. The materials and methodology for this experiment are given in Section 3.2.4.3.

Table 4.3 shows the thermal stability of ceria supports and catalysts. The BET surface area of fresh samples of CeO₂ (B) and CeO₂ (C) are 4-5 times larger than that of CeO₂ (A). After thermal treatment, surface areas of CeO₂ (B) and CeO₂ (C) supports and 1 % Pt/CeO₂ (B) and 1 % Pt/CeO₂ (C) drop drastically. It is interesting to note that, though BET surface area of fresh CeO₂ (C) is larger than CeO₂ (B), CeO₂ (B) has a larger BET surface area than CeO₂ (C) after heat treatment and so does the catalyst. The loss of BET surface areas can be attributed to loss of microporous surface followed by sintering of particles (Perrichon *et al.*, 1995).

Table 4.3 Thermal stability analysis of different ceria supports and catalysts

Support/Catalyst	BET surface area (Fresh sample), (m ² /g)	BET surface area after heating at 900 ° C in N ₂ flow for 24 hrs (m ² /g)
CeO ₂ (A)	17.3	5.1
CeO ₂ (B)	69.6	17.1
CeO ₂ (C)	84.7	6.1
1 % Pt/CeO ₂ (A)	9.9	6.7
1 % Pt/CeO ₂ (B)	65.8	15.5
1 % Pt/CeO ₂ (C)	80.4	5.5

A-Commercial ceria, B- Precipitation method, C- Decomposition method

4.2.5 Platinum dispersion studies

Platinum dispersion was measured for 1 % Pt/CeO₂ (A), 1 % Pt/CeO₂ (B), 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts. The materials and methodology are given in Section 3.2.5.2.

Table 4.4 gives platinum dispersion values for ceria and alumina supported platinum catalysts. The 1 % Pt/CeO₂ (A) catalyst has very poor platinum dispersion. Platinum dispersion of 1 % Pt/CeO₂ (C) is slightly higher than 1 % Pt/CeO₂ (B). The 1 % Pt/Al₂O₃ has the maximum platinum dispersion which is 46 %.

Table 4.4 Platinum dispersion of ceria and alumina supported Pt catalysts

Catalysts	Platinum dispersion (%)
1 % Pt/CeO ₂ (A)	8.4
1 % Pt/CeO ₂ (B)	34
1 % Pt/CeO ₂ (C)	35
1 % Pt/Al ₂ O ₃	46

4.2.6 Comparison of the catalysts

Figure 4.6 compares 1 % Pt/CeO₂ (A), 1 % Pt/CeO₂ (B), 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃. The figure compares the activity and product selectivities for partial oxidation of propane at 650 ° C and 700 ° C. The total flow rate is 300 scc/min and O₂/C₃H₈ ratio is 1.78.

Conversion of oxygen is always 100 % for all the catalysts. The 1 % Pt/CeO₂ (C), which has the largest BET surface area and platinum dispersion among all ceria-supported catalysts, shows the highest propane conversion ($X_{C_3H_8}$), the highest hydrogen selectivity (S_{H_2}) and carbon monoxide selectivity (S_{CO}) and the lowest carbon dioxide selectivity (S_{CO_2}) among all ceria-supported catalysts. 1 % Pt/Al₂O₃ gives the highest propane conversion, the highest hydrogen and carbon monoxide selectivities and the lowest carbon dioxide selectivity among all the catalysts. This can be explained by noting that BET surface area of 1 % Pt/Al₂O₃ (153 m²/g) is twice that of 1 % Pt/CeO₂ (C) (80.4 m²/g) and also it has higher platinum dispersion than 1 % Pt/CeO₂ (C). Also, the BET surface areas of the ceria catalysts are not stable, and the catalysts lose surface area with heat treatment.

Ruckenstein and Wang (1999) reported that Rh supported on irreducible oxides like Al_2O_3 was more active for partial oxidation of methane than Rh supported on reducible oxides like CeO_2 . The authors suggest that the lower activity of reducible oxides is due to coverage of Rh sites by partially reduced oxide and thus, in turn, loss in active sites during reaction. Pantu and Galvalas (2002) also studied methane partial oxidation over Pt supported on CeO_2 and Al_2O_3 . At lower temperatures, Pt/ CeO_2 gave higher conversion than Pt/ Al_2O_3 due to redox reactions. But at higher temperatures like 650°C and 700°C , conversions obtained for both catalysts are very close. This is due to reduction in the promotion effect of CeO_2 support.

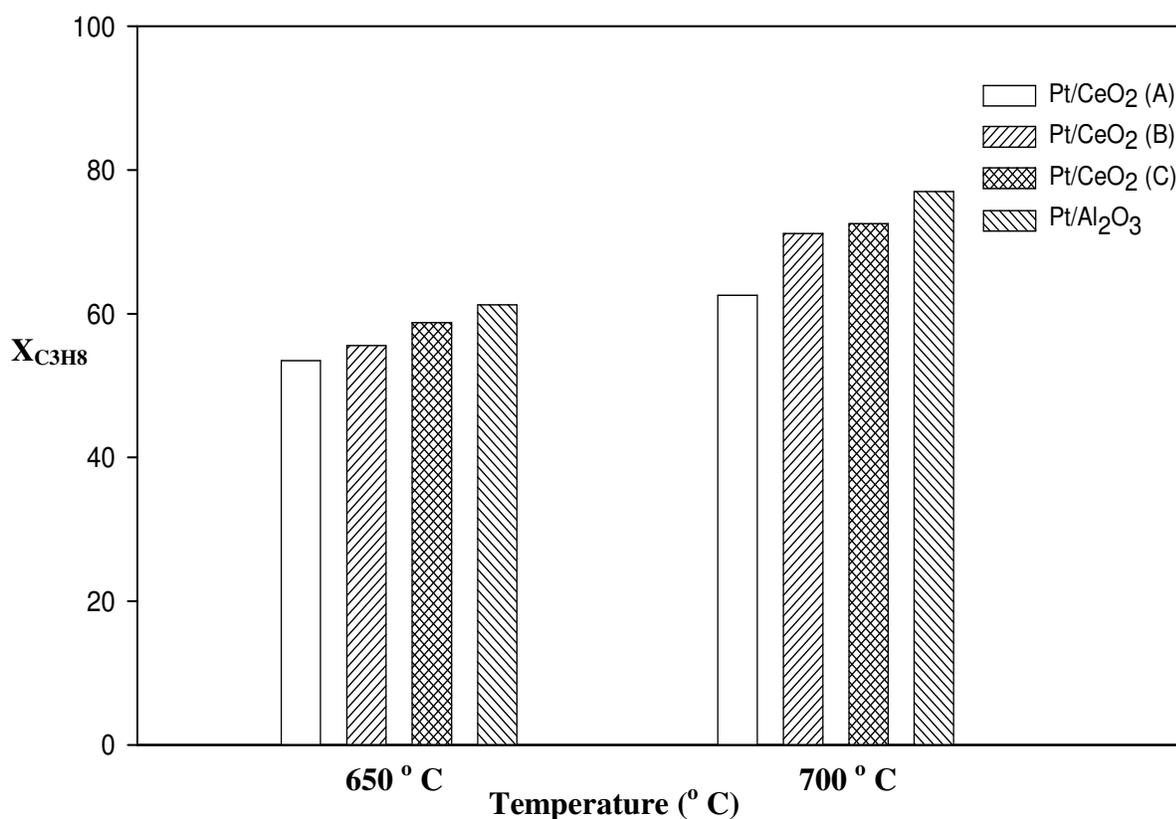


Figure 4.6 a Comparison of activities of 1 % Pt/ CeO_2 and 1 % Pt/ Al_2O_3 catalysts (Total flow rate = 300 scc/min, $\text{O}_2/\text{C}_3\text{H}_8 = 1.78$, amount of catalyst = 0.1 g)

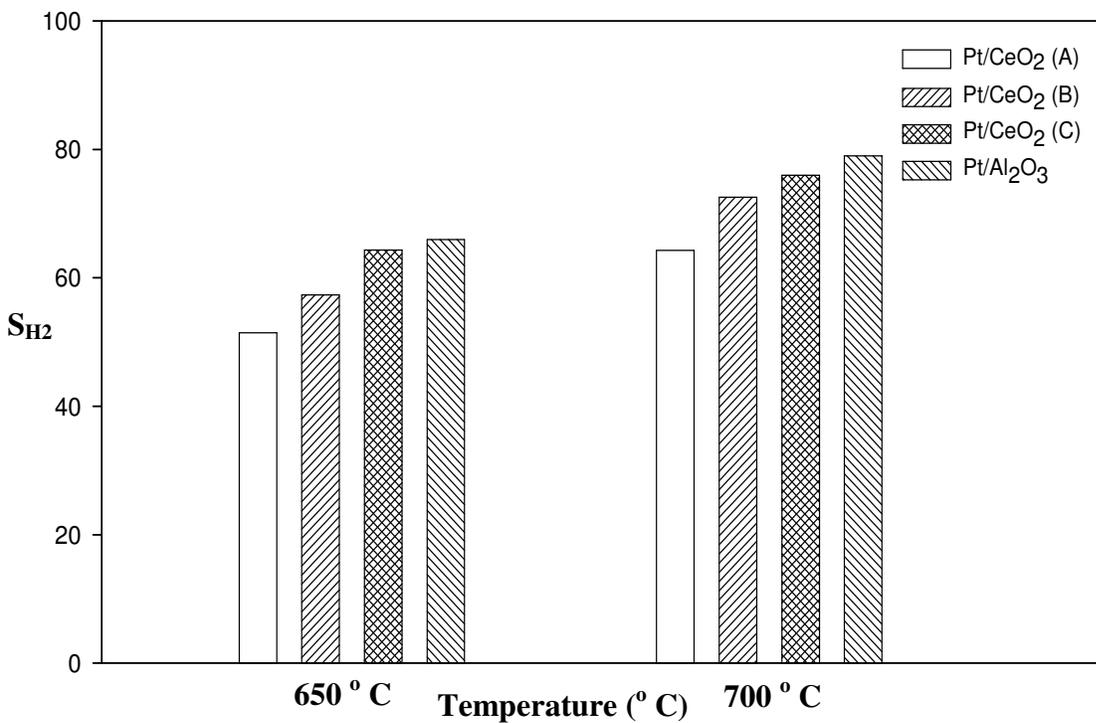


Figure 4.6 b Comparison of H₂ selectivities of 1 % Pt/CeO₂ and 1 % Pt/Al₂O₃ catalysts (Total flow rate = 300 scc/min, O₂/C₃H₈ = 1.78, amount of catalyst = 0.1 g)

