Formaldehyde Synthesis by Methanol Oxidation Using Platinised Oxides Catalysts

By

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons.)

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CERTIFICATION OF APPROVAL

Formaldehyde Synthesis by Methanol Oxidation Using Platinised Oxides Catalysts

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A project dissertation submitted to the
Chemical Engineering Programme
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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or person

(MOHD. RINALDI BIN HAMDI)

ABSTRACT

The main purpose of this study is to investigate the performance of platinised silicon dioxide and titanium (IV) oxide catalysts for oxidation of methanol to formaldehyde at room temperature (25 ^{O}C). The reaction was carried out using 100 mL of methanol (2.53 mol) in the presence of powdered (150 mg) catalyst. Samples were drawn at time intervals of 0, 10 20, 60, 90 and 120 minutes and the reaction was conducted up to 120 hours. Formaldehyde concentrations were determined by reacting 5 ml sample solution with the Hantzsch reagent. The complex formed in the samples were analysed using a UV Spectrophotometer. The amount of formaldehyde formed depends on the type of catalyst used. When 0.1 % Pt on silicon dioxide catalyst used, 0.012 mmol of formaldehyde was formed from 2.53 mol methanol after 60 minutes of reaction. Whereas using the 0.3 % Pt on silicon dioxide catalyst, 0.016 mmol of formaldehyde was formed. In the presence of 0.1 %, 0.3 %, 0.5 % and 1.1 % Pt on titanium (IV) oxide catalysts, 0.020, 0.032, 0.044 and 0.020 mmol of formaldehyde was formed, respectively. The percentage conversions of methanol using 0.1 %, 0.3 %, 0.5 % and 1.1 % Pt on titanium (IV) oxide catalysts are 0.0008, 0.0013, 0.0017 and 0.0008 %, respectively. The activity of the catalyst can be ranked in order of 0.5 % Pt on titanium (IV) oxide followed by 0.3 % Pt on titanium (IV) oxide, 0.1 % Pt on titanium (IV) oxide, 0.5 % Pt on silicon dioxide and 0.5 % Pt on silicon dioxide. The titanium (IV) oxide provides better support for platinum to create active sites for reactions. The best platinum loading is approximately 0.5 %. The formaldehyde yields were found to be decreased when elevating the reaction temperatures from 30 ^{O}C to 40 ^{O}C. The activation energy is 34 kJ/mol and the corresponding frequency factor is 0.26 $(\text{mol/L})^{-0.75}\text{s}^{-1}$ for this reaction temperature range. From the economic potential of view, the costs of produced catalysts are lower than silver catalyst.

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CHAPTER 1

INTRODUCTION

1. BACKGROUND OF STUDY

1.1 Methanol

Methanol (methyl alcohol) is produced from the distillation of wood and is a clear, colourless, volatile liquid with a weak odour that is somewhat sweeter than ethanol [1]. Methanol is used in the industrial production of many synthetic organic compounds and is a constituent of many commercially available solvents. Products that are available in the home that contain methanol include: windshield wiper fluids and de-icers, antifreeze, glass cleaner, canned heat, paints, varnishes, paint thinners and removers.

1.2 Formaldehyde

Formaldehyde on the other hand is a colourless, strong-smelling gas. Commonly known as a preservative in medical laboratories and mortuaries, formaldehyde is also found in other products such as chemicals, particle board, household products, glues, permanent press fabrics, paper product coatings, fibreboard, and plywood. It is also widely used as an industrial fungicide, germicide, and disinfectant [1].

Formaldehyde is common to the chemical industry. During both 1994 and 1995, Chemical & Engineering News reported U.S. production at 8.1 billion pounds [2]. This ranked it 24th overall. It is well known as a preservative in medical laboratories, as an embalming fluid, and as a sterilizer. Its primary use is in the production of resins and as a chemical intermediate. Urea-formaldehyde and phenol formaldehyde resins are used in foam insulations, as adhesives in the production of particle board and plywood, and in the treating of textiles.

1.3 Formaldehyde Synthesis

The world's production of formaldehyde from methanol is possible through 2 possible reactions: either by oxidation or dehydrogenation. For this research project, only oxidation of methanol is covered.

Both ways of formaldehyde synthesis are promising and largely used in the industrial practice. Until today, neither technology has established a leading role [3]. This proves that both methods are at par on each other. However, the choice must be taken into account of economic analysis so that the process will be both technically and commercially viable.

2. PROBLEM STATEMENT

2.1 Problem Identification

The project is focused on using platinised silicon dioxide and titanium (IV) oxide as alternative catalyst for formaldehyde synthesis. The current practice for formaldehyde synthesis requires temperature of 600 to 700 ^{O}C for silver catalyst and 270 – 400 ^{O}C for metal oxide catalysts. Since both metal oxide and silver catalysts are expensive, this research project intends to find alternative catalysts which are relatively cheaper and can operate at lower temperature.

2.2 Significant of the Project

Since its first commercial production at the beginning of this century formaldehyde has become a chemical of major industrial importance. The 1996 production capacity [3] is estimated to be almost 5 million tonnes as 100 % formaldehyde. This shows that formaldehyde is in demand and formaldehyde is used as raw material for other processes. Thus, there is an economic potential towards improving the formaldehyde production. By introducing new type of catalyst that reduces operating and maintenance cost (lower operating temperature and pressure, cheaper catalysts, higher activity, selectivity and life), the formaldehyde production will be more profitable.

3. OBJECTIVE AND SCOPE OF STUDY

3.1 Specific Objectives

3.1.1 To prepare silicon dioxide and titanium (IV) oxide catalysts with different platinum loading namely 0.1, 0.3, 0.5 and 1.1 wt% Pt.

3.1.2 To study formaldehyde reaction kinetics at the corresponding platinum loadings.

3.1.3 To determine the effect of temperature on the catalyst activity and formaldehyde reaction rate.

3.1.4 To characterise the catalyst using Temperature Programmed Desorption, Reduction and Oxidation (TPDRO).

3.2 General Objectives

3.2.1 To develop students' skills in the process of applying knowledge and expanding thoughts, solving problems independently and presenting findings through minimum guidance and supervision.

3.2.2 To give opportunity to students to work with individual project by application and practice of theoretical and knowledge that they gain throughout the semester.

3.2.3 To develop the potential of students creativity and innovativeness

3.3 The Relevancy of the Project

3.3.1 Formaldehyde production is still in demand

3.3.2 New type of catalyst that reduces operating and maintenance cost

3.3.3 Catalyst selectivity, increases formaldehyde yield, reduces methanol emission

Table 1: Reaction mechanism used for the microkinetic model. The * signifies a surface site and X* is an adsorbed specie.

$$
\begin{array}{rcll}
CH_3OH(g) + * & \rightleftharpoons & CH_3OH* & \text{(step 1)} \\
O_2(g) + * & \rightleftharpoons & O_2* & \text{(step 2)} \\
O_2* + * & \rightleftharpoons & 2O* & \text{(step 3)} \\
2CH_3OH* + O* & \rightleftharpoons & 2CH_3O* + H_2O* & \text{(step 4)} \\
CH_3O* + * & \rightleftharpoons & H_2CO* + H* \quad (slow) & \text{(step 5)} \\
H_2CO* & \rightleftharpoons & H_2CO(g) + * & \text{(step 6)} \\
2H* & \rightleftharpoons & H_2(g) + 2* & \text{(step 7)} \\
H_2O* & \rightleftharpoons & H_2O(g) + * & \text{(step 8)} \\
H_2CO* + O* & \rightleftharpoons & H* + HCOO* & \text{(step 9)} \\
HCOO* + * & \rightleftharpoons & H* + CO_2* \quad (slow) & \text{(step 10)} \\
CO_2* & \rightleftharpoons & CO_2(g) + * & \text{(step 11)}
\end{array}
$$

Figure 1 shows the simulation of the experimental conversion of methanol and selectivity towards formaldehyde and CO_2, respectively. The model clearly captures the trend that formaldehyde selectivity increases with temperature and saturates at high temperature. The model also captures the trend that CO_2 selectivity is high at low temperature but decrease with increasing temperature.

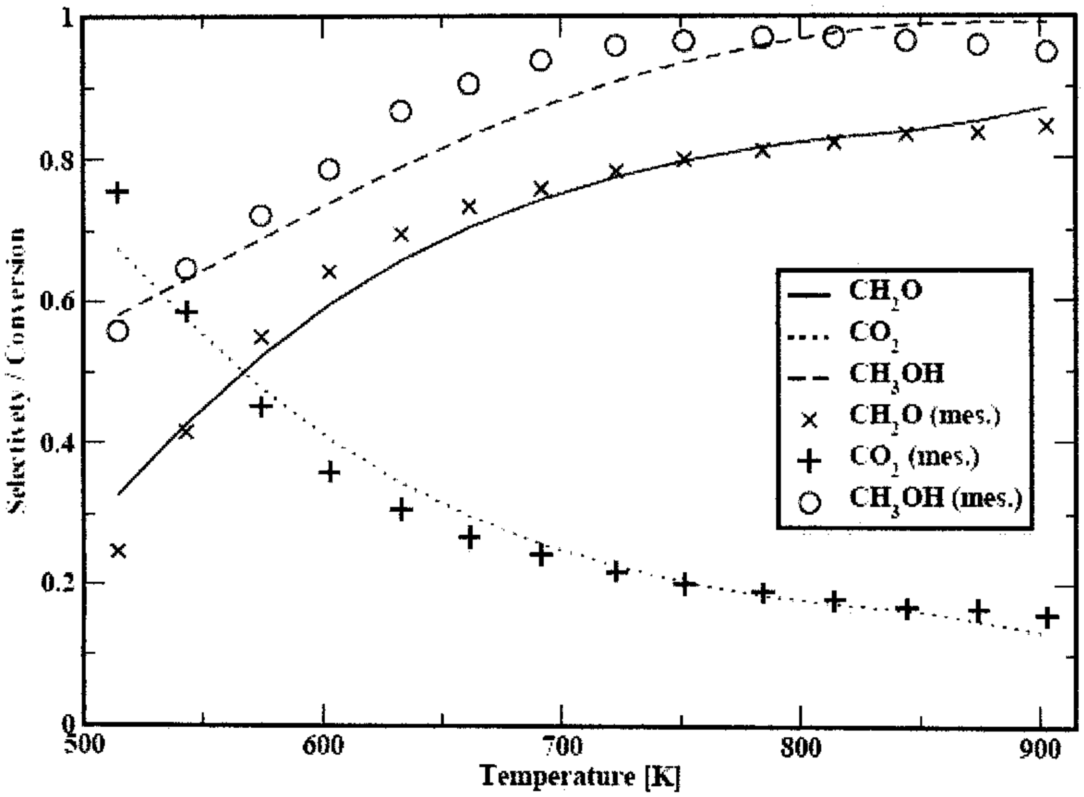


Figure 1: Simulation of the experiments by Nagy and Mestl. Points are experimental measurements and lines have been calculated with the microkinetic model. The figure shows the selectivity towards H$_2$CO and CO$_2$, respectively, and the conversion of methanol as a function of temperature.

The reaction orders can be derived from the following definition.

$$\alpha_i = \frac{d\ln(r_+)}{d\ln\left(\frac{p_i}{p^0}\right)}$$

For the formation of formaldehyde the following reaction orders can be derived.

$$\begin{aligned}
\alpha_{CH_3OH} &= 1 - 2\theta_{CH_3OH*} - 2\theta_{CH_3O*} \\
\alpha_{O_2} &= 1/4 - 2\theta_{O_2*} - \theta_{O*} - 1/2\theta_{CH_3O*} - \theta_{H_2CO*} \\
\alpha_{H_2CO} &= -2\theta_{H_2CO*} - 2\theta_{HCOO*} \\
\alpha_{CO_2} &= -2\theta_{CO_2} \\
\alpha_{H_2O} &= -1/2 + \theta_{CH_3O*} - 2\theta_{H_2O*}
\end{aligned}$$

As the coverage's of all intermediates except O* are low according to figure, the model explains the positive reaction order with respect to methanol observed experimentally

The reaction order of methanol, formaldehyde, water and carbon dioxide are independent of temperature and denotes values of 1, 0, - 0.5 and 0, respectively. The reaction order of oxygen varies between – 0.75 at low temperatures (high coverage of O*) to 0.25 at high temperatures (low coverage of O*). Generally the quantitative values of the reaction orders presented in figure reproduce the qualitative features discussed above.

As demonstrated in Figure 2 the apparent activation enthalpy of formaldehyde synthesis is always larger than the apparent activation enthalpy of formaldehyde combustion. Hence the rate of formaldehyde formation increases more rapidly than formaldehyde combustion at increasing temperature. In order to obtain a high selectivity the industrial process should be conducted at high temperatures. However the temperatures should not be high enough to promote the pyrolytic gas phase decomposition of formaldehyde. Furthermore a methanol rich feed should be used in the process to ensure high selectivity by achieving complete oxygen consumption. Otherwise the remaining oxygen would combust the formed formaldehyde. This is consistent with the work by Wachs et al. who show that the selectivity towards formaldehyde decreases from 92.3 % to 69.1 % when

CH3OH=O2 molar ratio decreases from 3.08 to 0.95 in a fixed bed reactor. The rate of formaldehyde combustion does not decrease with temperature it just does not increase as rapidly as the rate for formaldehyde formation.