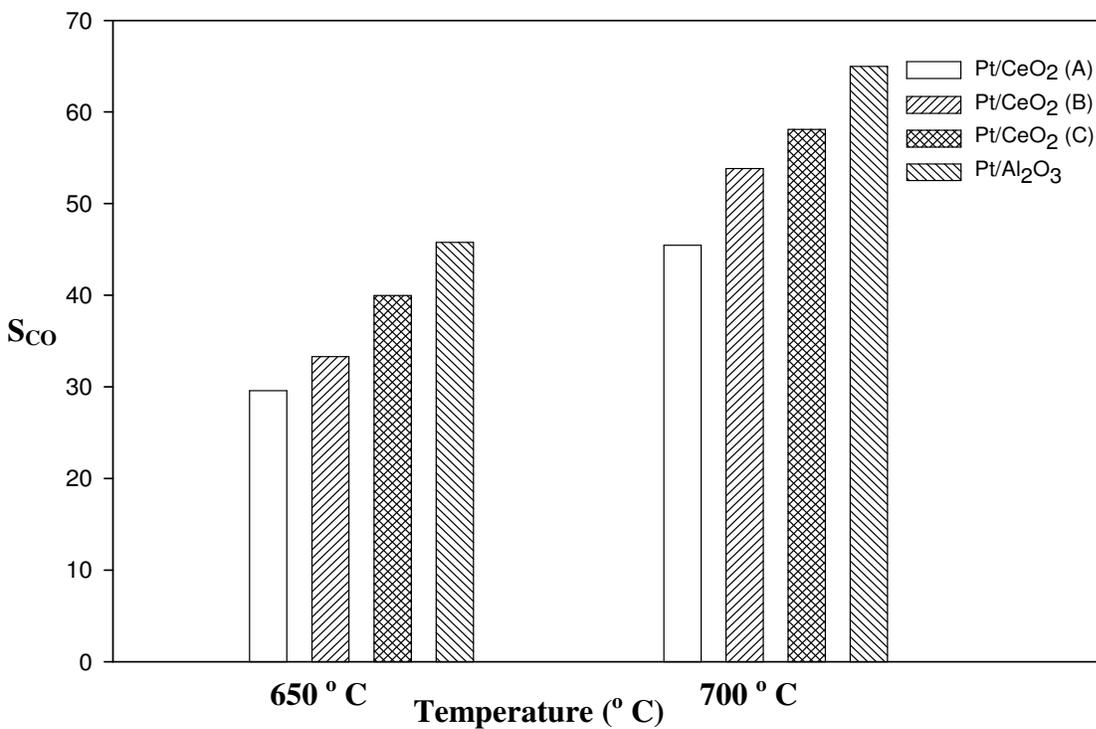


Figure 4.6 c Comparison of CO selectivities of 1 % Pt/CeO₂ and 1 % Pt/Al₂O₃ catalysts (Total flow rate = 300 scc/min, O₂/C₃H₈ = 1.78, amount of catalyst = 0.1 g)

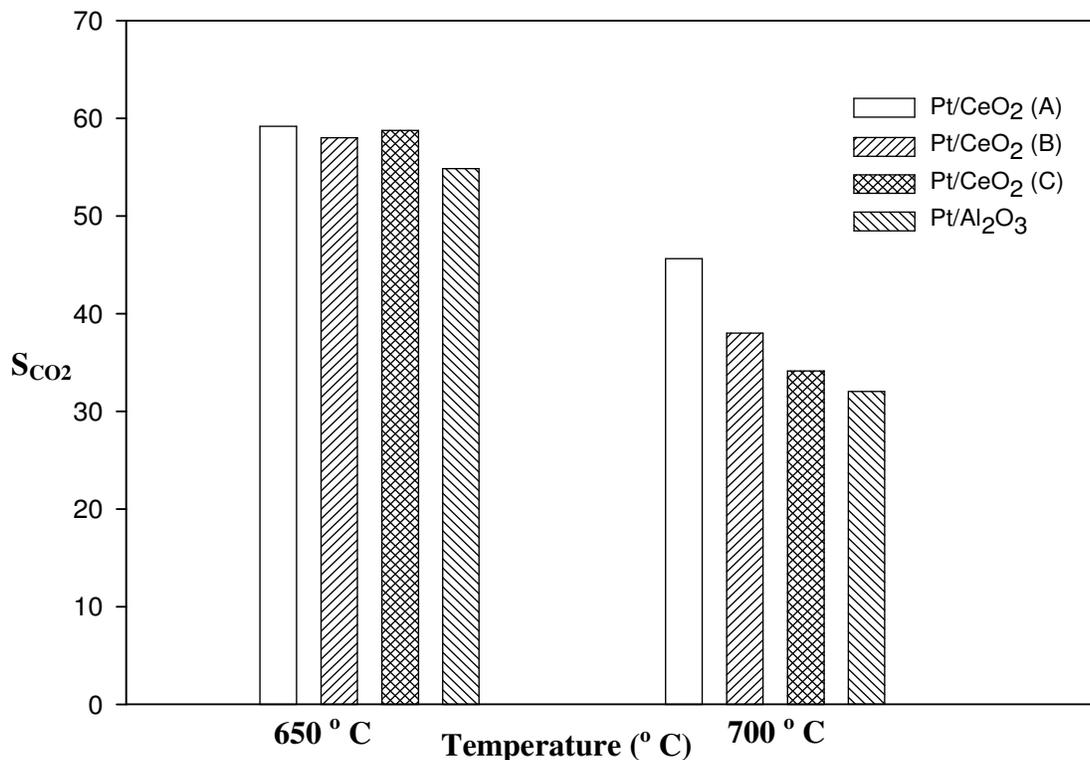


Figure 4.6 d Comparison of CO₂ selectivities of 1 % Pt/CeO₂ and 1 % Pt/Al₂O₃ catalysts (Total flow rate = 300 scc/min, O₂/C₃H₈ = 1.78, amount of catalyst = 0.1 g)

4.11 Summary

Studies of the effect of temperature for 1 % Pt/CeO₂ (A), 1 % Pt/CeO₂ (B), 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ show that there are two domains for partial oxidation reaction. Below 500 °C, complete oxidation of propane takes place to produce carbon dioxide and water. Above 500 °C, propane undergoes reforming reactions, producing hydrogen and carbon monoxide.

Ceria supports and the ceria-supported catalysts lose surface area upon heat treatment. The 1 % Pt/CeO₂ (C) catalyst, which has the largest initial BET surface area and platinum dispersion among ceria catalysts, gives the best activity and product selectivities for partial oxidation of propane among all ceria-supported catalysts. The 1 % Pt/Al₂O₃ catalyst, which has BET surface area twice that of 1 % Pt/CeO₂ (C) and higher platinum dispersion, gives higher propane conversion and hydrogen selectivity than 1 % Pt/CeO₂ (C).

Chapter 5: Effect of Time on Stream and Feed Ratio for 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃

5.1 Introduction

This chapter deals with the effect of O₂/C₃H₈ ratio on the performance of 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts for partial oxidation of propane. As noted in Chapter 4, 1 % Pt/CeO₂ (C) catalyst gives the highest activity at 650 ° C and 700 ° C for partial oxidation of propane among all ceria-supported catalysts used here. Also, this catalyst has the largest BET surface area and Pt dispersion among all ceria-supported catalysts used here. Hence the studies are carried out using the 1 % Pt/CeO₂ (C) catalyst. The effect of time on stream is also studied. The stable performance of the catalyst is very important for any reaction. Hence, the stability of the catalysts is studied to check if catalysts are stable and not deactivating with time on stream.

5.2 Effect of time on stream

5.2.1 1 % Pt/CeO₂ (C) catalyst

For the reasons mentioned above, the effect of time on stream on the performance of 1 % Pt/CeO₂ (C) catalyst was studied at 800 ° C for 15 hours on stream. The materials are given in Section 3.2.4.1 and methodology is given in Section 3.2.4.4.

Figure 5.1 shows the time-on-stream behavior of 1 % Pt/CeO₂ (C) catalyst for the partial oxidation of propane. The initial propane conversion is 91 % and hydrogen selectivity is 78 %. Oxygen conversion is always 100 %. At t = 15 hr, propane conversion is 88 % and hydrogen selectivity 71 %. The conversion of propane and selectivities of hydrogen, carbon monoxide and carbon dioxide do not change much over the time period. The rate of deactivation was calculated by linear regression of propane conversion to be

0.28 % propane conversion/hr. This indicates that the 1 % Pt/CeO₂ (C) catalyst is stable for partial oxidation of propane and not deactivating during the course of reaction.

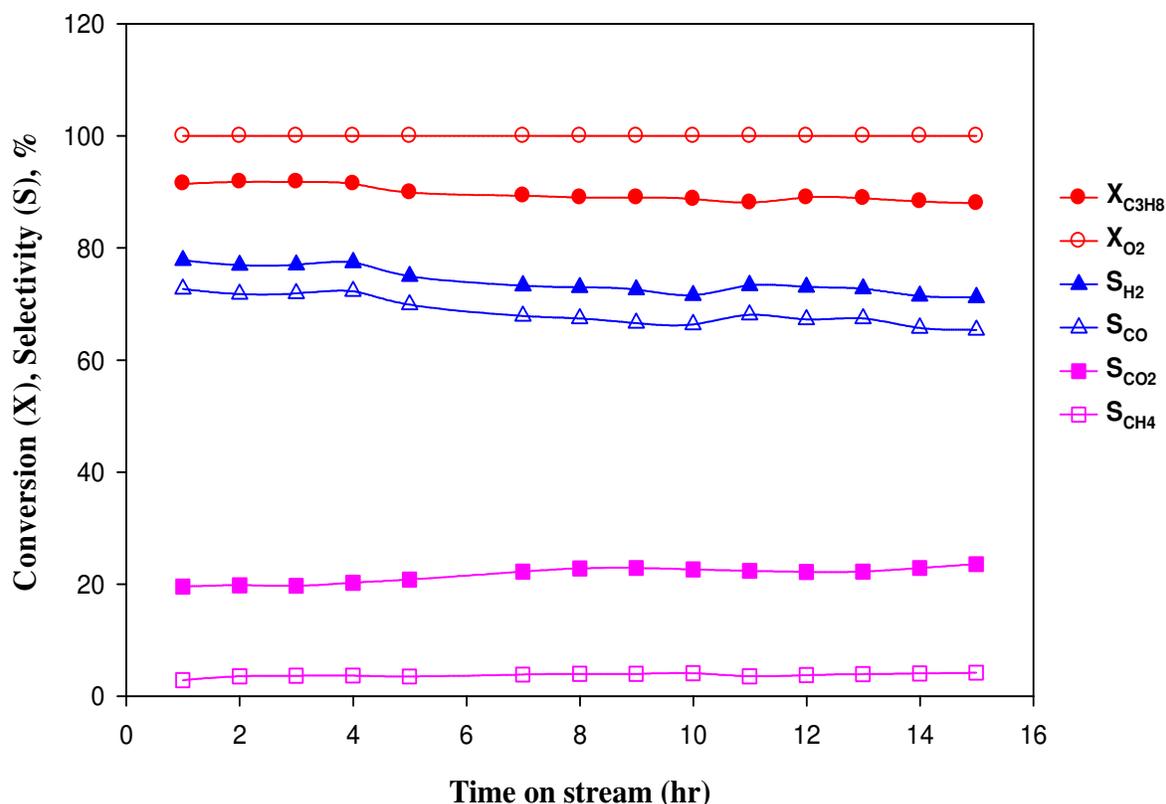


Figure 5.1 Stability of 1 % Pt/CeO₂ (C) for propane activity and product selectivities against time on stream (T = 800 ° C, total flow rate = 300 scc/min with 90 % inert)

5.2.2 1 % Pt/Al₂O₃ catalyst

The effect of time on stream on the performance of the 1 % Pt/Al₂O₃ catalyst was studied at 600 ° C for 16 hours on stream. The materials are given in Section 3.2.4.1 and methodology is given in Section 3.2.4.4.

Figure 5.2 shows the time-on-stream behavior of 1 % Pt/Al₂O₃ catalyst for the partial oxidation of propane at 600 ° C. The initial propane conversion is 50 % and hydrogen selectivity is 36 %. Oxygen conversion is always 100 %. At t = 16 hr, propane conversion is 46 % and hydrogen selectivity 29 %. After 5 hrs of time on stream, the catalyst is very stable. The conversion of propane and selectivities of hydrogen, carbon

monoxide and carbon dioxide do not change much over the time period. The rate of deactivation was calculated by linear regression of propane conversion to be 0.25 % propane conversion/hr. This indicates that the 1 % Pt/Al₂O₃ catalyst is stable for partial oxidation of propane and not deactivating during the course of reaction.

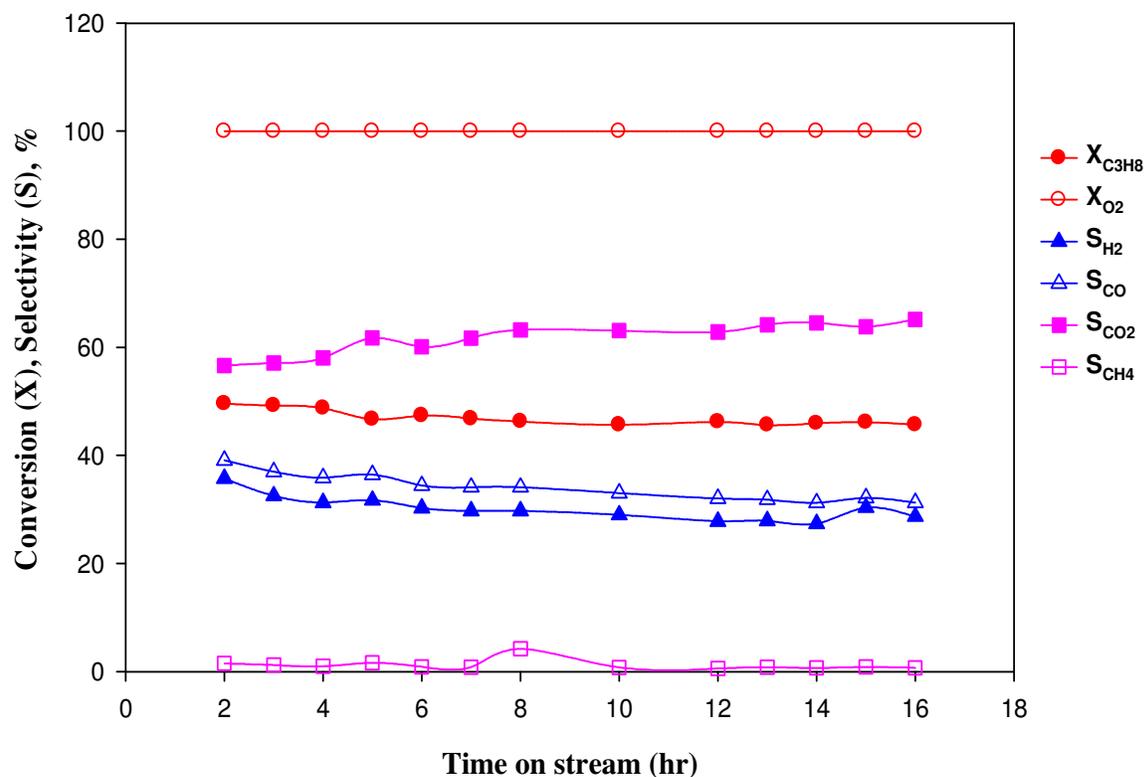


Figure 5.2 Stability of 1 % Pt/Al₂O₃ for propane activity and product selectivities against time on stream (T = 600 ° C, total flow rate = 300 sccm with 90 % inert)

5.3 Effect of O₂/C₃H₈ ratio

5.3.1 Pt/CeO₂ (C) catalyst

The 1 % Pt/CeO₂ (C) catalyst is studied for the effect of the O₂/C₃H₈ ratio. The materials are given in Section 3.2.4.1 and methodology for this reaction is given in Section 3.2.4.5.

Figure 5.3 shows the effect of the O₂/C₃H₈ ratio on partial oxidation of propane over 1 % Pt/CeO₂ (C) catalyst. Propane conversion and carbon dioxide selectivity increase as the O₂/C₃H₈ ratio increases. The hydrogen and carbon monoxide selectivities decrease with increase in the O₂/C₃H₈ ratio.

The stoichiometric ratio for partial oxidation is 1.5 while it equals 5 for total oxidation. Between O₂/C₃H₈ = 1.5 and O₂/C₃H₈ = 5, the selectivities of hydrogen and carbon monoxide decrease, and the selectivity of CO₂ increases. This indicates that, as O₂/C₃H₈ passes the stoichiometric point for partial oxidation and moves closer to the stoichiometric point for total oxidation, though the propane conversion is increasing, a small amount of propane is reacting through reforming reactions to form hydrogen and carbon monoxide while most of the propane is reacting through total oxidation to form carbon dioxide. Oxygen conversion is 100 % up to O₂/C₃H₈ = 5 (corresponds to complete combustion). Above O₂/C₃H₈ = 5, there is excess oxygen present, and it remains unreacted. Hence the conversion decreases.

At values of O₂/C₃H₈ greater than 5, all the reacted propane is converted into carbon dioxide. Below O₂/C₃H₈ = 1.5, conversion of propane is very low but very high hydrogen and carbon monoxide selectivities are obtained with very low carbon dioxide selectivity. The maximum hydrogen selectivity (94 %) is obtained at O₂/C₃H₈ = 0.5 but conversion of propane is very low, 28 %, under these conditions. The optimum O₂/C₃H₈ ratio is probably around 2 for high hydrogen selectivity and high propane conversion. At O₂/C₃H₈ values greater than 5, hydrogen, carbon monoxide and methane are not observed.

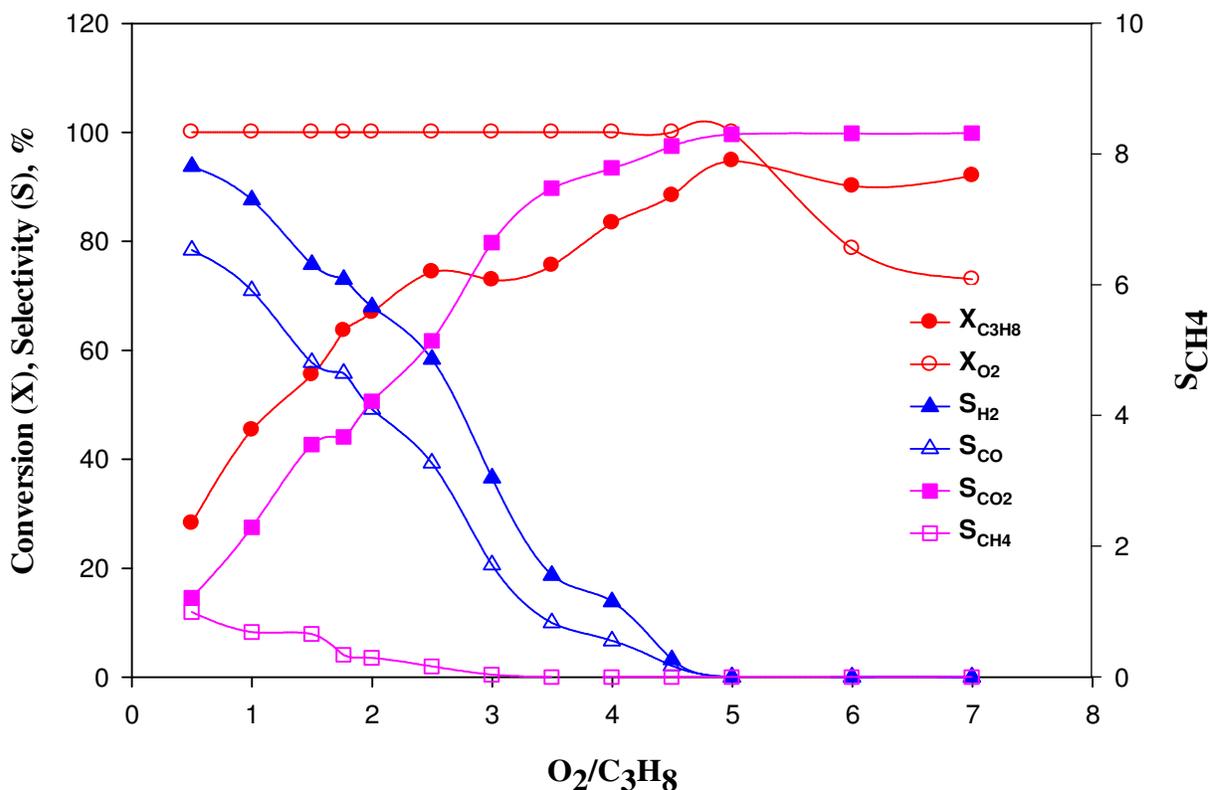


Figure 5.3 Effect of O₂/C₃H₈ ratio on partial oxidation of propane on 1 % Pt/CeO₂ (C) catalyst (T = 675 ° C, total flow rate = 300 scc/min with 90 % inert)

5.3.2 Pt/Al₂O₃ catalyst

The materials are given in Section 3.2.4.1 and methodology for this reaction is given in Section 3.2.4.5.

Figure 5.4 shows the effect of the O₂/C₃H₈ ratio on partial oxidation of propane over the 1 % Pt/Al₂O₃ catalyst. Similar behavior is observed for 1 % Pt/Al₂O₃ as it was observed for 1 % Pt/CeO₂ (C) catalyst. Propane conversion increases as O₂/C₃H₈ increases. The selectivities of hydrogen and carbon monoxide decrease, and the selectivity of CO₂ increases, with increase in the O₂/C₃H₈ ratio. Oxygen conversion is 100 % up to O₂/C₃H₈ = 5 (corresponds to complete combustion) and it decreases for higher values. At values of O₂/C₃H₈ greater than 5, all the reacted propane is converted into carbon dioxide.

The maximum hydrogen selectivity (81 %) is obtained at $O_2/C_3H_8 = 0.5$ but conversion of propane is very low, 22 %, under these conditions. The optimum O_2/C_3H_8 ratio is probably around 2 for high hydrogen selectivity and high propane conversion. At O_2/C_3H_8 values greater than 5, hydrogen, carbon monoxide and methane are not observed. The results confirm the observation made for 1 % Pt/CeO₂, that the optimum O_2/C_3H_8 ratio is around 2 for high conversion of propane and high selectivity of hydrogen.

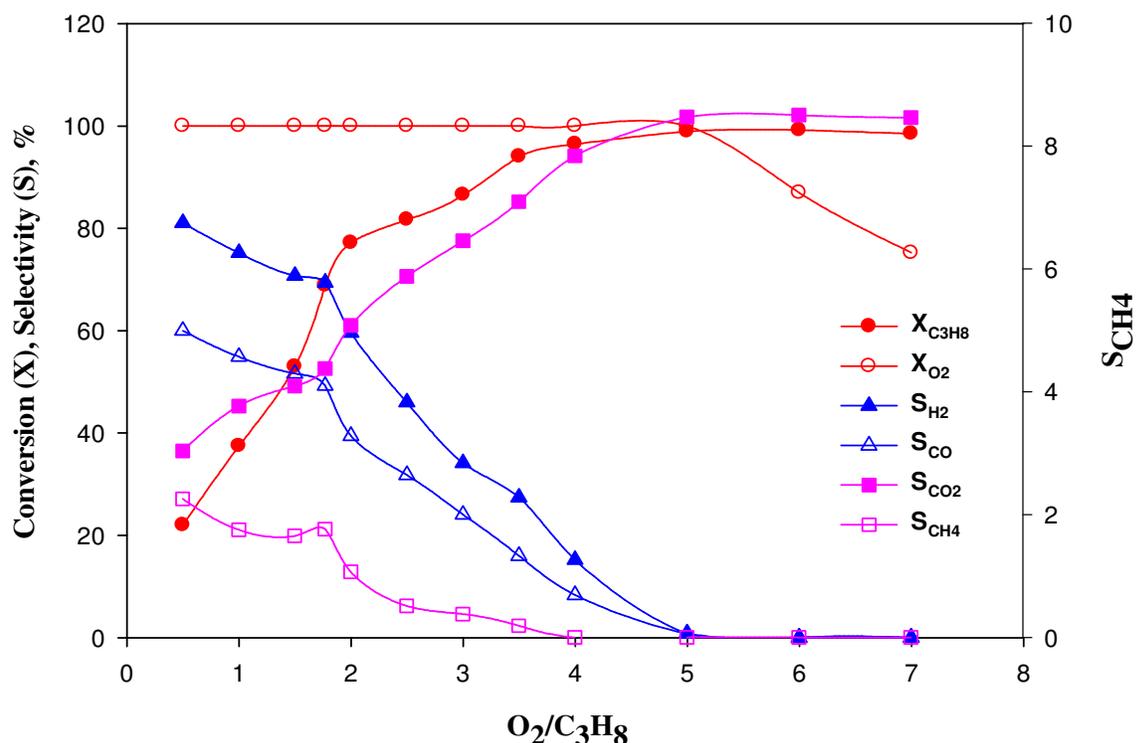


Figure 5.4 Effect of O_2/C_3H_8 ratio on partial oxidation of propane on 1 % Pt/Al₂O₃ catalyst (T = 675 ° C, total flow rate = 300 scc/min with 90 % inert)

5.4 Summary

The effect of time on stream on the performance of 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ show that both the catalysts are stable, with deactivation rates of 0.28 % and 0.25 % propane conversion/hr respectively.