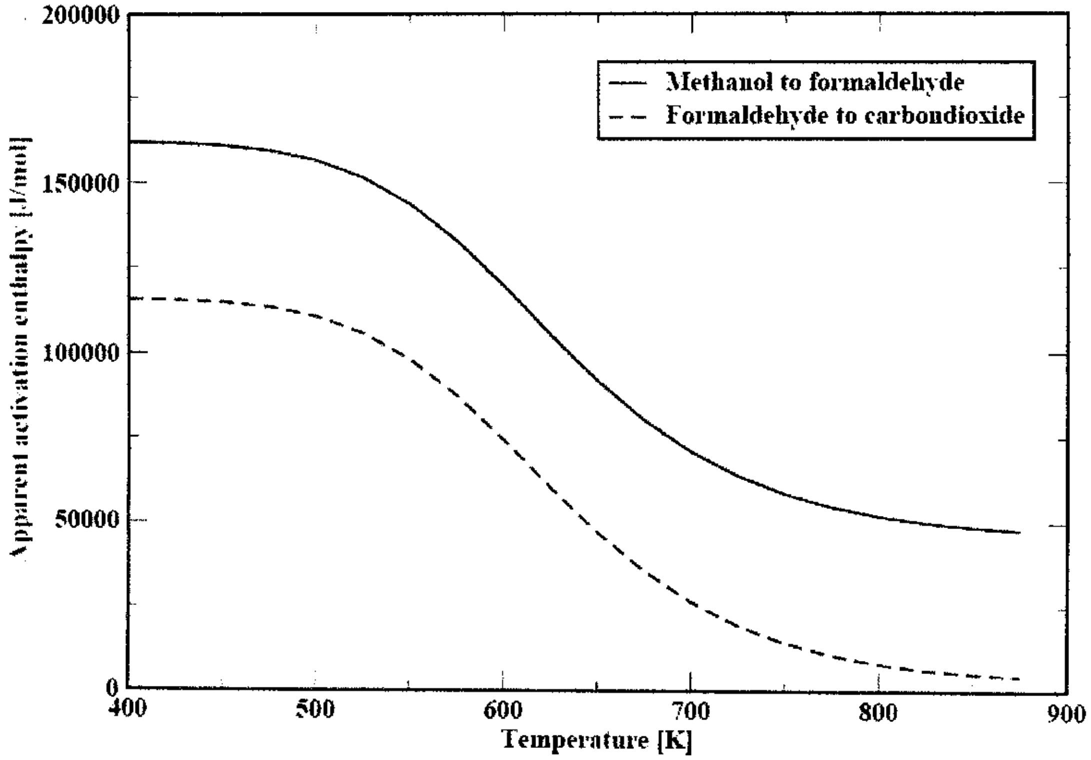


Figure 2: Apparent activation enthalpies for the oxidation of methanol to formaldehyde and further to carbon dioxide. Calculations have been performed at typical reaction conditions.

As a conclusion, they have formulated a simple microkinetic model for the oxidation of methanol on silver based on surface science at UHV and low temperatures. The mechanism contains two slow steps: methoxy decomposition to formaldehyde and formate decomposition.

2. ROBUST CONTROL OF A CATALYTIC FIXED BED REACTOR

In this paper [5] they consider control of a fixed bed reactor for formaldehyde synthesis in laboratory scale. It describes application of p-optimal controller design to control of an important chemical process, namely synthesis of formaldehyde in a catalytic fixed bed reactor. The plant oxidizes methanol CH_3OH and oxygen O_2 to the desired product formaldehyde *HCHO* which is an important primary product in the plastic industry. In a consecutive reaction Formaldehyde is further converted to the unwanted byproduct carbon monoxide CO. The experimental plant consists of the feed preparation of the gases included the mixer and the methanol valve, the reactor with a cooling jacket which is divided in three sections each connected with a thermostat, the absorption column and a process control system for process monitoring, operation and control.

Catalytic fixed bed reactors exhibit interesting control problems due to their nonlinear behaviour and their sensitivity to load changes and other disturbances. Because detailed nonlinear models of such reactors are too complex for use in controller design, a linear model description is identified here along with an appropriate structured uncertainty description. Experimental results involving a real reactor are given.

The process is very sensitive to load changes or other disturbances. Therefore control of the temperature profile is necessary to obtain a constant space time yield of formaldehyde. The influence of the inlet temperature T_{in} and the gas throughput Q are considered as disturbances. The set point of the first thermostat T_{hl} and the methanol-oxygen ratio *MR* are selected as control inputs. These two inputs have the strongest effect on the temperature profile. Two temperature measurements T_{m1} and T_{m2} are chosen as measured outputs. The position of the temperature measurements is at locations that allow inferring the form of the profile in a wide range. Thus control of the temperatures T_{m1} and T_{m2} will result indirectly in good control of the whole profile. Through this inferential control scheme we have thus reduced the problem of controlling a distributed output to the control of two lumped outputs.

3. A KINETIC STUDY OF METHANOL OXIDATION OVER SILICON DIOXIDE

The team [6] has studied the kinetics of methanol oxidation over SiO_2 in the temperature range of 400–600 ^{O}C to investigate the oxidation pathway of methanol. The experimental results indicated that methanol was first oxidized to formaldehyde, and then oxidized to CO. A kinetic model for methanol oxidation is proposed, and the rate constant and activation energy in each elemental reaction pathway is calculated.

Most studies have been carried out with metal oxides supported on SiO_2. Therefore, it is important to know whether SiO2, a carrier, is inactive in the oxidations of the reactant methane and the products methanol and formaldehyde. Pure SiO_2 (crushed quartz or silica gel) has an appreciable activity in formaldehyde formation from methane. The formaldehyde selectivity decreases if a metal oxide is supported on SiO_2. The influence of SiO_2 on the oxidation of produced methanol is not clear. Reportedly, the methoxide is oxidized to CO and CO_2 over MoO_3/SiO_2 at 600 and 625 ^{O}C via two different routes. One is that CH_3OM (M is the active site of the catalyst) is oxidized to $MOCH_2OM$, then it is further oxidized to CO_2. The other is that CH_3OM is oxidized to CH_2OM (formaldehyde), then further oxidized to CO. Methoxide oxidation over V_2O_5/SiO_2 has been reported to proceed only by the second route, followed by the oxidation of CO to CO_2.

SiO_2 sample and quartz glass wool were pretreated with a mixed gas of oxygen (3.73%) and He at 700 ^{O}C for 1 h. The oxidation products were analyzed with an on-line gas chromatograph (GC-130, Okura Riken; Porapak Q, 2m; FID). Methanol conversion and selectivities over SiO_2 at each reaction temperature are shown in Figure 3. Methanol conversion greatly increased above 400 ^{O}C. Selectivities of HCHO and CO_2 decreased and that of CO increased with the increase in reaction temperature. A low temperature was favorable for HCHO formation. The main product was CO at the temperature over 500 ^{O}C.

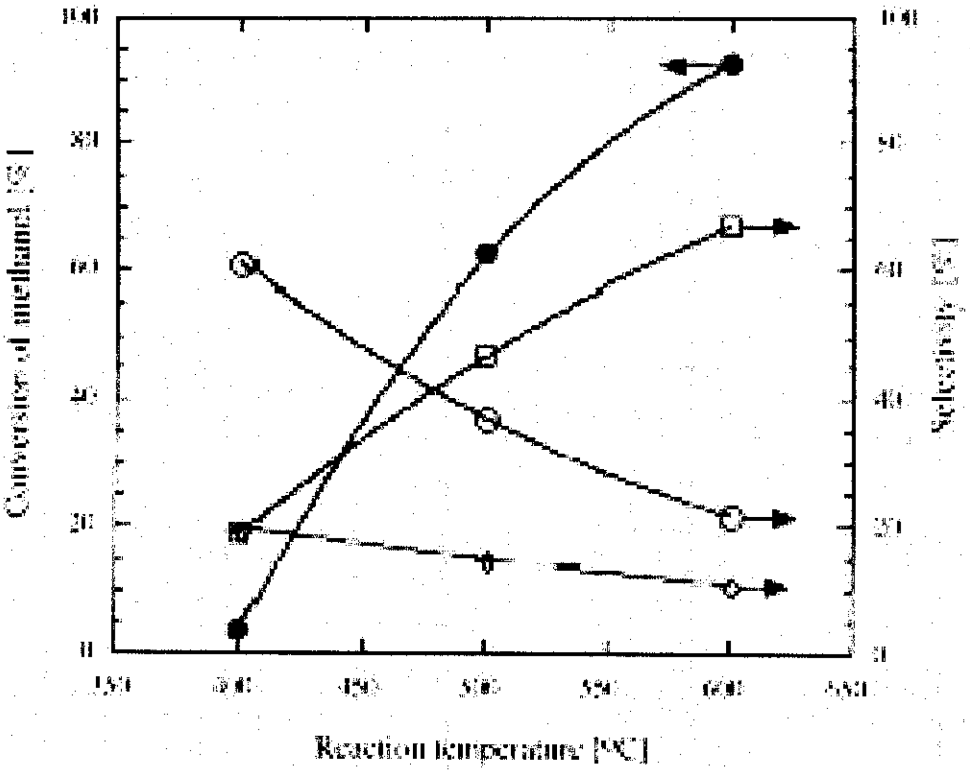


Figure 3: Methanol oxidation over SiO_2 at various temperatures. Helium gas (4.92 ml s^{-1}) containing methanol (1.0%) and oxygen (3.73%) was passed through the SiO_2 (0.10 g) bed. (•) Methanol conversion, (O) Formaldehyde selectivity, (☐) CO selectivity, (◊) CO_2 selectivity.

CHAPTER 3

METHODOLOGY AND PROJECT WORK

The project is divided into 5 primary procedures. These procedures are related to the laboratory work and experiment. The chemicals' names, suppliers and purities are tabulated in Appendix A1.

1. CATALYST PREPARATION

(i) The catalyst samples were prepared in batches at different platinum loading. The platinum was loaded at 0.1 %, 0.3 %, 0.5 % and 1.1 %. In order to prepare titanium catalyst loaded with 0.1 % platinum, the amount of chloroplatinic acid is to be determined [7]:

The amount of platinum for 0.1 % loading: 0.001 x 5.0 g = 0.005 g

The platinum molar mass: 195.09 g/mol

The chloroplatinic acid chemical formula: H_2PtCl_6; molar mass: 518.08 g/mol

Thus, the amount of chloroplatinic acid needed

$$= 0.005\text{ g platinum} \times \frac{1\text{ mol platinum}}{195.09\text{ g platinum}} \times \frac{1\text{ mol chloroplatinic acid}}{1\text{ mol platinum}} \times \frac{518.08\text{ g chloroplatinic acid}}{1\text{ mol chloroplatinic acid}}$$

$= 0.0133$ g chloroplatinic acid

The calculated amounts for chloroplatinic acid in other loadings are tabulated Table 2:

Table 2: Amounts for chloroplatinic acid in other loadings

Pt loading (wt %)	TiO_2 mass (g)	Pt mass (g)	Chloroplatinic acid mass (g)
0.30	5.0	0.015	0.0398
0.50	5.0	0.025	0.0664
1.11	5.0	0.055	0.1500

(ii) Since weighing 0.0133 g chloroplatinic acid is rather difficult and will involve huge errors and discrepancies, therefore the chloroplatinic acid was dissolved in distilled water to produce standard solution with known concentration. The chloroplatinic acid was weighed up to 0.24 g. This has taken into account the additional amount of acid needed to repeat the experiment. 0.24 g of chloroplatinic acid was dissolved in distilled water and filled up to 250 mL mark in the volumetric flask. The concentration of the standard solution is given by:

$$\text{Solution concentration} = \frac{\text{amount of solute}}{\text{volume of solution}} = \frac{0.24g}{250mL} \text{x} \frac{1000mL}{1L} = 0.96g/L$$

The reason of using g/L unit is for the sake of simplicity, where the volume of the solution will be obtained directly if the amount of acid needed is known. For example, for 0.1 % Pt, the mass of acid needed is 0.01333 g. The corresponding acid volume is:

$0.01333g\text{x}\frac{1L}{0.96g}\text{x}\frac{1000mL}{1L} = 13.89mL$, in which about 27 mL of distilled water and 10 mL of sodium citrate solution is added so that the volume becomes approximately 50 mL. The volumes of chloroplatinic acid for other loadings are tabulated in Table 3:

Table 3: Volumes of 0.96 g/L chloroplatinic acid for other loadings

Mass of chloroplatinic acid, g	Volume of chloroplatinic acid standard solution, mL	Volume of sodium citrate 1 wt % added to the solution, mL
0.0398	41.66	10
0.0664	69.17	10
0.1500	40 mL distilled water, as chloroplatinic acid was directly weighed	10

(iii) The above solution was refluxed until the yellowish solution turns black. **CAUTION**: Do not reflux the solution until it turns to colourless solution with black precipitate as that is the condition where platinum lost its activity.

The solution is let to cool to room temperature.

(iv) After the solution cooled to room temperature, 5.0 g titanium (IV) oxide and 5.85 g sodium chloride were added to the cooled solution. The mixture was stirred for approximately 20 minutes to ensure it was well mixed.

(v) The mixed solution was filtered with Whatman filter paper number 49. The solid precipitate obtained on the filter paper was dried in an oven at 110 ^{O}C overnight to ensure the solid precipitate (or rather sample catalyst) dried completely.

(vi) The dried sample catalyst was calcined at 450 ^{O}C for 3 days. Then, the sample catalyst was placed in a desiccator for future use.

2. PREPARATION OF HANTZSCH REAGENT[8]

Hantzsch reagent was used for detecting the presence of formaldehyde in the sample solution. The procedures to prepare Hantzsch reagent is as follows:

(i) 77 g of ammonium acetate was dissolved in 200 ml of deionised water.

(ii) The resulting solution was added with 1.5 mL of concentrated acetic acid (99.99 %) and 1.0 mL of acetyl acetone.

(iii) Deionised water was added to the solution in a 500 mL volumetric flask to obtain 500 mL of Hantzsch reagent.

3. PREPARATION OF STANDARD SOLUTION

The standard solution was prepared to construct a calibration diagram: absorbance versus formaldehyde concentration [8]. The targeted molarities for the prepared standard solutions range from 0.03 mmol/L to 0.1 mmol/L, including the blank solution.

(i) To prepare 50 mL 0.1 mmol/L formaldehyde solution from 37 % formaldehyde stock solution, the mass of stock solution was calculated.

Number of moles of formaldehyde in 37 % formaldehyde solution

= number moles of formaldehyde in 50 mL in 1.0 X 10^{-4} mol/L standard solution

Let m = mass of 37 % formaldehyde solution

$$\mathrm{m}\times\frac{37\mathrm{gCH_2O}}{100\mathrm{gso\ln}}\times\frac{1\mathrm{molCH_2O}}{30.03\mathrm{gCH_2O}}=1.0\times10^{-4}\mathrm{molCH_2O/L}\times0.05\mathrm{L}$$

$$\therefore \mathrm{m}=1.0\times10^{-4}\mathrm{molCH_2O/L}\times0.05\mathrm{L}\times\frac{100\mathrm{gso\ln}}{37\mathrm{gCH_2O}}\times\frac{30.03\mathrm{gCH_2O}}{1\mathrm{molCH_2O}}=0.0004\mathrm{gso\ln}$$

Thus, 0.0004 g 37 % formaldehyde solution was weighed with microbalance. In order to obtain lower solution concentration, the 1.0 X 10^{-4} mol/L standard solution was further diluted by adding methanol at the according volume. This was done by applying the dilution formula,

$$M_iV_i = M_fV_f,$$

where M is molarity, V is volume, subscript i is initial and subscripts f is final, respectively. For example, to dilute 1.0 X 10^{-4} mol/L standard solution to 50 mL 8.0 X 10^{-5} mol/L standard solution,

$$M_i = 1.0 \text{ X } 10^{-4} \text{ mol/L}$$

$$M_f = 8.0 \text{ X } 10^{-5} \text{ mol/L}$$

$$V_f = 0.05 \text{ L}$$

Thus, $M_iV_i = M_fV_f \Rightarrow V_i = \frac{M_fV_f}{M_i} = \frac{8.0\times10^{-5}mol/L\times0.05L}{1.0\times10^{-4}mol/L} = 0.02L$, or 20 mL 1.0 X 10^{-4} mol/L standard solution is needed to obtain 50 mL 8.0 X 10^{-5} mol/L standard solution. The above steps were repeated for 5.0 X 10^{-5} mol/L standard solution and 3.0 X 10^{-5} mol/L standard solution.

(ii) Five mL for each standard solution were reacted with 10 mL Hantzsch reagent. After that, all standard solutions were heated in a water bath for 1 hour duration at 37 ^{O}C.

(iii) After the standard solutions have been stabilised, the solutions were diluted with deionised water up to 100 mL mark. The resulting solutions were analysed by UV Spectrophotometer. The absorbance for each standard solution was plotted with respect to the corresponding concentration. The resultant plot, which is approximately linear plot will be used to measure the formaldehyde yield in the formaldehyde synthesis step.

4. CATALYST ACTIVITY TESTING [8]

The procedure of methanol oxidation was as follows:

(i) 150 mg of the catalyst under test was added to a conical flask.

(ii) 100 mL of methanol was added into the flask.

(iii) Rapidly 5 mL of the solution was filtered and reacted with Hantzsch reagent as zero time sample.

(iv) The solution was stirred and 5 mL of the solution was drawn at time, t = 10, 20, 60, 90 and 120 minutes through the septum and immediately filtered to the test tube.

(v) Each filtered sample solution drawn at time was reacted with 10 mL Hantzsch reagent and heated in a water bath for 1 hour duration in a water bath.

(vi) The sample solutions were allowed to cool to room temperature before they were diluted with deionised water to 100 mL mark.

(vii) A blank sample consists of 5 mL methanol and 10 mL Hantzsch reagent was also processed in the same way (repeat step v and vi).

(viii) The absorption spectrum of the standard solution was scanned with Ultra Violet Spectrophotometer at wavelength 413.0 nm.

(ix) The above steps were repeated with other sample solution.

(x) Sample catalyst that gave the best yield was used for formaldehyde synthesis elevated temperature (repeat same procedure but place conical flask in a water bath instead).

5. CATALYST CHARACTERISATION – TEMPERATURE PROGRAMMED REDUCTION (TPR) EXPERIMENT

(i) Approximately 0.6 g of catalyst sample was weighed and placed in the sample holder [7].

(ii) The Thermo Finnigan TPD/R/O 1100 equipment was set to have a cleaning procedure with 20 cc/min of nitrogen flow for 10 minutes.

(iii) The procedure was continued with sample pre-treatment with nitrogen gas flow of 20 cc/min, starting temperature at room temperature, the temperature ramp at 20 ^{O}C/min, final temperature at 110 ^{O}C and the sample was hold for 20 minutes.

(iv) The TPR process started with the 5.42 % hydrogen in nitrogen gas mixture at 20 cc/min, starting temperature at room temperature, the temperature ramp at 20 ^{O}C/min, final temperature at 800 ^{O}C and the sample was hold for 120 minutes.

CHAPTER 4

RESULTS AND DISCUSSION

1. GENERAL OBSERVATIONS

These are the observations recorded for the duration of project up to date. These include the observations during the sample catalysts preparation and standard solutions preparation.

Table 4: The observation obtained for the duration of the project.

No.	Observations	Explanation
1.	The orange powder turns to yellow solution upon diluted with distilled water.	The yellow colour shows the presence of chloroplatinic acid.
2.	The yellow solution turns to colourless solution with black precipitate after 4 hours of reflux.	The black precipitate is the solid platinum which has lost its activity.
3.	The yellow solution turns to black solution during reflux.	The black solution indicates the presence of platinum metal.[7]
4.	The black solution turns to grey solution and becomes more viscous upon adding the white powder.	The increase in viscosity is the attribute of silicon dioxide (white powder) added to aqueous solution.
5.	The filtered grey solution yield jelly and waxy solid.	The waxy and jelly solid represents the presence of silicon dioxide.
6.	The jelly and waxy solid becomes hard and brittle, grey solid.	The grey solid shows the complete drying of catalyst specimen.
7.	The black solution turns to greyish solution with suspended white solid adding the white powder.	The white suspended solid is titanium (IV) oxide.
8.	The sample catalyst becomes darker upon increasing the platinum loading	The darker sample catalyst has higher platinum loading.

9.	The standard solutions/sample solutions turn yellowish upon reacted with Hantzsch reagent.	The yellow colour comes from 3,5 – dietil – 1,4 – dihydrolutidine which indicates the presence of formaldehyde[8]. The yellow intensity increases as the formaldehyde concentration increases.

The yellow solution turns to colourless solution with black precipitate after 4 hours of reflux. The platinum solid is deactivated/lost its activity when it turns to black precipitate. The normal reflux period is 4 hours. However, in this experiment, after 4 hours, the platinum already turns to black precipitate. It was suggested either chloroplatinic acid or sodium citrate contain impurities which lead to the said observations. Moreover, the reflux temperature might be too high which makes the solution turns black faster.

The yellow solution turns to black solution during reflux. This is the desired reflux solution, whereby the platinum is at its active. The black solution turns to grey solution and becomes more viscous upon addition of silicon dioxide powder. The black solution thickens as white powder is being added.

The filtered grey solution yield jelly and waxy solid. By vacuum filtration, jelly and waxy solid material obtained on the filter paper. The solid that is grey in colour is the silica loaded with platinum. On the other hand, the solid is waxy and jelly due to the moisture in the silica that could not be removed from the solid material. The jelly and waxy solid becomes hard and brittle, grey solid. This is the condition of the filtered solid material after overnight drying. Since most of moisture has been removed, the solid material turns hard and brittle. The solid obtained, which is now grey in colour is ready to be calcined at elevated temperature.

The titanium (IV) oxide catalyst is a white powder. Upon adding titanium (IV) oxide into the refluxed solution, the solution turns grey with suspended titanium (IV) oxide. This is because titanium (IV) oxide is not soluble in aqueous solutions. The darker the solution indicates the higher concentration of platinum.

2. PREPARATION OF CALIBRATION CURVE

The standard solutions and sample solutions were reacted with Hantzsch reagent. This reagent acts as the formaldehyde indicator. Upon reaction with formaldehyde, 3,5 – dietil – 1,4 – dihydrolutidine will be formed which is yellow in colour. Thus, by measuring the absorbance of the sample solution, the concentration of formaldehyde in the solution could be determined. The apparatus used for this purpose is a UV Spectrophotometer. The wavelength selection was done by plotting the absorbance versus wavelength, as shown in Figure 4. From the graph, it could be seen the highest absorbance is at approximately wavelength = 413 nm. Figure 5 is the absorbance versus formaldehyde concentrations (calibration curve).