The effect of the O₂/C₃H₈ ratio on partial oxidation of propane for 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ show that the conversion of propane increases and the hydrogen selectivity decreases with increase in the O₂/C₃H₈ ratio. The optimum ratio is probably around 2 for high propane conversion and high hydrogen selectivity.

Chapter 6: Effect of Flow Rate on Partial Oxidation of Propane

6.1 Introduction

The effect of temperature on partial oxidation has been studied by many researchers. Partial oxidation, steam reforming, water gas shift reaction and dry reforming are the proposed reactions responsible for hydrogen production at high temperatures. Very few studies have been done to study the effect of flow rate on partial oxidation. Hence the effect of flow rate is studied for 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts to understand the partial oxidation reaction. This reaction is carried out at very low catalyst loadings and low temperature (600 ° C) so that the reactor can be studied as a differential reactor and the reaction scheme can be understood. Partial oxidation is also carried out on CeO₂ (C) and γ -Al₂O₃ supports to see if the support has any activity towards this reaction. Finally, dry reforming of propane is carried out to understand if this has any contribution to the overall reaction set.

Prior to catalytic testing, a blank reaction is carried out in a quartz reactor. Table 6.1 shows the results for the blank reaction. There is only 3 % conversion of propane and all the reacted propane is converted into carbon dioxide.

Table 6.1 Effect of temperature on the activity of the quartz reactor for partial oxidation of propane (total flow rate = 300 scc/min, O₂/C₃H₈ = 1.78)

Temperature (° C)	X _{C₃H₈} , %	X _{O₂} , %	S _{H₂} , %	S _{CO} , %	S _{CO₂} , %
300	0	0	0	0	0
400	0	0	0	0	0
500	0.7	2.6	0	0	99.2
600	2.8	7.9	0	0	100
700	6.5	13.2	1.2	3.2	68.7
800	86.7	75.5	5.2	14.2	17.1

6.2 Study of support for partial oxidation of propane

Partial oxidation of propane was studied for CeO₂ (C) and γ -Al₂O₃ supports. The materials and methodology are given in Section 3.2.4.6.

Table 6.2 shows results for partial oxidation of propane on the CeO₂ (C) and γ -Al₂O₃ supports. For the CeO₂ (C) support, as the flow rate decreases, the conversion of propane and of oxygen increase. Conversion of oxygen is 100 % at the lower flow rate (50 scc/min). The reaction on CeO₂ (C) support gives 17.39 % and 35.81 % propane conversion at 300 scc/min and 50 scc/min respectively. Hydrogen selectivity is less than 3 %, independent of flow rate. There is no carbon monoxide formation; the largest part of the reacted propane forms carbon dioxide. The FID detector shows peaks for propylene and methane. The results for the blank reaction indicate that the reactor is not active at 600 °C and the activity for total oxidation of propane is coming from the support.

Propane is converted into carbon dioxide and water with no carbon monoxide production for partial oxidation of propane on support alone. Similar results are observed with the alumina support. Conversion of propane and oxygen increases with decrease in the flow rate. Propane is converted into carbon dioxide and water. Hydrogen selectivity is very low. Some amount of carbon monoxide is observed at 50 scc/min, but it is very low. The alumina support shows less conversion of propane and oxygen (as compared to the ceria support) at both high and low flow rates. This indicates that the ceria support is more active for total oxidation than the alumina support.

For both the supports, hydrogen formation can be explained by the reaction of propane decomposition into propylene and hydrogen which is shown below.



The results for partial oxidation of propane for the CeO₂ (C) and γ -Al₂O₃ support show that the supports are active for total oxidation of propane but not for reforming reactions of propane to produce hydrogen.

Table 6.2 Partial oxidation of propane on CeO₂ (C) and γ -Al₂O₃ supports (Temperature = 600 ° C, O₂/C₃H₈ = 1.78, amount of catalyst = 0.02 g)

Catalyst Support	CeO ₂ (C)		γ -Al ₂ O ₃	
	300	50	300	50
Total flow (scc/min)	300	50	300	50
X _{C₃H₈} , %	17.4	35.8	5.9	26.8
X _{O₂} , %	41.2	100	15.9	68.0
S _{H₂} , %	2.6	1.5	2.3	2.9
S _{CO} , %	0	0	0	5.7
S _{CO₂} , %	81.3	90.8	87.3	90.4

6.3 Effect of flow rate

6.3.1 1 % Pt/CeO₂ (C) Catalyst

The effect of flow was studied for 0.01 g and 0.02 g of 1 % Pt/CeO₂ (C) catalyst. The reaction was carried out in the quartz reactor at 600 ° C. The materials and methodology are given in Section 3.2.4.7.

Figure 6.1 shows the effect of flow rate on catalyst activity and selectivity for partial oxidation of propane over 1 % Pt/CeO₂ (C). The results are shown for both 0.01 g and 0.02 g loading. Oxygen outlet flow rates are not shown in the graph, as oxygen is completely consumed at all flow rates and all catalyst loadings used. From Figure 6.1, the outlet flow rate of propane at 0.02 g is less than that at 0.01 g at all the flow rates. This indicates that, as expected, the conversion of propane increases with increase in catalyst weight at all flow rates. Similarly, the production of hydrogen increases with increase in catalyst weight at all flow rates. The conversion of propane does not change much with respect to total inlet flow rate, which indicates that the reaction is not mass transfer controlled under these operating conditions.

All the total oxidation of propane takes place in the first half of the reactor (0.01 g), as all the oxygen is consumed at 0.01 g catalyst loading itself. For the second half of the reactor containing 0.01 g catalyst, the unreacted propane undergoes reforming reactions such as steam reforming and dry reforming by reacting with the products formed in total oxidation.

Further, the production of carbon dioxide increases with increase in catalyst weight at all the flow rates. Finally, the outlet flow rate of carbon monoxide at 0.02 g is almost the same as the outlet flow rate at 0.01 for lower flow rates, i.e. 50, 100 and 200 scc/min. For the higher flow rates, i.e. 300 scc/min and 400 scc/min, the outlet flow rate of carbon monoxide at 0.02 g is less than that at 0.01 g. This shows that, at the lower space times (higher space velocities), the carbon monoxide formed at 0.01 g loading is reacting further

as the amount of catalyst increases. Most probably this overall loss of CO and overall gain in CO₂ is due to consumption of carbon monoxide through water gas shift reaction (Equation 2.6).

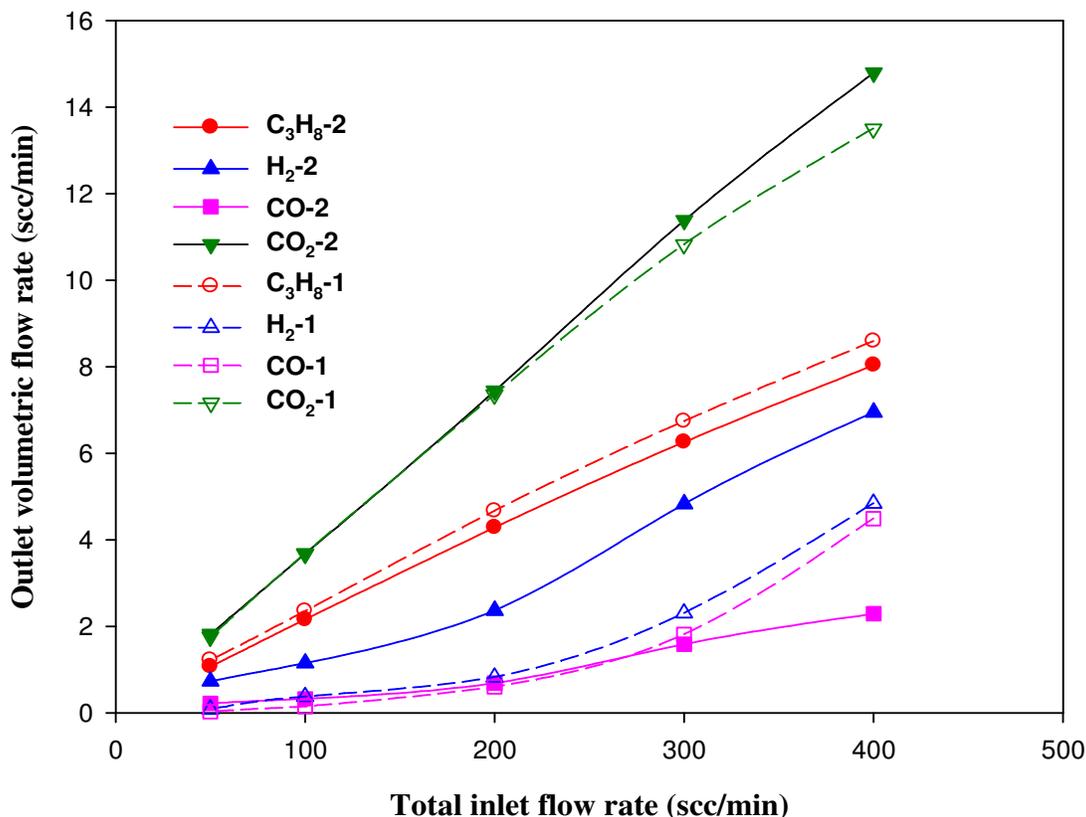


Figure 6.1 Effect of flow rate on 1 % Pt/CeO₂ (C) catalyst activity and product distribution for partial oxidation of propane (T= 600 ° C, O₂/C₃H₈ = 1.77, 90 % inert; 1- 0.01 g and 2-0.02 g catalyst weight)

6.3.2 1 % Pt/Al₂O₃ Catalyst

As for the 1 % Pt/CeO₂ (C) catalyst, the effect of flow was studied for 0.01 g and 0.02 g of 1 % Pt/Al₂O₃ catalyst. The reaction was carried out in the quartz reactor at 600 ° C. The materials and methodology are given in Section 3.2.4.7.

Figure 6.2 shows the effect of flow rate on catalyst activity and selectivity for partial oxidation of propane over 1 % Pt/Al₂O₃. The results are shown for both 0.01 g and 0.02 g loading. Figure 6.2 compares conversion of propane and product selectivities at catalyst weight 0.01 g and 0.02 g, similar to Figure 6.1 for 1 % Pt/CeO₂ (C) catalyst.

The behaviors of oxygen, propane and hydrogen are qualitatively similar in Figures 6.1 and 6.2. Production of carbon monoxide increases with increase in catalyst weight at all the flow rates. However, at higher flow rates such as 300 scc/min and 400 scc/min, the outlet flow rate of carbon dioxide at 0.02 g is less than the outlet flow rate at 0.01 g. This indicates that the carbon dioxide formed at 0.01 g loading is reacting further as the catalyst loading increases.