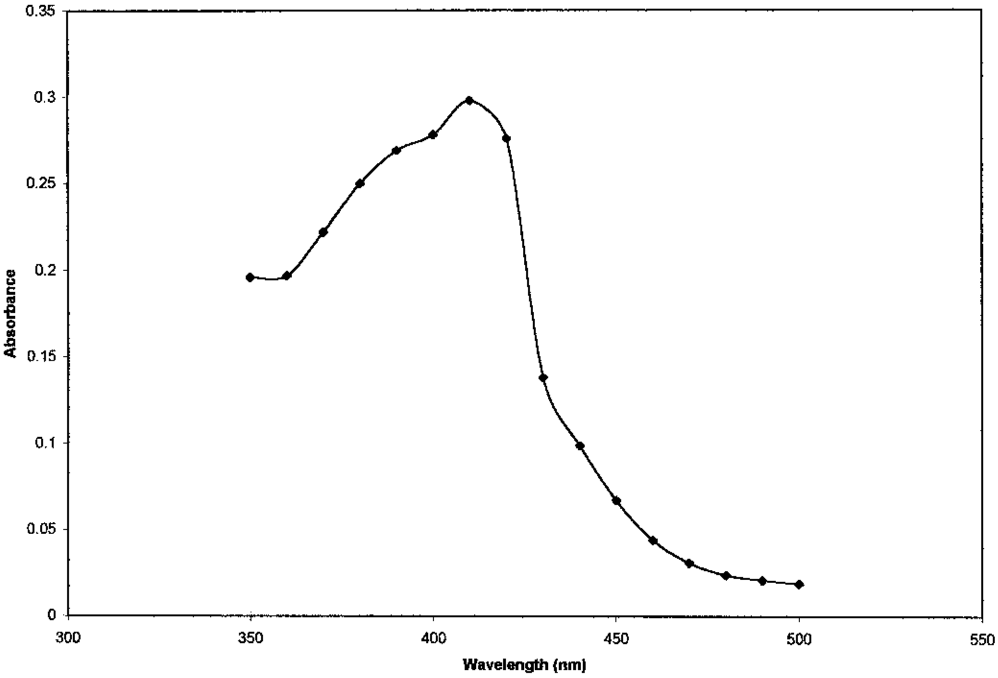


Figure 4: Absorbance versus wavelength

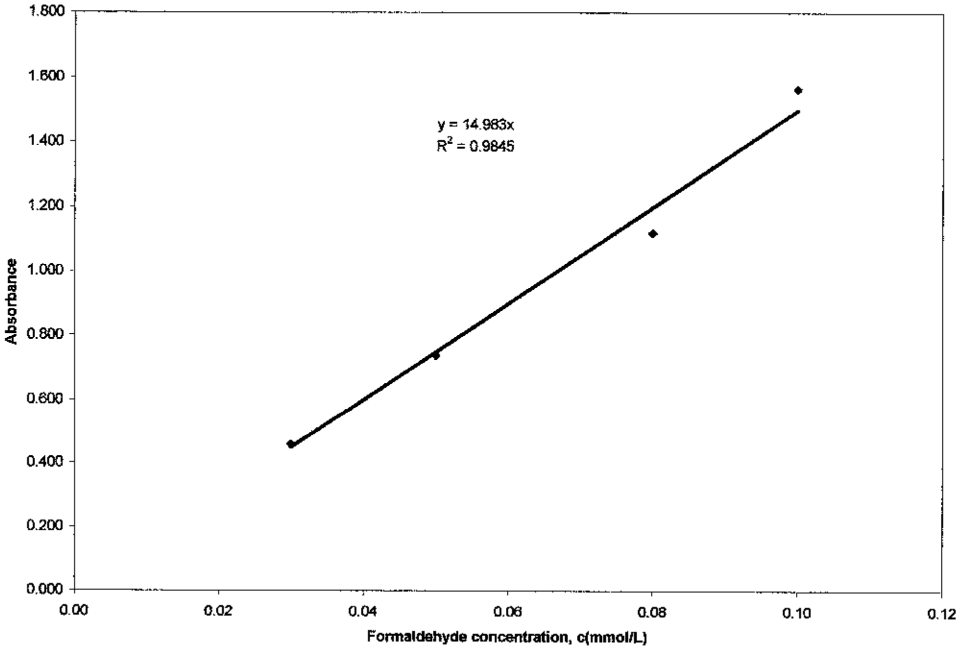


Figure 5: Standard calibration curve for formaldehyde

3. PERFORMANCE OF PLATINISED SILICON DIOXIDE FOR METHANOL CONVERSION TO FORMALDEHYDE

3.1 Methanol Oxidation By Using 0.1 % Platinum Loaded On Silicon Dioxide

The concentrations of formaldehyde synthesised using 0.1 % Pt on silicon dioxide are tabulated in Table 5.

Table 5: Concentrations of formaldehyde using 0.1 % Pt on silicon dioxide

Time (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.006	0.063
10	0.005	0.054
20	0.005	0.056
60	0.006	0.062

The corresponding graph representation for this experiment is shown Figure 6:

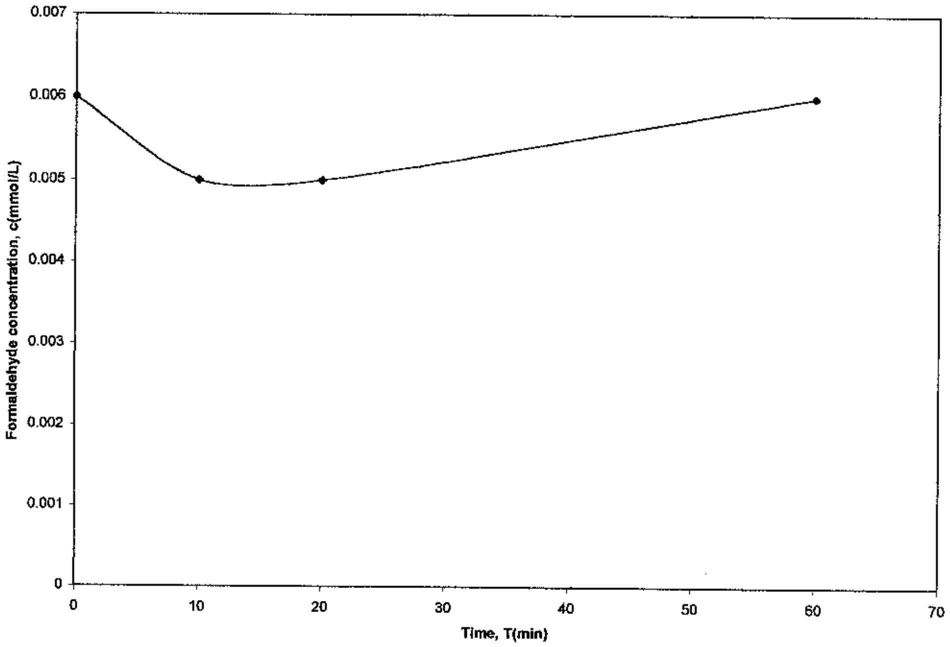


Figure 6: Formaldehyde concentrations versus time using 0.1 % Pt on silicon dioxide

3.2 Methanol Oxidation By Using 0.3 % Platinum Loaded On Silicon Dioxide

The concentrations of formaldehyde synthesised in the presence of 0.3 % Pt on silicon dioxide are tabulated in Table 6.

Table 6: Concentrations of formaldehyde using 0.3 % Pt on silicon dioxide

Time (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.005	0.055
10	0.007	0.088
20	0.007	0.076
90	0.008	0.093

The corresponding graph representation for this experiment is shown in Figure 7:

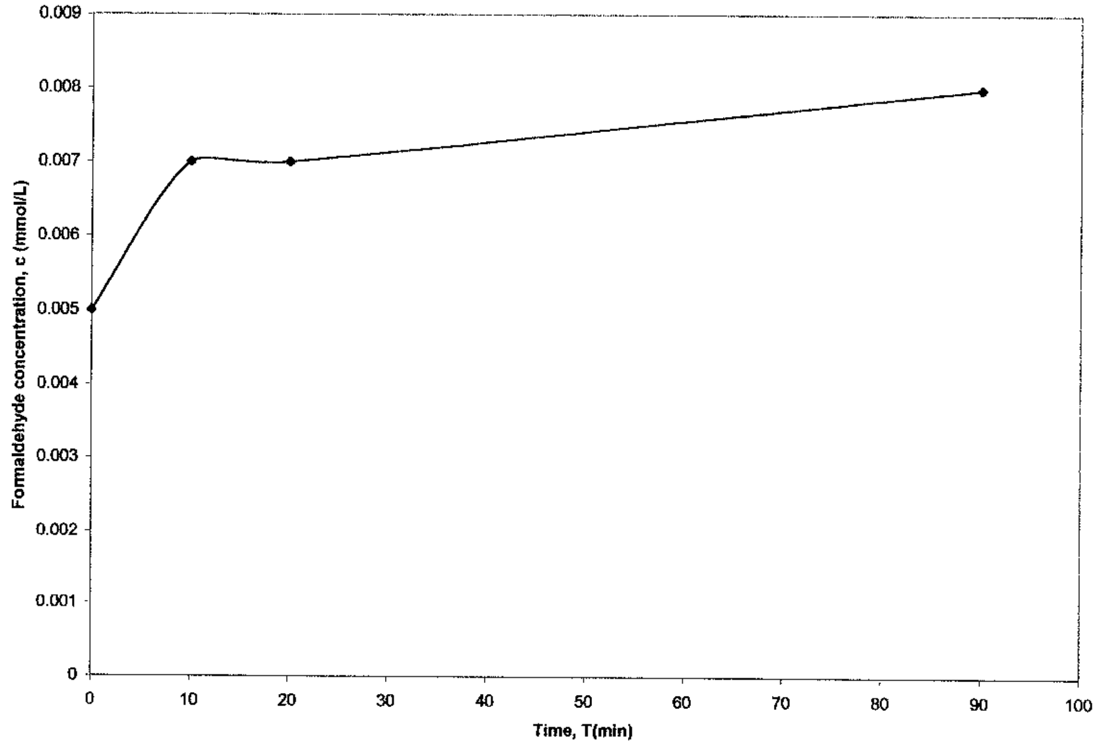


Figure 7: Formaldehyde concentrations versus time using 0.3 % Pt on silicon dioxide

4. PERFORMANCE OF PLATINISED TITANIUM (IV) OXIDE FOR METHANOL OXIDATION TO FORMALDEHYDE

4.1 Methanol Oxidation By Using 0.1 % Platinum Loaded On Titanium (IV) Oxide

The concentrations of formaldehyde synthesised using 0.1 % Pt on titanium (IV) oxide are tabulated in Table 7.

Table 7: Concentrations of formaldehyde using 0.1 % Pt on titanium (IV) oxide

Time (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.006	0.064
10	0.007	0.080
20	0.007	0.088
60	0.010	0.135
90	0.014	0.186
120	0.016	0.225

The corresponding graph representation for this experiment is shown in Figure 8.

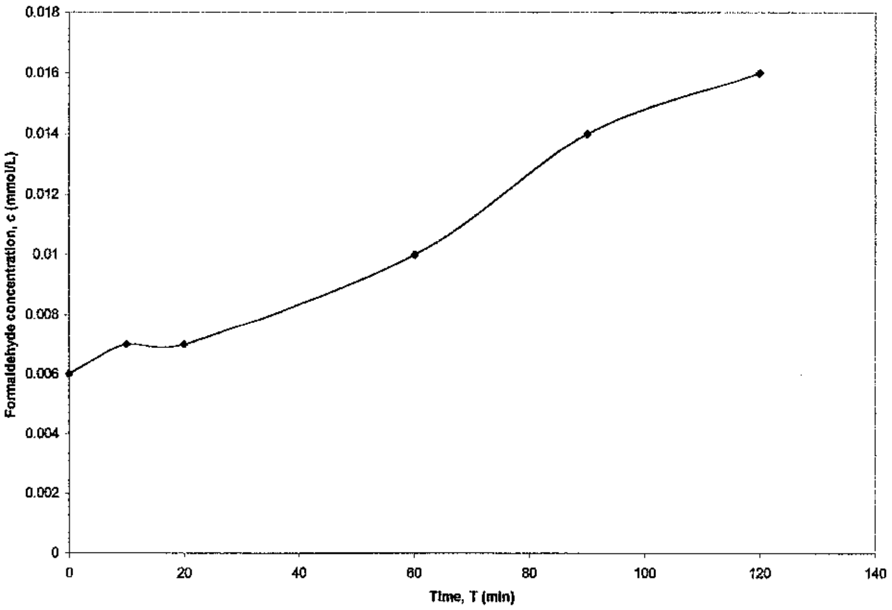


Figure 8: Formaldehyde concentrations versus time using 0.1 % Pt on titanium (IV) oxide

4.2 Methanol Oxidation By Using 0.3 % Platinum Loaded on Titanium (IV) Oxide

The concentrations of formaldehyde synthesised using 0.3 % Pt on titanium (IV) oxide are tabulated in Table 8.

Table 8: Concentrations of formaldehyde using 0.3 % Pt on titanium (IV) oxide

Time (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.011	0.138
10	0.012	0.166
20	0.013	0.181
60	0.016	0.224
90	0.015	0.213
120	0.016	0.220

The corresponding graph representation for this experiment is shown in Figure 9.

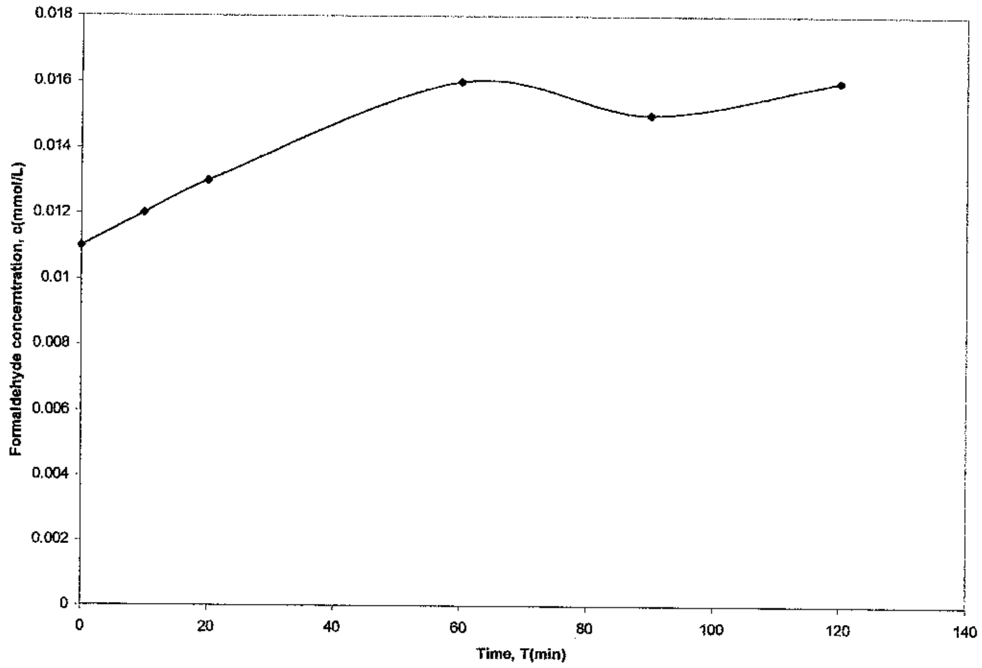


Figure 9: Formaldehyde concentrations versus time using 0.3 % Pt on titanium (IV) oxide

4.3 Methanol Oxidation By Using 0.5 % Platinum Loaded On Titanium (IV) Oxide

The concentrations of formaldehyde synthesised using 0.5 % Pt on titanium (IV) oxide are tabulated in Table 9.

Table 9: Concentrations of formaldehyde using 0.5 % Pt on titanium (IV) oxide

Time (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.005	0.050
10	0.008	0.102
20	0.014	0.188
60	0.022	0.310
90	0.011	0.138
120	0.010	0.129

The corresponding graph representation for this experiment is shown in Figure 10.

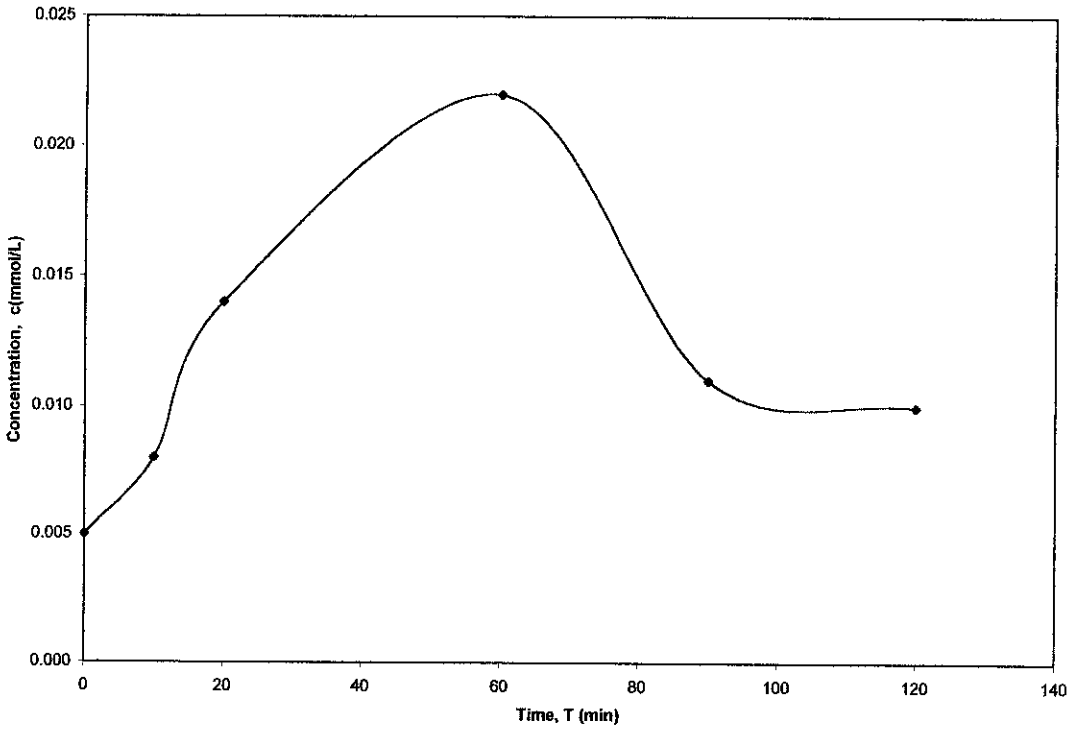


Figure 10: Formaldehyde concentrations versus time using 0.5 % Pt on titanium (IV) oxide

4.4 Methanol Oxidation By Using 1.1 % Platinum Loaded On Titanium (IV) Oxide

The concentrations of formaldehyde synthesised using 1.1 % Pt on titanium (IV) oxide are tabulated in Table 10.

Table 10: Concentrations of formaldehyde using 1.1 % Pt on titanium (IV) oxide

Time (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.004	0.030
10	0.006	0.073
20	0.008	0.100
60	0.010	0.129
90	0.012	0.161
120	0.015	0.203

The corresponding graph representation for this experiment is shown in Figure 11.

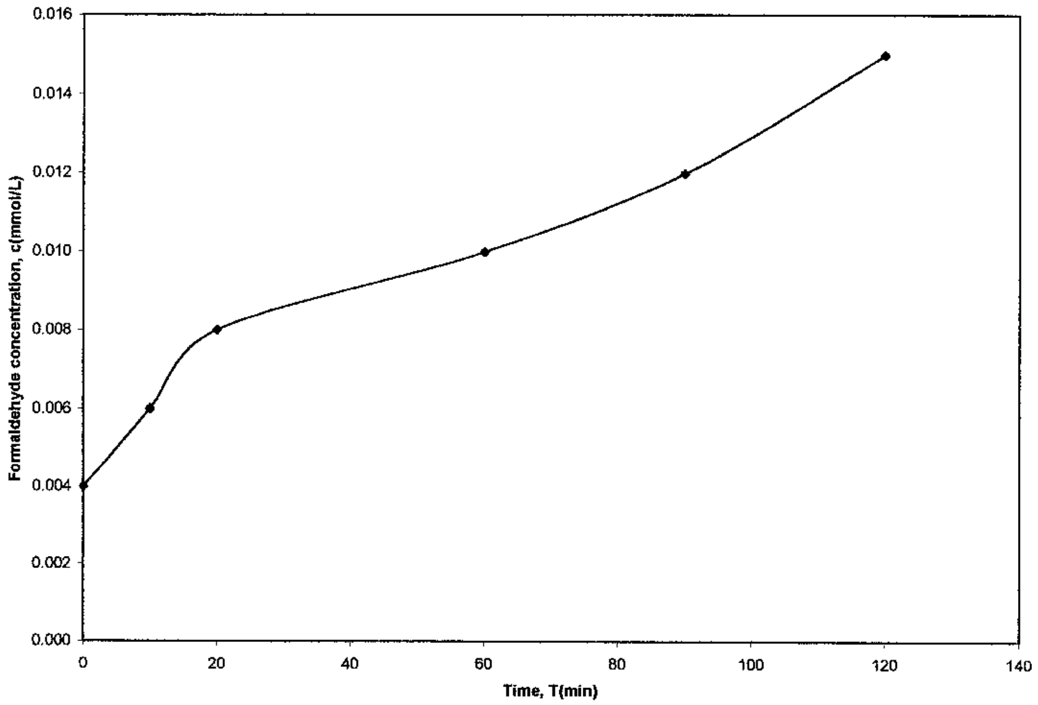


Figure 11: Formaldehyde concentrations versus time using 1.1 % Pt on titanium (IV) oxide

5. COMPARISON OF PERFORMANCE BETWEEN SILICON DIOXIDE AND TITANIUM (IV) OXIDE CATALYST CARRIERS

The above results of catalysts' activity testing are tabulated as below in Table 11. The sample catalysts involve platinised silicon dioxide (SiO_2) at 0.1 % and 0.3 % platinum loading, as well as platinised titanium (IV) dioxide (TiO_2) at 0.1 %, 0.3 %, 0.5 % and 1.1 % platinum loading.

Table 11: Comparisons of formaldehyde concentration with various catalysts

Catalyst / Time (min)	Concentrations of formaldehyde (mmol/L)					
	0.1 % Pt on SiO_2	0.3 % Pt on SiO_2	0.1 % Pt on TiO_2	0.3 % Pt on TiO_2	0.5 % Pt on TiO_2	1.1 % Pt on TiO_2
0	0.006	0.005	0.006	0.011	0.005	0.004
10	0.005	0.007	0.007	0.012	0.008	0.006
20	0.005	0.007	0.007	0.013	0.014	0.008
60	0.006	N/A	0.010	0.016	0.022	0.010
90	N/A	0.008	0.014	0.015	0.011	0.012
120	N/A	N/A	0.016	0.016	0.010	0.015

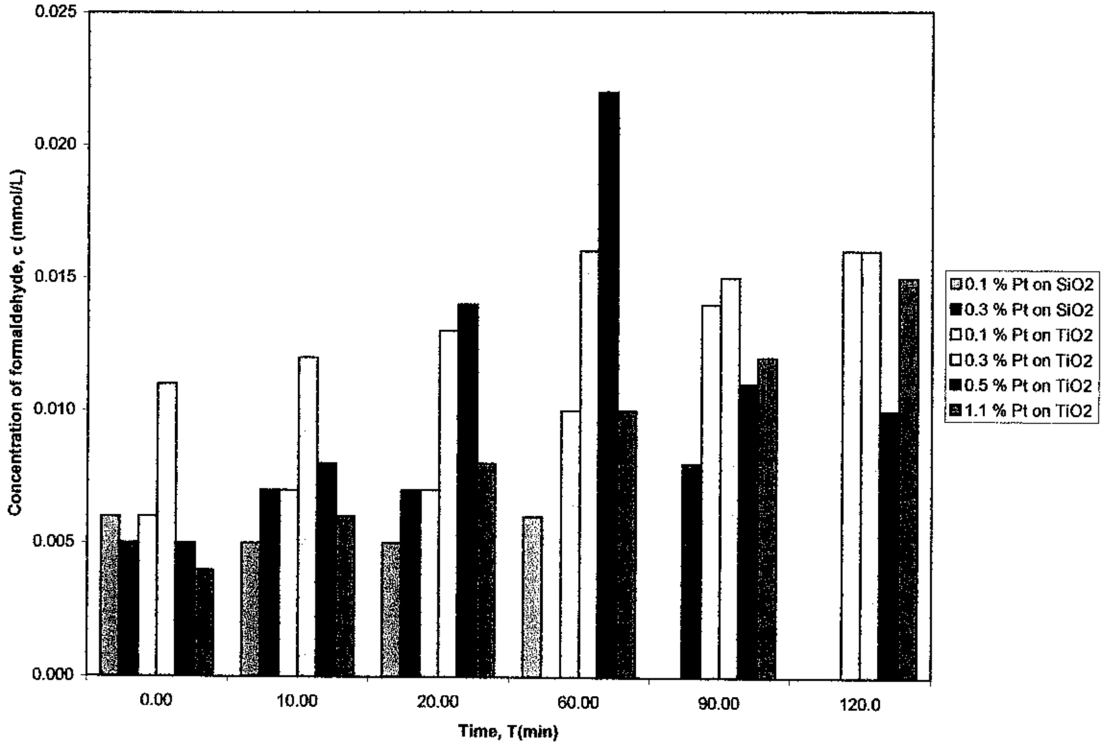


Figure 12: Formaldehyde concentration versus time using various catalysts

From Figure 12, it can be seen that 0.5 % Pt on titanium (IV) oxide catalyst gave the highest activity compared to 0.1 % and 0.3 % platinum on silicon dioxide catalysts and 0.1 %, 0.3 and 1.1 % Pt on titanium (IV) oxide catalysts. The highest formaldehyde concentration is 0.022 mmol/L by using 0.5 % Pt on titanium (IV) oxide catalyst at time = 60 minutes. The formaldehyde concentrations after 60 minutes dropped to 0.011 mmol/L and 0.010 mmol/L due to the effect of overheating samples. Thus the data is disregarded. Hence, 0.5 % Pt on titanium (IV) is the best among of sample catalysts.

For silicon dioxide catalysts, the effect of loading platinum did not give any enhanced performance. This could be seen in Figure 6 and Figure 7. The formaldehyde concentration shows as if no reaction took place because the formaldehyde concentrations were nearly constants.

6. PERCENTAGE CONVERSION

The percentage conversion [9] is given by:

$$\text{Percentage Conversion} = \frac{N_{AO} - N_A}{N_{AO}} \times 100\%,$$

where N_{AO} is the initial moles of methanol and N_A is the moles of methanol at any point of time. This expression is identical to the expression using concentration parameter C_{AO} and C_A by dividing the above equation with the reactive volume of the reactor, V. Note that this expression is valid for constant volume reaction (none or negligible volume changes). Since 1 mol of formaldehyde is formed from 1 mol of methanol, it is concluded that instantaneous moles of methanol is given by $N_A = N_{AO} - N_B$, or rather $N_B = N_{AO} - N_A$. The assumption is valid according to the literature review whereby formaldehyde selectivity is approaching 1 at low temperature (refer Figure 3 in literature review). Thus, the above percentage conversion expression is simplified to

$$\text{Percentage Conversion} = \frac{N_B}{N_{AO}} \times 100\%.$$

The sample calculation could be viewed in Appendix A6. The percentage conversions are tabulated in the Table 12 below:

Table 12: Percentage conversion of methanol with various catalysts

Catalyst / Time min)	Percentage Conversion (%)					
	0.1 % Pt on SiO_2	0.3 % Pt on SiO_2	0.1 % Pt on TiO_2	0.3 % Pt on TiO_2	0.5 % Pt on TiO_2	1.1 % Pt on TiO_2
0	0.0005	0.0004	0.0005	0.0009	0.0004	0.0003
10	0.0004	0.0006	0.0006	0.0009	0.0006	0.0005
20	0.0004	0.0006	0.0006	0.0010	0.0011	0.0006
60	0.0005	N/A	0.0008	0.0013	0.0017	0.0008
90	N/A	0.0006	0.0011	0.0012	0.0009	0.0009
120	N/A	N/A	0.0013	0.0013	0.0008	0.0012

The best percentage conversion from Chang Oon Yuen [8] is 0.01871 % with 5 % Pt on alumina. The percentage conversion of methanol obtained by Min Qian, M. A. Liauw and G. Emig (in Chang Oon Yuen Dissertation, Ref. 8) is 0.4 % at 723 K. By comparing the percentage conversion obtained in the lab with the two percentage conversions, it can be said that the percentage conversion obtained (0.0017 % at 25 ^{O}C for 0.5 % Pt on titanium (IV) oxide) is relatively good since the reaction temperature is relatively low.