Carbon dioxide could be getting consumed by dry reforming (Equation 2.7) or by the Reverse Boudouard reaction (Equation 2.8) or by both. Accordingly, experiments were carried out to see if the 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts are active for dry reforming. These results are reported in the next section.

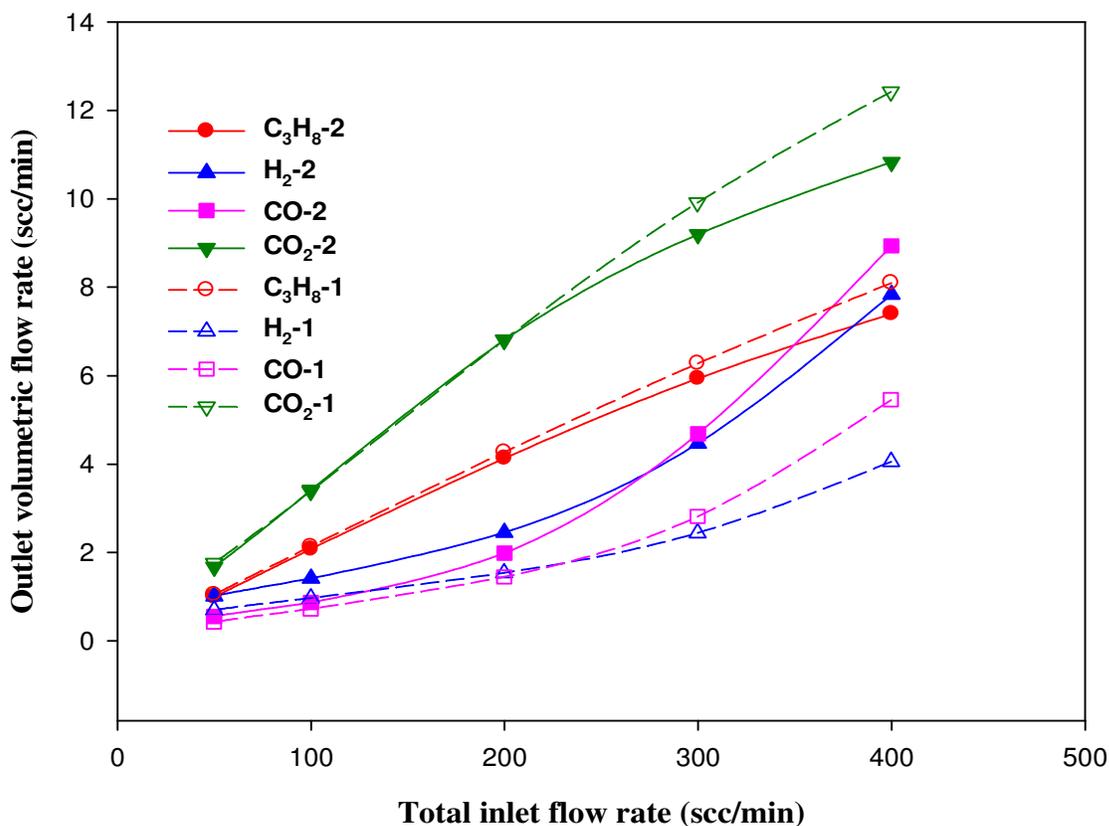


Figure 6.2 Effect of flow rate on 1 % Pt/Al₂O₃ catalyst activity and product distribution for partial oxidation of propane (T = 600 ° C, O₂/C₃H₈ = 1.77, 90 % inert; 1- 0.01 g and 2-0.02 g catalyst weight)

6.4 Dry reforming of propane

The argument was made in the previous section which dealt with effect of flow rate on partial oxidation of propane that the propane reacts with total oxidation first and then the unreacted propane undergoes reforming reactions such as steam and dry reforming. Accordingly, dry reforming of propane is carried out over 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts. The materials and methodology are given in Section 3.2.4.8.

The partial oxidation of propane was carried out over 1 % Pt/CeO₂(C) and 1 % Pt/Al₂O₃ catalysts for a few flow rates before carrying out the dry reforming reaction. Then the dry reforming reaction is carried out, varying the total flow rate from 300 scc/min to 100 scc/min. Table 6.3 shows the results for dry reforming of propane, compared with those of the partial oxidation of propane at same total flow rate.

The catalysts were active for the partial oxidation reaction. The results for dry reforming of propane on 1 % Pt/Al₂O₃ show a conversion of propane of only 2-3 %. Conversion of carbon dioxide is also very low, around 2 %. The outlet flow rates of hydrogen and carbon monoxide are also very low, as compared to those obtained in partial oxidation. Recall that the blank test carried out for the quartz reactor alone at 600 ° C gives 2 % propane conversion, with all the reacted propane converted into carbon dioxide and water with no carbon monoxide and hydrogen production. These results confirm that the carbon monoxide and hydrogen produced in the dry reforming run are due to the presence of the catalyst and not because of activity of the reactor.

Similar results are obtained for dry reforming over 1 % Pt/CeO₂ (C) catalyst. Conversions of propane and carbon dioxide over 1 % Pt/CeO₂ (C) are slightly higher than those on 1 % Pt/Al₂O₃. Prior studies (Pantu and Gavalas, 2002) show that dry reforming of methane over noble metals supported on cerium oxide is faster than over the metals supported on aluminum oxide.

The results of Table 6.3 for dry reforming of propane on 1 % Pt/Al₂O₃ and 1 % Pt/CeO₂ (C), indicate that dry reforming is not a major component of reforming reactions over either catalyst, and can be neglected.

Table 6.3 Comparison of dry reforming and partial oxidation of propane (Temperature = 600 ° C, Catalyst amount = 0.02 g, Dry Reforming: CO₂ /C₃H₈ = 3, 86 % inert (N₂+Ar); Partial Oxidation: O₂ /C₃H₈ = 1.78, 90 % inert (N₂+Ar))

Reaction		Dry Reforming				Partial Oxidation		
Catalyst	Total flow rate (scc/min)	X _{C₃H₈}	X _{CO₂}	H ₂ (scc/min)	CO (scc/min)	X _{C₃H₈}	H ₂ (scc/min)	CO (scc/min)
1 % Pt/Al ₂ O ₃	300	2.07	2.58	0.04	0.28	46.16	4.92	4.98
	200	2.09	1.14	0.03	0.29	-	-	-
	100	3.51	1.85	0.02	0.19	43.11	1.6	0.78
1 % Pt/CeO ₂ (C)	300	3.85	4.46	0.12	1.39	41.12	4.43	1.38
	200	4.43	4.78	0.10	1.06	-	-	-
	100	5.16	4.84	0.09	0.79	42.12	1.3	0.4

6.5 Reaction scheme

The effect of flow rate and catalyst loading indicate that total oxidation of propane is occurring first,



and unreacted propane is then reacting with steam to form hydrogen and carbon monoxide (steam reforming)



The results of the previous section indicate that dry reforming is not occurring. For 1 % Pt/CeO₂ (C), at high flow rates, carbon monoxide is consumed and carbon dioxide production rate is increasing with catalyst loading. However, for 1 % Pt/Al₂O₃, at high flow rates, carbon dioxide is consumed and carbon monoxide production rate increases with catalyst loading. To explain this difference in the behavior of two catalysts, two reactions are considered.

The first is the water gas shift reaction, in which carbon monoxide reacts with steam to form carbon dioxide and hydrogen.



The second is the reverse Boudouard reaction (RB), in which carbon dioxide reacts with carbon formed by dissociation of propane to form carbon monoxide.



For each of these reactions, we compare experimentally determined outlet conditions with equilibrium values, to determine whether the reaction is far from equilibrium, near (or at) equilibrium, or proceeding in the reverse direction.

6.5.1 Calculation of Activity Ratio

For the water gas shift reaction, we define the activity ratio, J_{WGS} , the ratio of activities of products to activities of reactants, (Balzhiser and Samuels, 1972) as:

$$J_{WGS} = \frac{a_{CO_2} \times a_{H_2}}{a_{CO} \times a_{H_2O}} \quad \text{Equation 6.6}$$

where a_i is the activity of species I. This ratio can be approximated as:

$$J_{WGS} = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} \quad \text{Equation 6.7}$$

where p_i is partial pressure of species I, in atm. Hence J_{WGS} can be calculated from reactor exit stream compositions corresponding to entry flow rate.

Further, the equilibrium constant for the Water Gas Shift reaction, K_{WGS} , can be calculated from thermodynamic parameters as:

$$K_{WGS} = \exp\left(-\frac{\Delta G_{WGS}^o}{RT}\right) \quad \text{Equation 6.8}$$

where ΔG_{WGS}^o is the standard state free energy change on reaction, R is the universal gas constant and T is the temperature. K_{WGS} for temperatures other than 25 °C can be calculated from the chart of K against temperature which is given for standard reactions (Sandler, 1999).

If $J_{WGS} < K_{WGS}$, then the water gas shift reaction will go in the forward direction. On the other hand, if $J_{WGS} > K_{WGS}$, then the water gas shift reaction will go in the reverse direction.

So by calculating the activity ratio J_{WGS} and comparing with K_{WGS} , the direction of the reaction can be determined for the different flow rates.

Similarly J_{RB} can be approximated as:

$$J_{RB} = \frac{(a_{CO})^2}{a_{CO_2} \times a_C} = \frac{(p_{CO})^2}{p_{CO_2}} \quad \text{Equation 6.9}$$

K_{RB} is given by

$$K_{RB} = \exp\left(-\frac{\Delta G_{RB}^o}{RT}\right) \quad \text{Equation 6.10}$$

and J_{RB} and K_{RB} can be compared to find the direction for the reverse Boudouard reaction.

The values of K_{WGS} and K_{RB} at 600 °C are:

$$K_{WGS} = 2.82 \quad \text{Equation 6.11}$$

$$K_{RB} = 0.089 \quad \text{Equation 6.12}$$

6.5.2 Role of Water Gas Shift and Reverse Boudouard Reactions

The studies for effect of flow rate and catalyst loading indicate that, at higher flow rates, there is an overall loss in CO production and overall gain in CO₂ production for 1 % Pt/CeO₂ (C), whereas there is an overall loss in CO₂ production and overall gain in CO production for 1 % Pt/Al₂O₃. To explain this behavior, we put forward a hypothesis that both water gas shift and reverse Boudouard reaction are taking place on both 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts.

For the 1 % Pt/CeO₂ (C) catalyst, the rate of carbon monoxide consumption by the water gas shift reaction is higher than the rate of production of carbon monoxide by the reverse Boudouard reaction and the rate of formation of carbon dioxide by water gas shift is higher than the rate of consumption of carbon dioxide by the reverse Boudouard reaction.

Hence there is an overall increase in carbon dioxide production and an overall decrease in carbon monoxide production with increase in catalyst loading. Water gas shift is faster than reverse Boudouard reaction since ceria is known to promote water gas shift reaction (Pantu and Gavalas, 2002). Here the water gas shift reaction dominates over reverse Boudouard reaction.

On the other hand, for the 1 % Pt/Al₂O₃ catalyst, the rate of carbon dioxide consumption by the reverse Boudouard reaction is higher than the rate of production of carbon dioxide by water gas shift reaction, and the rate of formation of carbon monoxide by the reverse Boudouard reaction is higher than the rate of consumption of carbon monoxide by water gas shift. Hence there is an overall increase in carbon monoxide production and an overall decrease in carbon dioxide production with increase in catalyst loading. Here the reverse Boudouard reaction dominates over water gas shift reaction.

6.5.3 Comparison for ceria-and-alumina supported catalysts

Figure 6.3 gives activity ratios for water gas shift reaction (Equation 6.4) for 1 % Pt/CeO₂ and 1 % Pt/Al₂O₃ catalysts. Similarly Figure 6.4 gives activity ratios for reverse Boudouard reaction (Equation 6.5) for 1 % Pt/CeO₂ and 1 % Pt/Al₂O₃ catalysts. Values of K_{WGS} and K_{RB} are also shown.