7. RATE OF REACTION

The rate of reaction [10] is given by:

$$-r_A = \frac{1}{V_r}\frac{dN_A}{dt},$$

where N_A is the moles of methanol, V_r is volume of reactive part of the ideal reactor (in this case is volume of methanol) and r_A is the rate of methanol consumption. The average methanol consumption is estimated from:

$$r_A = \frac{1}{V_r}\frac{N_A - N_{A0}}{t}$$

To determine the average rate of methanol consumption, the final moles of methanol were taken. The final moles of formaldehyde were taken as the amount of methanol consumed by assuming all reacted methanol convert to formaldehyde. The rates of reactions using different catalysts are tabulated in Table 13.

Table 13: Average rate of reaction of formaldehyde synthesis with various catalysts

Catalyst	Average Rate of Reaction (mol/L.s)
0.1 % Pt on Silicon Dioxide	$1.6667 \text{ X } 10^{-9}$
0.3 % Pt on Silicon Dioxide	$2.9630 \text{ X } 10^{-8}$
0.1 % Pt on Titanium (IV) Oxide	$4.4444 \text{ X } 10^{-8}$
0.3 % Pt on Titanium (IV) Oxide	$4.4444 \text{ X } 10^{-8}$
0.5 % Pt on Titanium (IV) Oxide	$1.2222 \text{ X } 10^{-7}$
1.1 % Pt on Titanium (IV) Oxide	$4.1667 \text{ X } 10^{-8}$

From the above table, it could be seen that 0.5 % Pt on titanium (IV) oxide is the catalyst with the highest reaction rate among the above 6 catalysts. From the table, it could be seen that the reaction rate for 0.1 % and 0.3 % Pt on titanium (IV) oxide are similar ($4.4444 \text{ X } 10^{-8}$ mol/L.s). 0.1 % Pt on titanium (IV) oxide already offers similar performance at lower loading. The rate of reaction is highest when titanium (IV) oxide is loaded up to 0.5 % platinum in which reaction rate ($1.2222 \text{ X } 10^{-7}$ mol/L.s) are approximately three times higher than 0.1 % platinum. Increasing platinum loading, however does not guarantee the reaction rate will further increase. This is clearly shown with the decreased reaction rate to 4.1667 X 10^{-8} mol/L.s, in which is lower than 0.1 % Pt on titanium (IV) oxide.

The average reaction rates for platinised silicon dioxide are very low. The reaction rate when using 0.1 % Pt on silicon dioxide is the lowest among of the catalysts that is 1.6667 X 10^{-9} mol/L.s. From the literature review [4], it was cited that silicon dioxide has appreciable methanol conversion when the reaction temperature is above 400 ^{O}C. Thus, the formaldehyde yield is very low in this experiment since the reaction temperature was at room temperature (approximately 25 ^{O}C).

8. EFFECT OF PLATINUM LOADING ON TITANIUM (IV) OXIDE CATALYST CARRIER.

The effect of platinum loading is tabulated Table 14. The sample catalysts involve pure titanium (IV) oxide and platinised titanium (IV) dioxide (TiO_2) at 0.1 %, 0.3 %, 0.5 % and 1.1 % platinum loading. The catalysts' performance are compared at time = 60 minutes. The pure titanium (IV) oxide performance data was taken from the study of methanol oxidation to formaldehyde, which was done previously in January 2004 semester.

Table 14: Formaldehyde concentrations at time = 60 minutes as a function of platinum loading on titanium (IV) oxide carrier

Percentage of platinum loading (%)	Formaldehyde concentration (mmol/L)
0	0.00157
0.1	0.01000
0.3	0.01600
0.5	0.02200
1.1	0.01000

The corresponding graph representation for this comparison is shown in Figure 13.

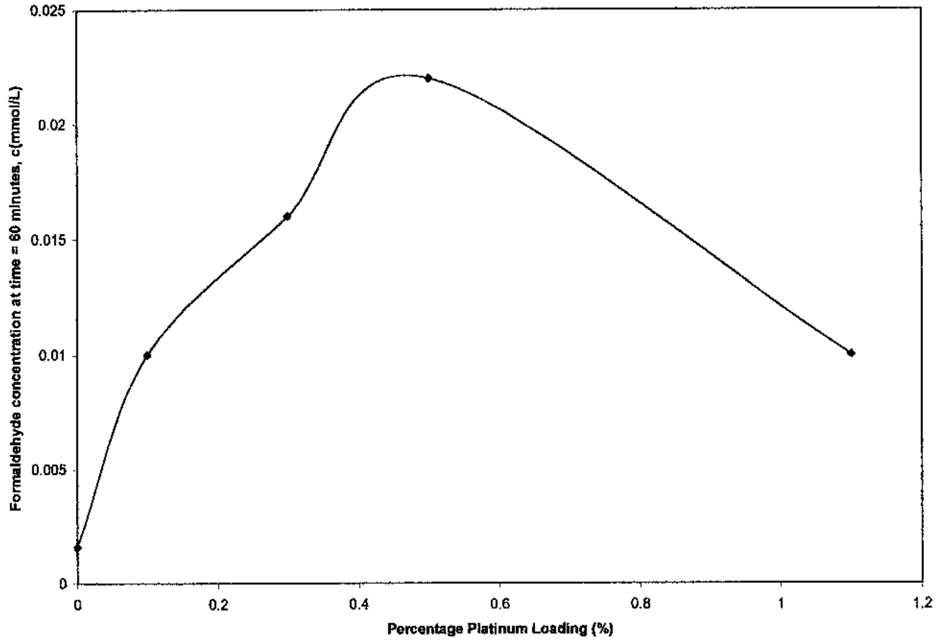


Figure 13: Formaldehyde concentrations at time = 60 minutes as a function of platinum loading

From the Figure 13, it could be clearly seen the catalyst performance is sharply enhanced by loading platinum on titanium (IV) oxide 0 % (pure titanium (IV) oxide) to 0.5 % platinum. The titanium (IV) oxide is the best when platinum loading is approximately 0.5 % (formaldehyde concentration = 0.022 mmol/L) when gradually the catalyst's performance decreases when titanium (IV) oxide loaded with 1.1 % platinum. This is shown by the deficit of formaldehyde concentration (0.010 mmol/L). It was suspected upon platinum addition, the certain part of titanium (IV) oxide surface was accumulated with platinum atoms. Thus the dispersion degree of platinum would be decreased and the active site on the catalyst also decreased. The discussion on dispersion degree of platinum will confirm the hypothesis.

9. PERFORMANCE OF 0.5 % PLATINUM ON TITANIUM (IV) OXIDE FOR METHANOL OXIDATION TO FORMALDEHYDE AT ELEVATED TEMPERATURES

9.1 Methanol Oxidation At 30 ^{O}C

The concentrations of formaldehyde synthesised using 0.5 % Pt on titanium (IV) oxide at 30 ^{O}C are tabulated in Table 15.

Table 15: Concentrations of formaldehyde using 0.5 % Pt on titanium (IV) oxide at 30 ^{O}C

ime (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.005	0.053
10	0.008	0.103
20	0.007	0.086
60	0.011	0.148
90	0.011	0.145
120	0.012	0.156

The corresponding graph representation for this experiment is shown in Figure 14.

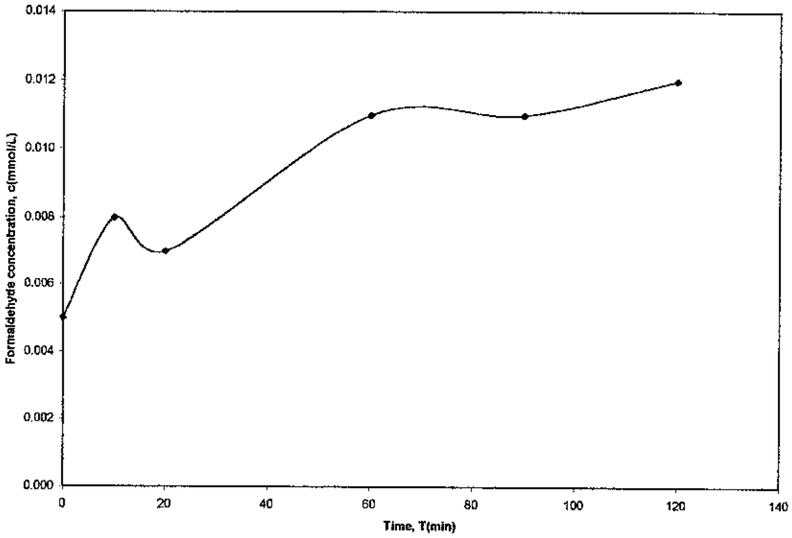


Figure 14: Formaldehyde concentrations versus time using 0.5 % Pt on titanium (IV) oxide at 30 ^{O}C

9.2 Methanol Oxidation At 35 ^{O}C

The concentrations of formaldehyde synthesised using 0.5 % Pt on titanium (IV) oxide at 35 ^{O}C are tabulated in Table 16.

Table 16: Concentrations of formaldehyde using 0.5 % Pt on titanium (IV) oxide at 35 ^{O}C

ime (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.004	0.040
10	0.005	0.045
20	0.006	0.074
60	0.009	0.108
90	0.008	0.095
120	0.010	0.126

The corresponding graph representation for this experiment is shown in Figure 15.

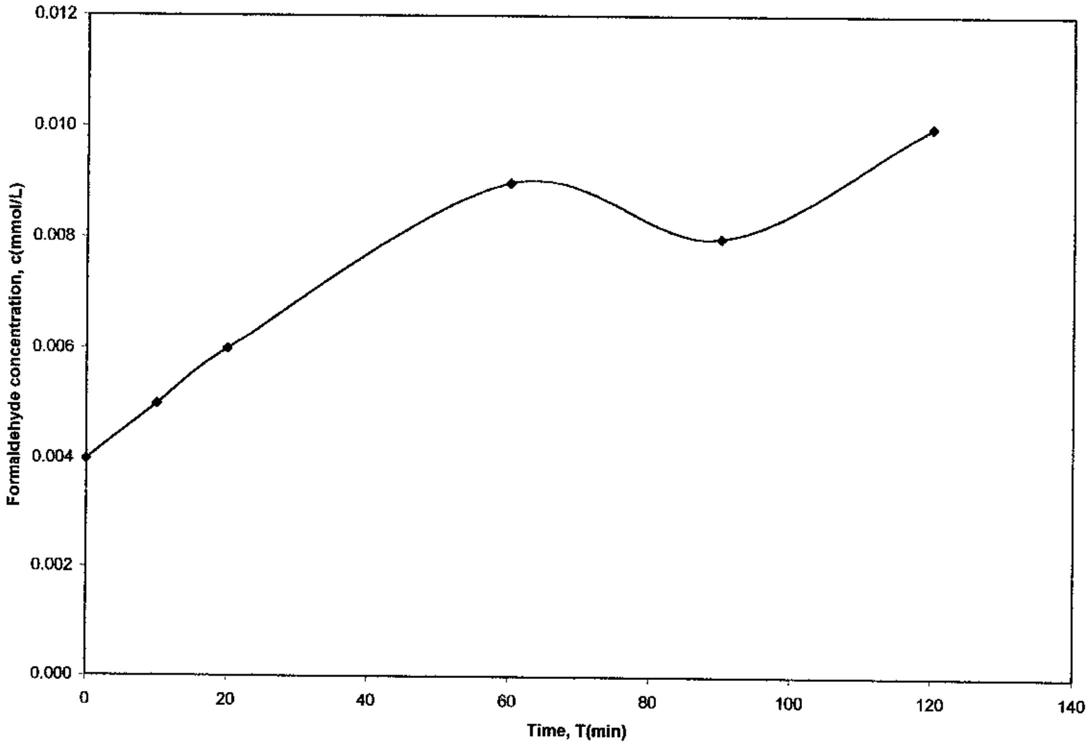


Figure 15: Formaldehyde concentrations versus time using 0.5 % Pt on titanium (IV) oxide at 35 ^{O}C

9.3 Methanol Oxidation At 40 ^{O}C

The concentrations of formaldehyde synthesised using 0.5 % Pt on titanium (IV) oxide at 40 ^{O}C are tabulated in Table 17.