From Figure 6.3, the activity ratios are less than K_{WGS} at all flow rates for 0.01 g catalyst loading for 1 % Pt/Al₂O₃ catalyst. Hence the water gas shift is far from equilibrium and the reaction takes place only in the forward direction. The activity ratios at 0.02 g are generally higher than those at 0.01 g catalyst loading, and are generally closer to, but still less than, the value of K_{WGS} . This indicates that reaction is closer to equilibrium, but still takes place in the forward direction.

Activity ratios for 0.01 g of 1 % Pt/CeO₂ (C) are larger than those for 0.01 g of 1 % Pt/Al₂O₃, but less than K_{WGS} . However, for 0.02 g of 1 % Pt/CeO₂ (C), activity ratios are

very close to equilibrium constant. Hence water gas shift can be expected to be very close to equilibrium for 0.02 g of 1 % Pt/CeO₂ (C). These calculations support the argument made before that water gas shift is faster on 1 % Pt/CeO₂ than on 1 % Pt/Al₂O₃ and is very near to equilibrium. For 1 % Pt/Al₂O₃, water gas shift is far from equilibrium.

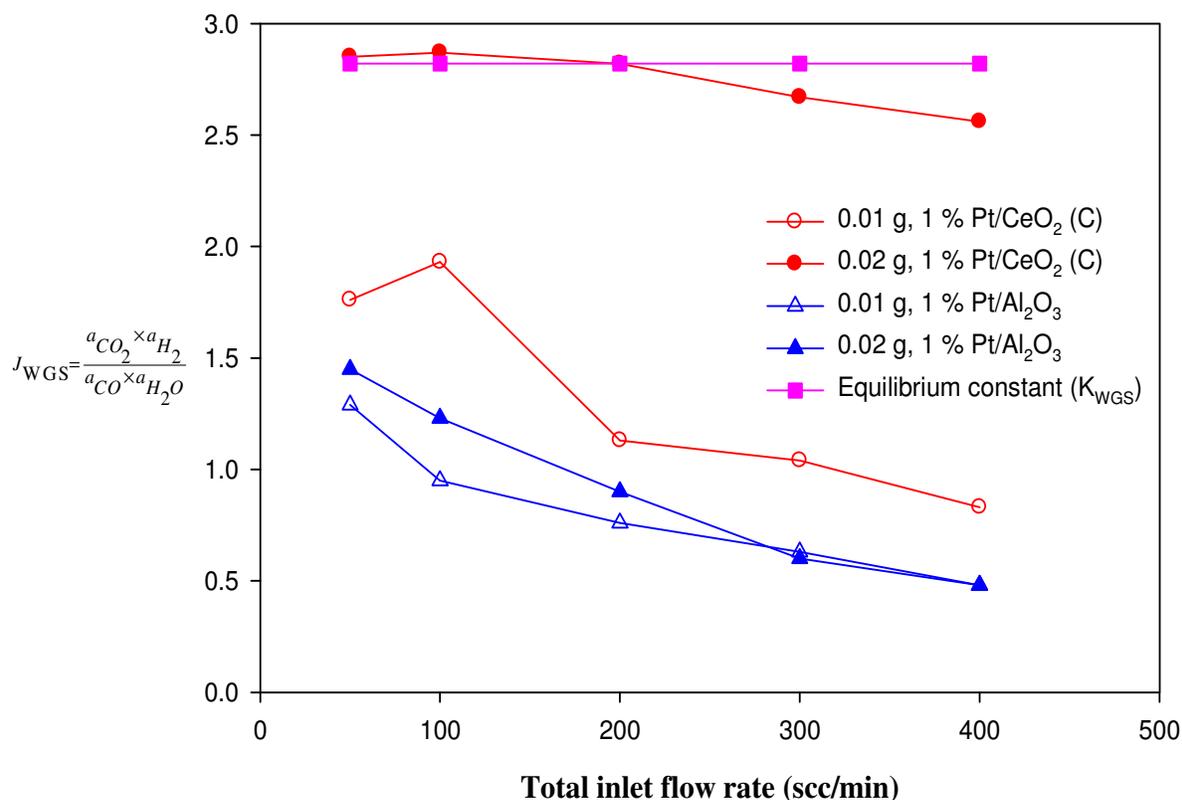


Figure 6.3 Effect of catalyst amount and support on activity ratio J_{WGS} at different flow rates ($T = 600^\circ \text{C}$, $\text{O}_2/\text{C}_3\text{H}_8 = 1.77$, 90 % inert)

From Figure 6.4, the activity ratios are less than K_{RB} at all flow rates for both 0.01 g and 0.02 g catalyst loading for 1 % Pt/CeO₂. Hence reverse Boudouard is far from equilibrium and the reaction takes place only in forward direction. The activity ratios at 0.02 g are generally higher than those at 0.01 g catalyst loading, but still less than, the value of K_{RB} . This indicates that reaction takes place in forward direction.

Activity ratios for 0.01 g of 1 % Pt/Al₂O₃ are 10 times larger than those for 0.01 g of 1 % Pt/CeO₂ (C), but less than K_{RB} . However for 0.02 g of 1 % Pt/Al₂O₃, activity ratios are close to equilibrium constant. Hence the reverse Boudouard can be expected to be very close to equilibrium for 0.02 g of 1 % Pt/Al₂O₃. These calculations support the argument made before that reverse Boudouard reaction is faster on 1 % Pt/Al₂O₃ than on 1 % Pt/CeO₂ and is near to equilibrium. For 1 % Pt/CeO₂ (C), reverse Boudouard is far from equilibrium.

For the 1 % Pt/CeO₂ catalyst, water gas shift is fast and close to equilibrium, whereas the reverse Boudouard reaction is far from equilibrium. Hence water gas shift dominates over the reverse Boudouard reaction. For 1 % Pt/Al₂O₃ water gas shift is far from equilibrium and the reverse Boudouard reaction is close to equilibrium. Hence the reverse Boudouard reaction dominates over water gas shift reaction.

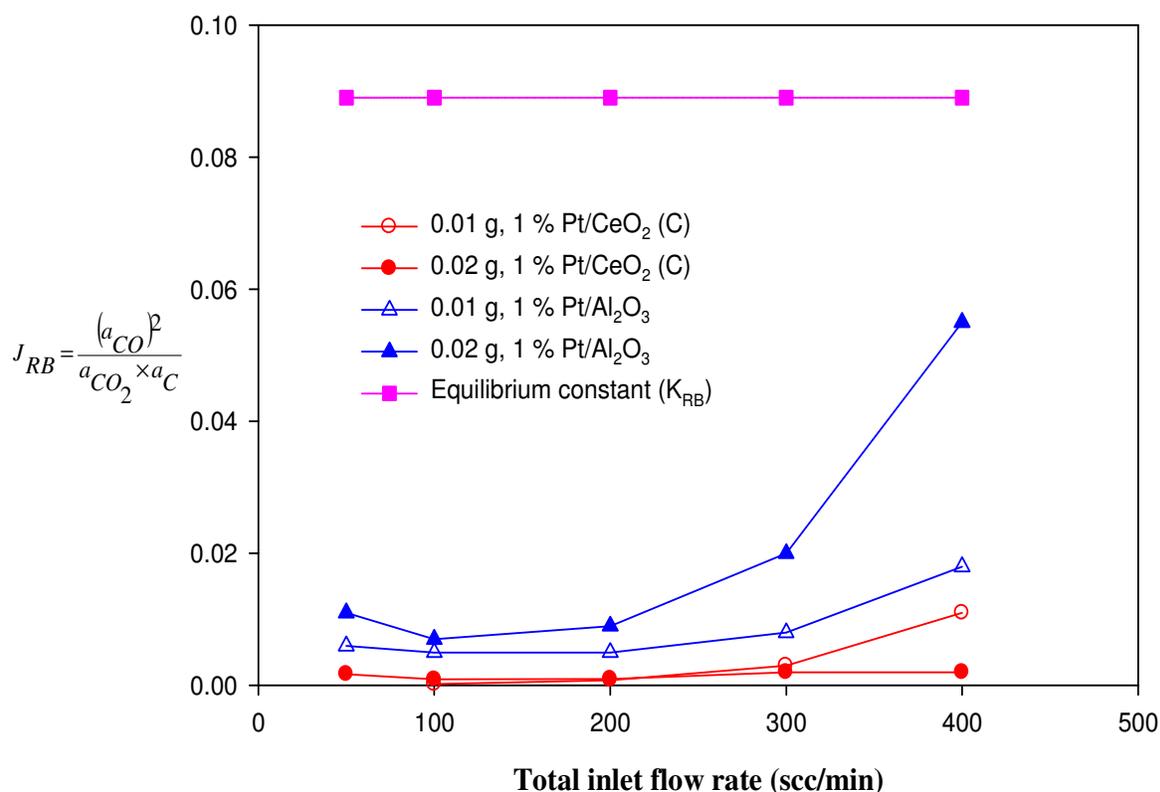


Figure 6.4 Effect of catalyst amount and support on activity ratio J_{RB} at different flow rates ($T = 600^\circ \text{C}$, $\text{O}_2/\text{C}_3\text{H}_8 = 1.77$, 90 % inert)

6.6 Summary

Study of CeO_2 (C) and $\gamma\text{-Al}_2\text{O}_3$ supports for partial oxidation show that the supports are active for total oxidation of propane to produce carbon dioxide and water. Dry reforming of propane is not a significant reaction for either 1 % Pt/ Al_2O_3 or 1 % Pt/ CeO_2 . Effect of flow rates on 1 % Pt/ Al_2O_3 and 1 % Pt/ CeO_2 catalysts show that propane first undergoes total oxidation to produce carbon dioxide and water, then unreacted propane undergoes steam reforming to form carbon monoxide and water. The water gas shift reaction dominates over the reverse Boudouard reaction over 1 % Pt/ CeO_2 catalyst. Hence there is an overall loss of carbon monoxide production and an overall gain in carbon dioxide production at higher flow rates. On the other hand, the reverse Boudouard reaction dominates over water gas shift over 1 % Pt/ Al_2O_3 . Hence there is an overall loss in carbon dioxide production and an overall gain in carbon monoxide production at higher flow rates.

Chapter 7: Summary and Recommendations for Future Work

7.1 Summary

Partial oxidation of propane was studied over 1 % Pt/CeO₂ (A), 1 % Pt/CeO₂ (B) and 1 % Pt/CeO₂ (C) catalysts. The performance of ceria catalysts was compared with 1 % Pt/Al₂O₃ catalyst. All the catalysts are active for partial oxidation reaction.

Ceria supports and catalysts lose surface areas after heat treatment at 900 ° C. Among all the ceria supports and the ceria-supported catalysts, CeO₂ (B) support and 1 % Pt/CeO₂ (B) catalysts are the most stable after heat treatment. The 1 % Pt/CeO₂ (C) catalyst shows the highest activity and hydrogen selectivity for partial oxidation reaction among all the ceria-supported catalysts. This is because it has the largest BET surface area and the highest platinum dispersion among all the ceria-supported catalyst. The 1 % Pt/Al₂O₃ catalyst gives higher activity and hydrogen selectivity than 1 % Pt/CeO₂ (C) catalyst. This can be explained by the fact that it has BET surface area, twice that of 1 % Pt/CeO₂ (C) and also it shows higher platinum dispersion than that of 1 % Pt/CeO₂ (C).

Studies of the effect of time on stream on the performance of 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts at 800 ° C and 600 ° C respectively show that both the catalysts give stable performance for partial oxidation with deactivation rate 0.28 % and 0.25 % propane conversion/hr respectively.

The effect of temperature shows that the reaction contains two domains. In the first domain (below 500 ° C), the propane is converted into carbon dioxide and water and in the second domain (above 500 ° C), propane undergoes reforming reaction to produce carbon monoxide and hydrogen.

The study of effect of the O₂/C₃H₈ ratio on partial oxidation of propane shows that conversion of propane increases and hydrogen selectivity decreases with increase in the

O₂/C₃H₈ ratio. The optimum O₂/C₃H₈ ratio is probably around 2 for high propane conversion and high hydrogen selectivity.

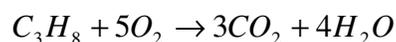
Partial oxidation was studied on the CeO₂ (C) and γ-Al₂O₃ supports alone. Both the supports are active for total oxidation of propane to carbon dioxide and water, with no activity for propane reforming reactions to form hydrogen and carbon monoxide.

Dry reforming of propane is carried out to understand the contribution of dry reforming reaction in the reforming reactions. Results show that dry reforming is not a significant reforming reaction for both 1 % Pt/CeO₂ (C) and 1 % Pt/Al₂O₃ catalysts.

Effect of flow rate was studied for partial oxidation reaction with very low catalyst loadings such as 0.01 g and 0.02 g. The following reaction scheme can be proposed. Initially propane undergoes total oxidation to form carbon dioxide and water. The unreacted propane undergoes steam reforming to form carbon monoxide and hydrogen. Water gas shift and the reverse Boudouard reactions take place on both catalysts.

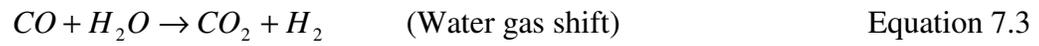
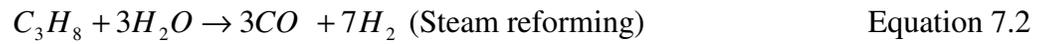
Activity ratios are compared with equilibrium constants. The results indicate that water gas shift is near equilibrium for the 1 % Pt/CeO₂ (C) catalyst, but is far from equilibrium for the 1 % Pt/Al₂O₃ catalyst. The reverse Boudouard reaction is close to equilibrium for the 1 % Pt/Al₂O₃ catalyst, but is far from equilibrium for 1 % Pt/CeO₂ (C) catalyst. Activity ratios for the 1 % Pt/CeO₂ (C) are 10 times smaller than those for 1 % Pt/Al₂O₃. Water gas shift dominates over the reverse Boudouard reaction for 1 % Pt/CeO₂ (C), resulting in an increase in carbon dioxide production with decrease in carbon monoxide production at higher flow rates. However, reverse Boudouard dominates over water gas shift for 1 % Pt/Al₂O₃ catalysts resulting in decrease in carbon dioxide production at higher flow rates. The proposed reaction sequence is:

1. Total oxidation of propane



Equation 7.1

2. Steam reforming of propane in parallel with water gas shift reaction and reverse Boudouard reaction.



7.2 Recommendations for future work

The effect of flow rate was studied for 0.01 g catalyst loading. The oxygen was completely consumed even at such a low catalyst loading. Whether partial oxidation of propane is taking place or total oxidation of propane is taking place first can not be found out when the oxygen is completely consumed. So the reaction conditions should be chosen such that there is some oxygen at the outlet which is left unreacted. Some oxygen is observed at outlet of the reactor at lower temperatures (500 ° C and 550 ° C). So one option is to carry out experiments at 500 ° C or 550 ° C on the effect of flow rate. These experiment will help to elucidate whether partial oxidation is taking place or total oxidation is taking place first.

Ayabe *et al.* (2003) studied partial oxidation of propane on Ni/Al₂O₃ catalyst. They observed that addition of steam in the reaction mixture increases hydrogen yield. Addition of steam also suppresses carbon formation. Steam should be added in the propane and oxygen reaction mixture when partial oxidation of propane is carried out on 1 % Pt/CeO₂ (C) or 1 % Pt/Al₂O₃ catalyst to see if it has any effect in increasing hydrogen yield.

Results show that 1 % Pt/Al₂O₃ gives better activity than 1 % Pt/CeO₂ (C). This is due to higher BET surface area and Pt dispersion of 1 % Pt/Al₂O₃. 1 % Pt/ CeO₂ (C) catalyst showed 35 % Pt dispersion whereas 1 % Pt/Al₂O₃ catalyst showed 46 % Pt dispersion. Pantu and Gavalas (2002) have prepared cerium oxide support using the citrate complexation technique. Platinum was added to the support by incipient wetness impregnation and 0.5 % Pt/ CeO₂ showed 69 % Pt dispersion. This method of preparation for ceria support and the catalyst could be used. It could help in getting higher platinum dispersion values and thus getting higher catalyst performance.

Kinetic studies could be carried out by varying partial pressures of propane and oxygen to find order of reaction. Product gases such as hydrogen, carbon monoxide and carbon dioxide could also be added with reactants to see if they have any inhibitive effects on reaction kinetics.

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Appendices

Appendix A: Gas Chromatograph Program

Gas Chromatograph Model: Varian 3600

Detectors used:

A: Thermal conductivity detector (TCD)

B: Flame ionization detector (FID)

Carrier Gas: Argon

Reference flow: 58 cc/min

Carrier flow: 19 cc/min

Columns used: Haysep D packed column and an alumina capillary column

Period of analysis: 44 minutes

Method 1

Initial column temperature: 35 ° C

Initial hold time: 6 minutes

Final column temperature: 200 ° C

Column rate in ° C/min: 5

Column hold time: 5 minutes

Injector A temperature: 200 ° C

Injector B temperature: 100 ° C

Detector A temperature: 250 ° C

Detector B temperature: 275 ° C

TCD A initial attenuation: 8

TCD A filament temperature: 300 ° C

TCD A polarity negative

FID B initial attenuation: 8

Initial relays: -1-2-3-4

Program 1 relay time in minutes: 0.30

Program 1 relays: -12-3-4

Program 2 relay time in minutes: 1

Program 2 relays: -1-2-3-4

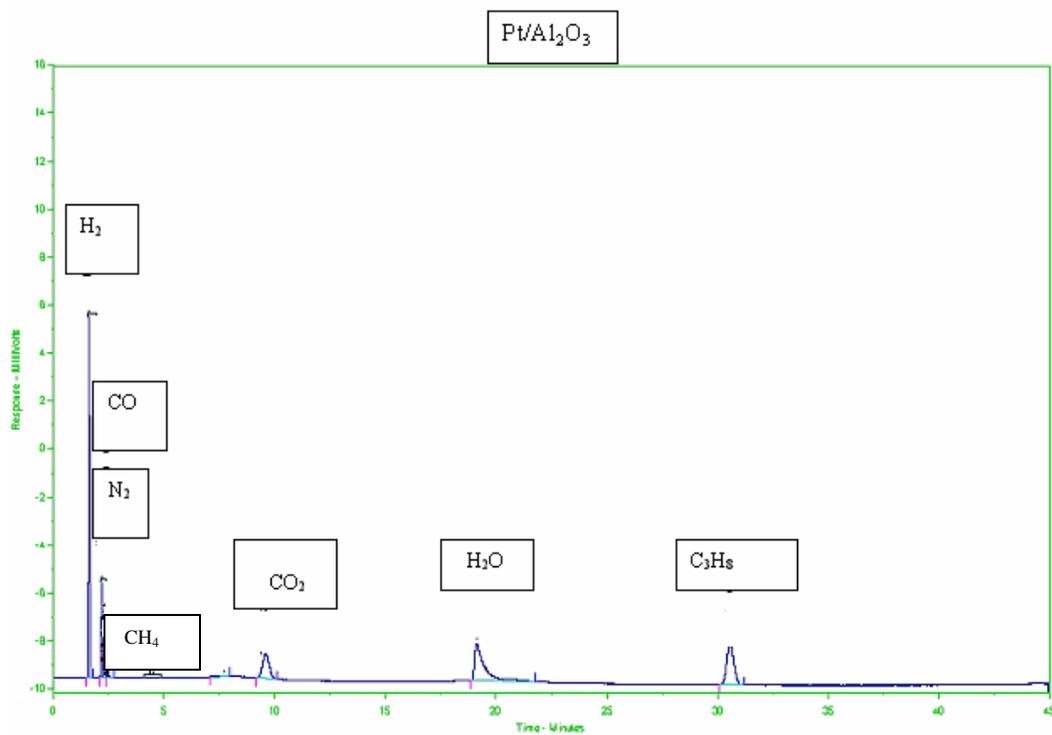


Figure A.1 A typical chromatograph obtained from TCD for partial oxidation of propane over commercial 5 % Pt/Al₂O₃ catalyst (Reaction conditions: T = 500 ° C, Feed ratio = C₃H₈:O₂:N₂:Ar = 10.8:19.2:10.8:259)

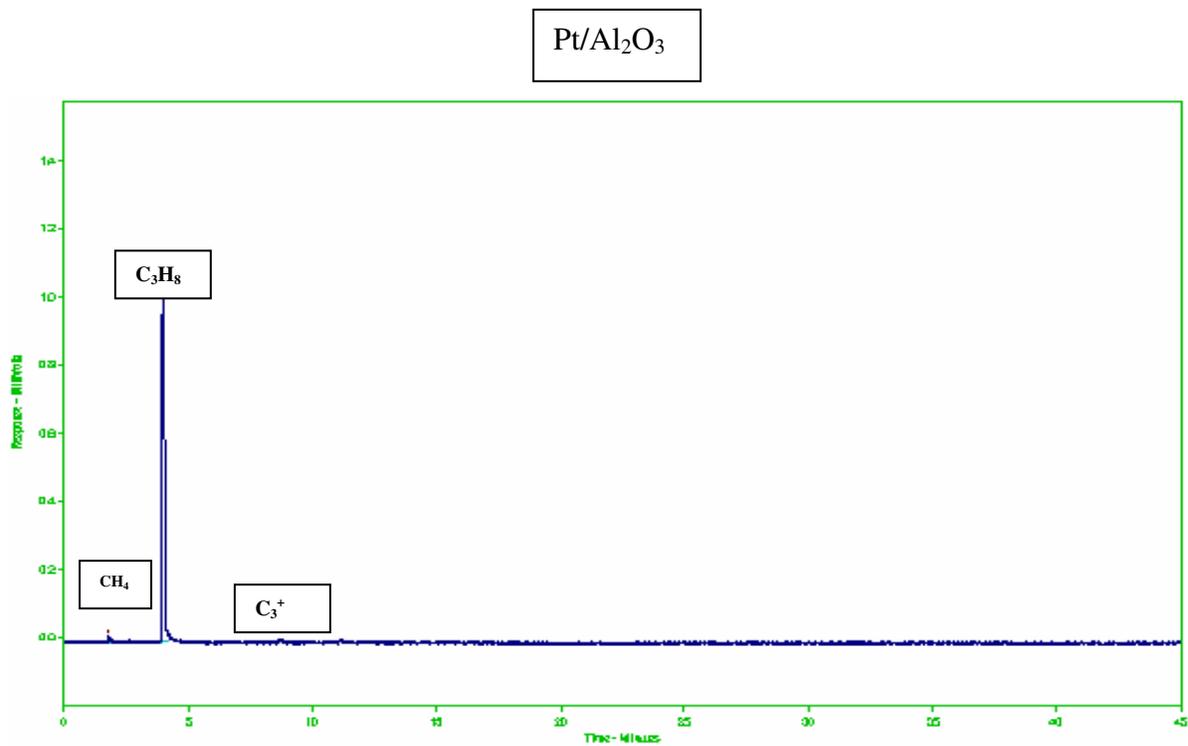


Figure A.2 A typical chromatograph obtained from FID for partial oxidation of propane over commercial 5 % Pt/Al₂O₃ catalyst (Reaction conditions: T = 500 ° C, Feed ratio = C₃H₈:O₂:N₂:Ar = 10.8:19.2:10.8:259)

Appendix B: Mass Flow Controller Calibration Curves

This appendix provides calibration curves for the Brooks mass flow controllers used for reaction of partial oxidation of propane and dry reforming of propane.