Table 17: Concentrations of formaldehyde using 0.5 % Pt on titanium (IV) oxide at 40 ^{O}C

ime (min)	Concentration of formaldehyde (mmol/L)	Absorbance at wavelength = 413.0 nm
0	0.001	-0.004
10	0.009	0.110
20	0.009	0.118
60	0.012	0.153
90	0.014	0.190
120	0.017	0.228

The corresponding graph representation for this experiment is shown in Figure 16.

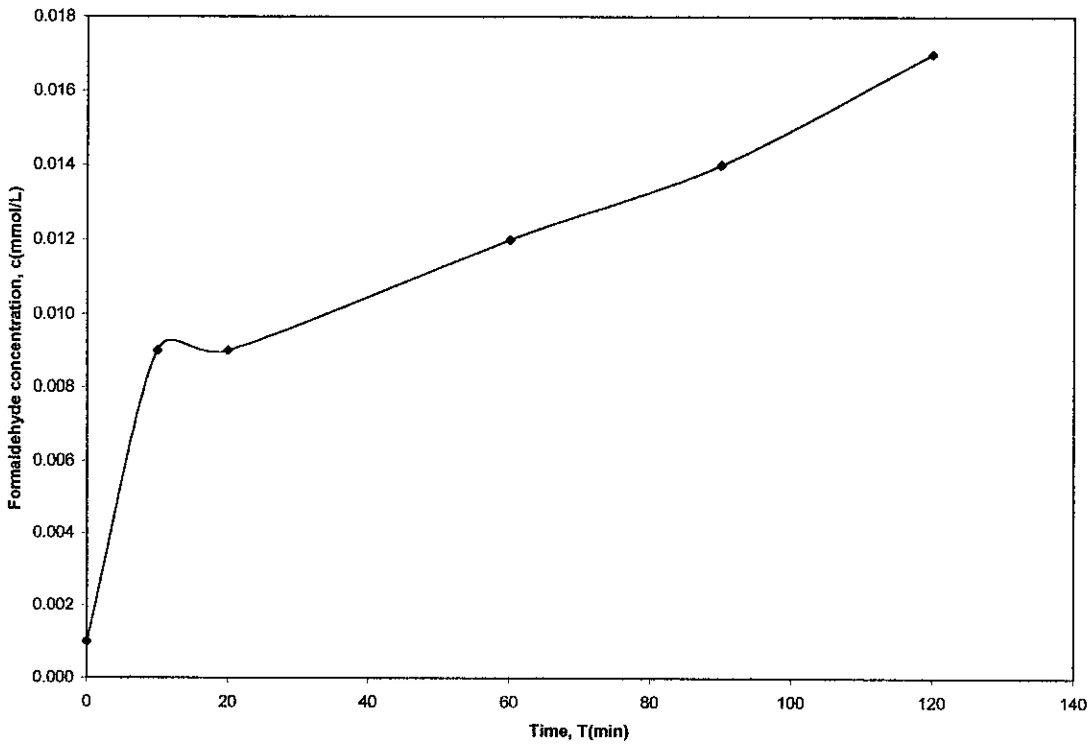


Figure 16: Formaldehyde concentrations versus time using 0.5 % Pt on titanium (IV) oxide at 40 ^{O}C

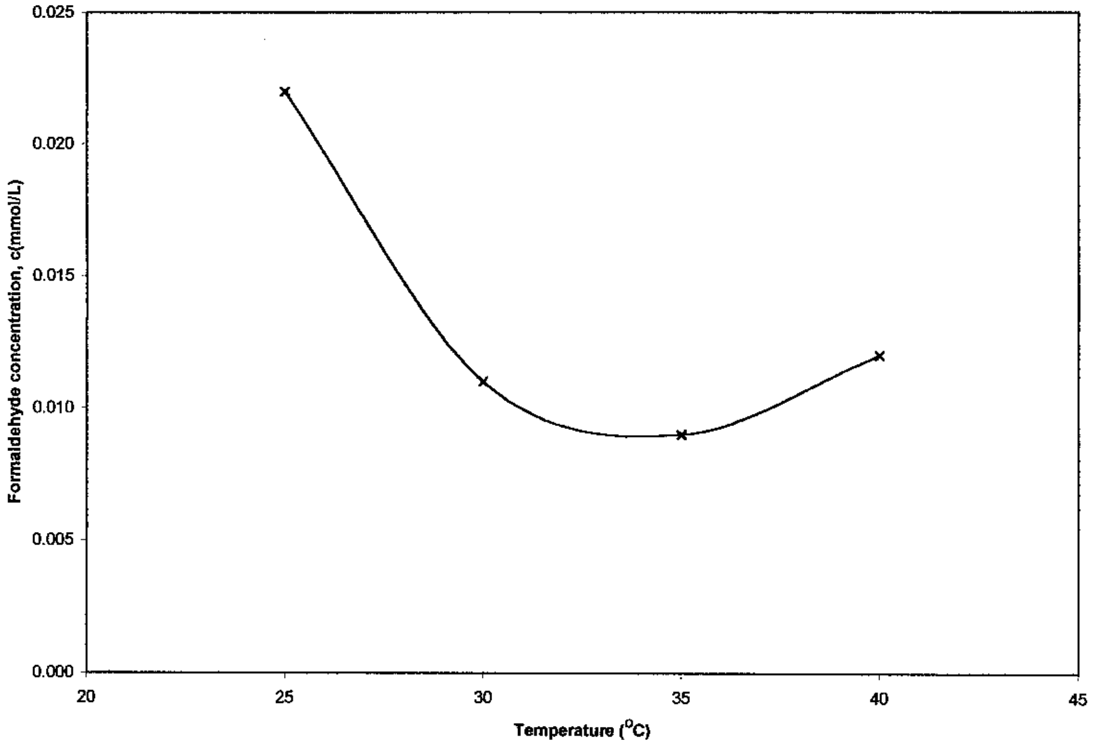


Figure 17: Formaldehyde concentrations at various temperatures (time = 60 minutes) using 0.5 % Pt on titanium (IV) oxide catalyst

From Figure 17, the highest formaldehyde concentration is when reacted at room temperature (approximately 25 ^{O}C). The reason is the colligative properties of solution, whereby gas solubility decreases by increasing the temperature. Since oxygen gas for methanol oxidation is from air, the air solubility decreases when reaction temperature is increased. Hence, the formaldehyde concentration decreased when reaction temperature increased to 30 ^{O}C and further increased to 35 ^{O}C. It was when the reaction temperature of 40 ^{O}C that the formaldehyde concentration increased. This might be due to more energy transferred to the system to reach the activation energy of the reaction which compensated the drop in formaldehyde concentrations.

10. ACTIVATION ENERGY AND FREQUENCY FACTOR

In order to obtain the activation energy and pre-exponential/frequency factor, the rate expression must be expressed according to the rate law. According to the literature review [4], reaction orders for methanol and oxygen gas are first order and 0.75 respectively. By assuming the experiment follows reaction orders in the model and the fact that methanol oxidation to formaldehyde is irreversible reaction and no further reactions, the rate equation could be written as:

$$-r_A = kC_AC_B^{0.75}$$

Where C_A : concentration of methanol in mol/L

C_B : concentration of oxygen gas O_2 in mol/L

$-r_A$: rate of methanol consumption in mol/L.s

k : rate constant in $(mol/L)^{-0.75}s^{-1}$

according to Arrhenius law, the rate constant could be represented as [10]

$$k = k_0 e^{\frac{-E}{RT}}$$

Where k_O : pre-exponential/frequency factor in $(mol/L)^{-0.75}s^{-1}$

E : activation energy in kJ/mol

R : universal gas constant in kJ/mol

T : absolute temperature in K

The expression now becomes: $-r_A = k_0 e^{\frac{-E}{RT}} C_A C_B^{0.75}$

If the rate of reaction, reactant concentrations and reaction temperature data available, the activation energy E and frequency factor k_O could be determined.

The rate of reactions, reaction temperatures, Henry's Law constants [9,12], oxygen gas concentration in liquid phase, rate constants and their respective natural logarithm are tabulated in Table 18.

Table 18: Rate constants at different temperature.

action rate ol/L.s)	Reaction temperature (K)	Inverse temperature (K^{-1})	Henry's Law constant (atm)	Oxygen gas concentration (mol/L)	Rate constant $(mol/L)^{-0.75}s^{-1}$	ln k
$X\ 10^{-8}$	303	0.0033003300	47500	0.000533026	$3.75\ X\ 10^{-7}$	-14.79
$X\ 10^{-8}$	308	0.0032467532	50700	0.000499384	$3.28\ X\ 10^{-7}$	-14.92
$X\ 10^{-8}$	313	0.0031948882	53500	0.000473248	$5.81\ X\ 10^{-7}$	-14.35

The natural logarithm of rate constant ln k is plotted with respect to the inverse of absolute temperature 1/T, as shown in Figure 18 below. The slope of the graph represents the ratio E/R.

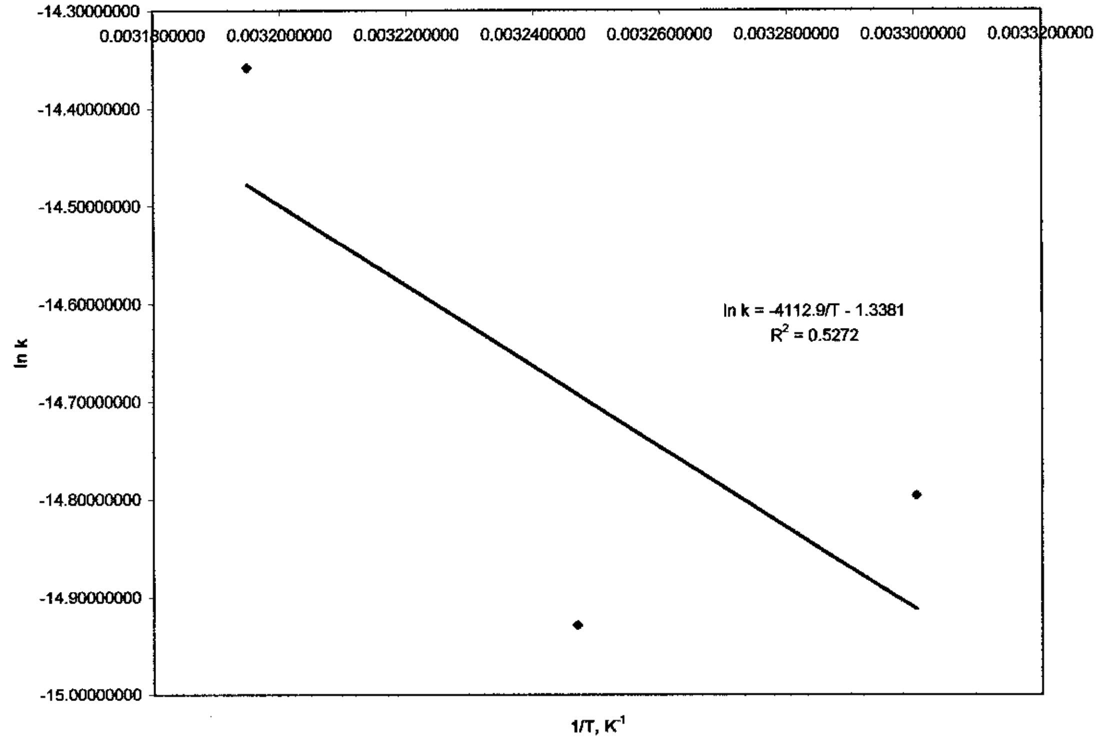


Figure 18: Temperature dependency of reaction rate

From the results, the activation energy obtained (34.19 kJ/mol) is lower than cited in the literature review (approximately 163 kJ/mol at 400 K). This might be due to the different mechanism that take place at 400 K, in which the reaction is rather gaseous reaction rather than liquid phase reaction done in the lab. The pre-exponential/frequency factor, k_o for this reaction is 0.2623 $(mol/L)^{-0.75}s^{-1}$

11. CATALYST CHARACTERISATION USING TPDRO

The catalyst characterisation covered in this project is temperature programmed reduction (TPR) using Temperature Programmed Desorption-Oxidation-Reduction (Thermo Finnigan TPD/R/O 1100) equipment. The TPR experiments will give information to decide the reduction conditions of the metal oxide precursor. TPR also recognises the presence of different precursor phases, their oxidation state and their interaction with the support. In this experiment, the TPR purpose is to determine the dispersion degree of platinum on titanium (IV) oxide. In Figure 13, it is shown increasing platinum loading on titanium (IV) oxide does not necessarily increases the formaldehyde yield. The initial hypothesis is the 1.1 % loading has lower dispersion degree of platinum compared to 0.5 % loading. Thus, the active site on of 1.1 % loading on titanium (IV) oxide is lower.

The TPR experiments have been conducted for only 0.5 and 0.3 % Pt on titanium (IV) oxide catalysts samples. The metal surface area and dispersion degree for 0.5 and 0.3 % Pt on titanium (IV) oxide catalysts are tabulated in Table 19. The sample calculation is attached in Appendix A9.