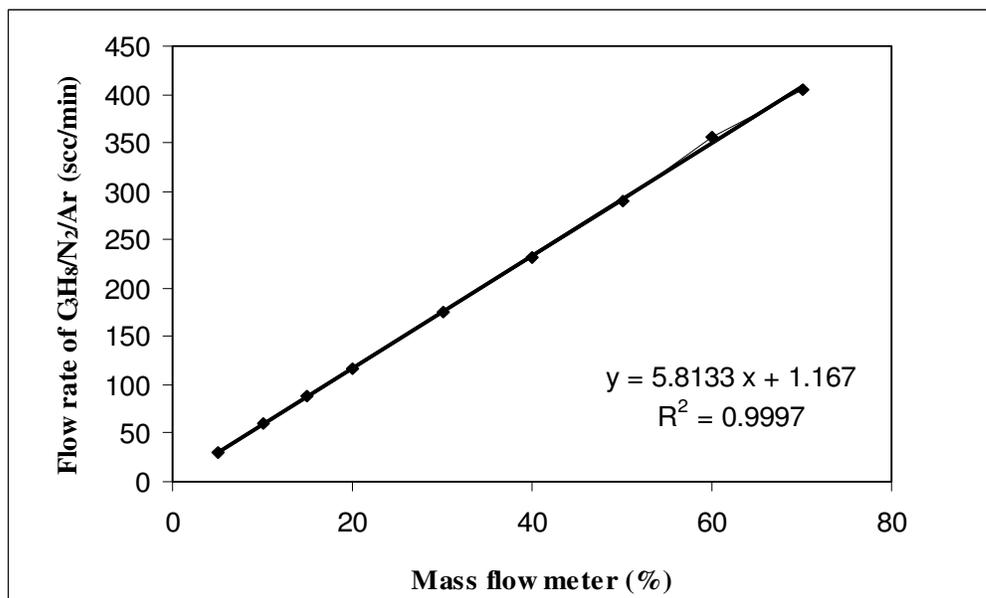


Figure B.1 MFC calibration curve for C₃H₈/N₂/Ar mixture

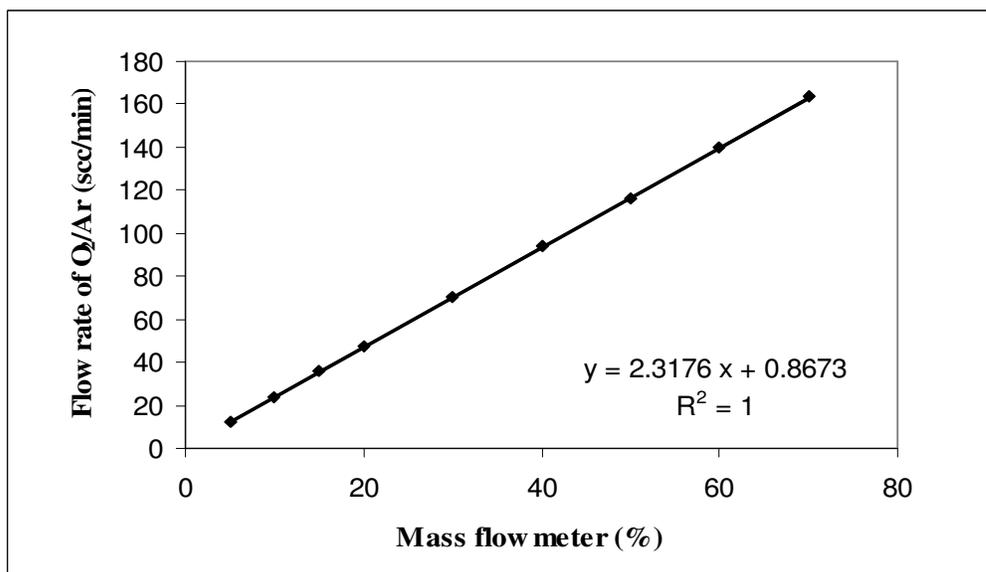


Figure B.2 MFC calibration curve for O₂/Ar mixture

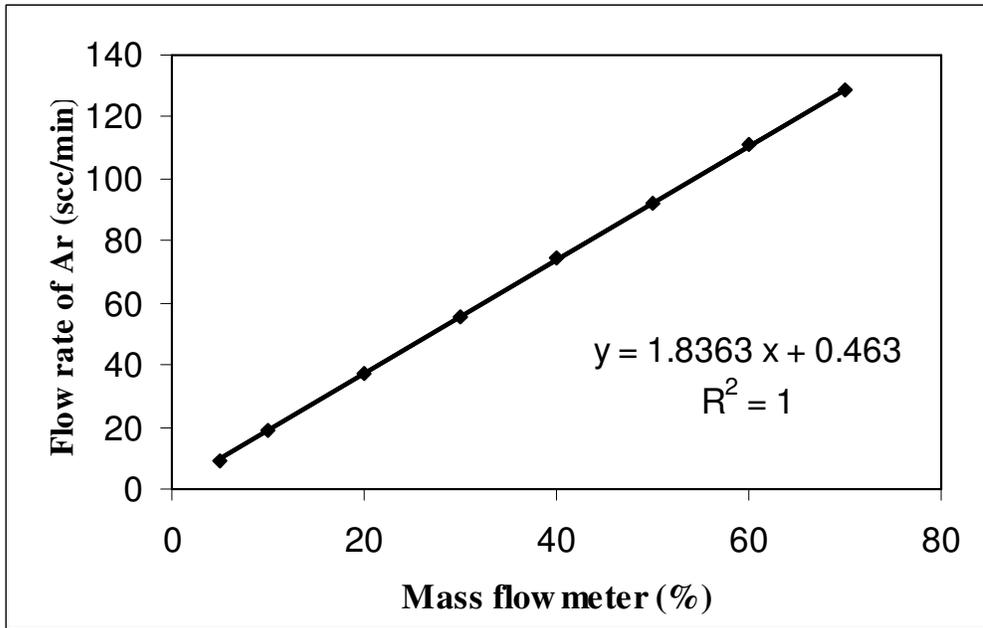


Figure B.3 MFC calibration curve for Ar

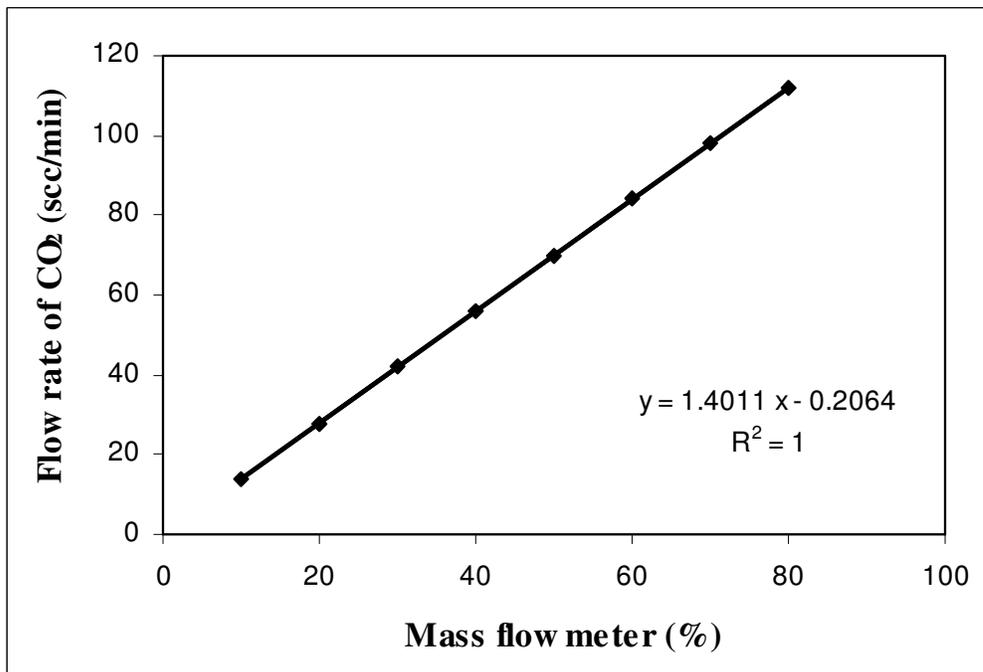


Figure B.4 MFC calibration curve for CO₂

Appendix C: Calculations for Conversions and Selectivities

The procedure for calculations of conversions and selectivities is given in this Appendix. The relative response factors for various gases which are detected in TCD detector are given in Table C.1.

Table C.1 Relative response factors for the reactants and products

Gases	Retention time (min)	Relative response factors (rRF)
H ₂	3.71	0.089
N ₂	4.81	1.000
O ₂	4.94	0.836
CO	5.28	0.987
CH ₄	8.45	0.269
CO ₂	14.55	0.880
C ₃ H ₆	34.00	0.286
C ₃ H ₈	35.28	0.286

Nitrogen is an internal standard. Now outlet flow rate of any gas (x) can be calculated as:

$$(V_x)_{out} = \frac{rRF_X \times A_X \times V_{N_2,in}}{rRF_{N_2} \times A_{N_2}} \quad (\text{scc/min})$$

where,

A_X = TCD peak area of component X

A_{N_2} = TCD peak area of N₂

rRF_X = Relative response factor of component X

rRF_{N_2} = Relative response factor of component N₂

$V_{N_2,in}$ = Inlet flow rate of N₂ in scc/min

Thus by calculating outlet flow rates of reactant and product gases, conversions and selectivities can be calculated as:

1. Conversion of propane, $X_{C_3H_8}$, %

$$X_{C_3H_8} = \frac{V_{C_3H_8,in} - V_{C_3H_8,out}}{V_{C_3H_8,in}} \times 100 \quad \text{Equation C.1}$$

where

$V_{C_3H_8,in}$ = Inlet flow rate of C_3H_8 in scc/min

$V_{C_3H_8,out}$ = Outlet flow rate of C_3H_8 in scc/min

2. Conversion of oxygen, X_{O_2} , %

$$X_{O_2} = \frac{V_{O_2,in} - V_{O_2,out}}{V_{O_2,in}} \times 100 \quad \text{Equation C.2}$$

$V_{O_2,in}$ = Inlet flow rate of O_2 in scc/min

$V_{O_2,out}$ = Outlet flow rate of O_2 in scc/min

3. Selectivity of hydrogen, S_{H_2} , %

$$S_{H_2} = \frac{V_{H_2,out}}{[V_{C_3H_8,in} - V_{C_3H_8,out}] * 4} \times 100 \quad \text{Equation C.3}$$

$V_{H_2,out}$ = Outlet flow rate of H_2 in scc/min

4. Selectivity of carbon monoxide, S_{CO} , %

$$S_{CO} = \frac{V_{CO,out}}{[V_{C_3H_8,in} - V_{C_3H_8,out}] * 3} \times 100 \quad \text{Equation C.4}$$

$V_{CO,out}$ = Outlet flow rate of CO in scc/min

5. Selectivity of carbon dioxide, S_{CO_2} , %

$$S_{CO_2} = \frac{V_{CO_2,out}}{[V_{C_3H_8,in} - V_{C_3H_8,out}] * 3} \times 100$$

Equation C.5

$V_{CO_2,out}$ = Outlet flow rate of CO_2 in scc/min

6. Selectivity of methane, S_{CH_4} , %

$$S_{CH_4} = \frac{V_{CH_4,out}}{[V_{C_3H_8,in} - V_{C_3H_8,out}] * 3} \times 100$$

Equation C.6

$V_{CH_4,out}$ = Outlet flow rate of CH_4 in scc/min