Table 19: Surface area and dispersion degree for platinised titanium (IV) oxide catalysts

Platinum loading (%)	Amount of gas adsorbed, μmol/g	Metal surface area, m^2/g	Dispersion Degree, %
0.3	23.02	2.27×10^{-23}	299.5115323
0.5	13.91	1.37×10^{-23}	108.5533824

From the results obtained, the dispersion degree for 0.3 % loading is approximately three times higher than that of 0.5 % loading. This contradicts the previous hypothesis that the catalyst with higher yield has higher platinum dispersion and thus more active site. The result of TPR experiment however, is questionable. From the chromatogram reports, there were valleys (negative peak) formed instead of peaks. The typical result of TPR experiment comes with one significant peak without valleys. Moreover, 0.3 % loading has higher metal surface area. In addition to that, the result does not agree with the general facts about catalyst. Levenspiel [10], in his book (1999) says: A large readily accessible surface in easily handled materials is desirable (p. 378). The fact that higher 0.3 % has higher surface area and dispersion degree but lower formaldehyde yield clearly contradicts this statement. The dispersion degrees obtained is also non logical, as the figures exceed 100%. These abnormal figures were expected, as the calibration for signals are used from previous TPR experiment for other sample.

The existence of the valleys' plot questions the reliability of TPDRO equipment. The valley plot might come from residual sample from previous test. Most probably, the error and uncertainties come from the TPDRO equipment itself. This is because of the TPDRO has been used extensively to test samples from various resources. Thus, it is recommended to put TPDRO equipment under maintenance. In the mean time, the catalyst samples could be tested by using other equipment, such as scanning electron microscopy (SEM) device.

12. COST OF CATALYST

The cost of catalyst is important to determine the commercial viability of the produced catalyst. A catalyst might have outstanding activity. However, if the cost of the catalyst is very high, that does not make the catalyst as the optimised choice. The target is to maximise profit but at the same time minimise cost. The selected catalyst must have a high activity and selectivity and at reasonable cost. The cost of catalyst [13] is tabulated in Table 20.

Table 20: Price/Cost of catalyst per 50 g

Catalyst	Price/cost per 50 g (RM)
Silver	937.00
Iron molybdate	165.00
0.1% Pt on silicon dioxide	41.21
0.3% Pt on silicon dioxide	93.13
0.1% Pt on titanium (IV) oxide	149.96
0.3% Pt on titanium (IV) oxide	201.66
0.5% Pt on titanium (IV) oxide	253.56
1.1% Pt on titanium (IV) oxide	416.72

Silver and iron molybdate are the commercial catalysts. These catalysts are used in practice for formaldehyde synthesis through methanol oxidation. The rest are the catalysts produced in through experiment in laboratory. The most expensive catalyst still goes to silver, where for 50 g, it worth RM 937.00. The cheapest catalyst on the other hand is 0.1% Pt on silicon dioxide, where it costs RM 41.21. The best catalyst from this experiment, 0.5% Pt on titanium (IV) oxide costs RM 253.56, which is approximately 3 to 4 times cheaper than that of silver. However, this catalyst is still more expensive when compared to iron molybdate which costs only RM 165.00. Nevertheless, apart from price, there are several characteristics such as catalyst selectivity and catalyst life which are not known for 0.5% Pt on titanium (IV) oxide. The activity of this catalyst at the reaction conditions for silver and iron molybdate could not be justified since no explicit experiment has been done in order to fairly justify the best catalyst among of those tabulated in Table 20. Thus, it is suggested that further investigation and experiment need to be commenced in order to verify the actual catalysts activity, selectivity and life.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

1. CONCLUSION

The objective to load silicon dioxide and titanium (IV) oxide is achieved. The activities towards formaldehyde synthesis of both catalysts carriers when supported with platinum have also been tested. The following conclusions are founded:

- The best catalyst is 0.5 % Pt on titanium (IV) oxide, followed by 0.3 % Pt on titanium (IV) oxide, 1.1 Pt on titanium (IV) oxide, 0.1 % Pt on titanium (IV) oxide, 0.3 % on silicon dioxide and 0.1 % Pt on silicon dioxide. The titanium (IV) oxide provides better support for platinum to create active sites for reactions. This is proven from the formaldehyde yield in Table 12.
- The effect of elevating reaction temperature decreased the formaldehyde yield. This is because the experiment was conducted in liquid phase and solubility of oxygen decreases as temperature increases. This might not be true if the experiment is executed in gaseous phase at higher temperature and pressure.
- The activation energy is 34.19 kJ/mol and the corresponding frequency factor is 0.2623 $(mol/L)^{-0.75}s^{-1}$. The low activation energy indicates the reaction is temperature insensitive and thus increasing reaction temperature doesn't give appreciable increase in rate of reaction.
- From the TPR experiment, the dispersion degree and as well as metal surface area are inversely proportional to the activity of the catalyst. Thus, good platinum dispersion gives a catalyst with low activity. The reliability of the TPDRO equipment is questionable.
- The costs of produced catalysts are below the cost of silver catalysts. The cost of catalyst becomes higher upon loading more platinum and when changing from silicon dioxide carrier to titanium (IV) oxide carrier. The titanium (IV) oxide catalysts are more expensive that silicon dioxide catalysts. The commercial catalyst iron molybdate is a strong competing catalyst since it is cheaper than 0.3 %, 0.5 % and 1.1 % Pt on titanium (IV) oxide.

2. RECOMMENDATION

From the results obtained in the experiment, several areas of improvement could be identified and recommended:

- It might be timely to consider platinising the commercial catalyst in order to increase the activity, selectivity and the catalyst's life. Such catalysts that could be platinised are silver, iron molybdate and iron-cobalt catalysts. By platinising those catalysts, there might be probability for them to operate at lower temperatures at similar rate of reaction. This experiment proves platinising the available catalysts might improve the catalysts activity.
- The results comes from TPDRO equipment is questionable. Thus alternative tests should be made to verify the results. In the mean time, the TPDRO equipment might require professional calibration and maintenance to ensure the reliability of experimental results.
- The experiment is redone in gaseous phase and higher reaction temperature and pressure so that the formaldehyde yield is improved and proves the catalysts have good catalytic activity. The reactor should also have control features, whereby temperature and pressure could be manipulated.

REFERENCE:

1. OSHA Fact Sheet: Formaldehyde

www.osha.gov/OshDoc/data_General_Facts/formaldehyde-factsheet.pdf

2. Safety and Health Topics: Formaldehyde

http://www.osha.gov/SLTC/formaldehyde/

3. Formaldehyde First Listed in the Second Annual Report on Carcinogens Reasonably Anticipated to be a Human Carcinogen 10th Report On Carcinogens / NATIONAL TOXICOLOGY PROGRAM 1nov02

http://www.mindfully.org/Pesticide/2002/Formaldehyde-Carcinogen-OC1nov02.htm

3. Davies P., Donald R. T., Harbord N. H., (Authors for Methanol Paperwork), Twigg M. V. (Editor), Catalyst Handbook, 2nd Edition, 1996, Manson Publishing Ltd., p. 1 – 26, p. 460, p490 – 502.

4. A. Andreasen, H. Lynggard, C. Stegelmann, P. Stoltze, "A Microkinetic Model of the Methanol Oxidation Over Silver", Surface Science Volume 544, Issue 1 , 10 October 2003, p5-23.

5. A. Kremling and F. Allgower, "Robust Control of a Catalytic Fixed Bed Reactor", Proc. 33rd Conference on Decision and Control, Lake Buena Vista, Florida, December 1994, Vol. 4, No. 5, p10.

6. Shuiliang Yao, Feng Ou Yang, Satoshi Shimumora, Hiroaki Sakurai, Kenji Tabata, Eiji Suzuki, "A Kinetic Study of Methanol Oxidation Over Silicon Dioxide", Applied Catalysis A: General 198 (2000) p43–50.

7. Amiruddin, N. A., Surface characterisation of platinised TiO_2 powder, January 2002, p. 20 – 28.

8. Chang, O. Y., Catalytic Oxidation of Methanol to Formaldehyde Using Metal Oxide Catalysts, May 2004, p14 – 59.

9. Felder, M. R., Rousseau R. W., Elementary Principle of Chemical Processes, John Wiley and Sons, 2000, USA, 3rd Edition, p123.

10. Levenspiel, O., Chemical Reaction Engineering, John Wiley and Sons, 2000, USA, 3rd Edition, p376 – 391.

11. Fogler, H. S., Elements of Chemical Reaction Engineering, Prentice Hall, 1999, Upper Saddle River, New Jersey, USA, 3rd Edition, P592 – p613.

12. Perry R. H., Green D. W., Maloney J. O., Perry's Chemical Engineers Handbook, 7th edition, Mc-Graw Hill, New York, 1997, 2-125.
13. Science Lab.com, Chemical and Laboratory Equipment, Price Quotation.
http://www.sciencelab.com/page/S/PVAR/23014/SLC5086

APPENDICES

A1. Chemicals

Table A1: Chemicals' Names and Formulas, Suppliers and Purities

Chemical's name and formula	Supplier	Purity
Titanium (IV) Oxide, TiO_2	GCE Laboratory Chemicals	99 %
Sodium Citrate Dihydrate, $Na_3C_6H_5O_7.2H_2O$	Calbio Chem EMD Biosciences Inc. La Jolla	Molecularbiology Grade
Acetic Acid, $C_2H_4O_2$	Hamburg Chemicals	99.8 %
Methanol, C_2H_5OH	Merck KGaA, Darmstadt, Germany	99.8 %
Ammonium Acetate, CH_3COONH_4	Merck KGaA, Darmstadt, Germany	98 %
Chloroplatinic Acid, $H_2PtCl_6.xH_2O$	Merck Schuchardt	40 % Pt
Sodium Chloride, NaCl	HmbG Chemicals	Extra Pure
Silicon Dioxide, SiO_2	Systerm	Extra Pure

A4. Calculation for amount of chloroplatinic acid

In order to prepare 5.0 g silicon dioxide and titanium (IV) oxide catalyst loaded with 0.1 % platinum, the amount of chloroplatinic acid is to be determined:

The amount of platinum for 0.1 % loading: 0.001 x 5.0 g = 0.005 g

The platinum molar mass: 195.09 g/mol

The chloroplatinic acid chemical formula: H_2PtCl_6; molar mass: 518.08 g/mol

Thus, the amount of chloroplatinic acid needed

$$= 0.005 \text{ g platinum} \times \frac{1 \text{ mol platinum}}{195.09 \text{ g platinum}} \times \frac{1 \text{ mol chloroplatinic acid}}{1 \text{ mol platinum}} \times \frac{518.08 \text{ g chloroplatinic acid}}{1 \text{ mol chloroplatinic acid}}$$

$$= 0.0133 \text{ g chloroplatinic acid}$$

The rest is tabulated as Table 2, identical with the table in Chapter 3:

Table 2: Amounts for chloroplatinic acid in other loadings

Pt loading (wt %)	Pt mass (g)	Chloroplatinic acid mass (g)
0.30	0.015	0.0398
0.50	0.025	0.0664
1.11	0.055	0.1500

The chloroplatinic acid was dissolved in distilled water The concentration of the standard solution is given by:

$$\text{Solution concentration} = \frac{\text{amount of solute}}{\text{volume of solution}} = \frac{0.24g}{250mL} \text{x} \frac{1000mL}{1L} = 0.96g/L$$

The reason of using g/L unit is for the sake of simplicity, where the volume of the solution will be obtained directly if the amount of acid needed is known. For example, for 0.1 % Pt, the mass of acid needed is 0.01333 g. The corresponding acid volume is:

$$0.01333g\text{x}\frac{1L}{0.96g}\text{x}\frac{1000mL}{1L} = 13.89mL$$

The rest is tabulated as Table 3, identical with the table in Chapter 3:

$M_i = 1.0 \text{ X } 10^{-4}$ mol/L

$M_f = 8.0 \text{ X } 10^{-5}$ mol/L

$V_f = 0.05$ L

Thus, $M_iV_i = M_fV_f \Rightarrow V_i = \dfrac{M_fV_f}{M_i} = \dfrac{8.0\times10^{-5}\,mol/L\times0.05L}{1.0\times10^{-4}\,mol/L} = 0.02L$, or 20 mL 1.0 X 10^{-4} mol/L standard solution is needed to obtain 50 mL 8.0 X 10^{-5} mol/L standard solution.

To dilute 8.0 X 10^{-5} mol/L standard solution to 50 mL 5.0 X 10^{-5} mol/L standard solution,

$M_i = 8.0 \text{ X } 10^{-5}$ mol/L

$M_f = 5.0 \text{ X } 10^{-5}$ mol/L

$V_f = 0.05$ L

Thus, $M_iV_i = M_fV_f \Rightarrow V_i = \dfrac{M_fV_f}{M_i} = \dfrac{5.0\times10^{-5}\,mol/L\times0.05L}{8.0\times10^{-5}\,mol/L} = 0.03125L$, or 31.25 mL 8.0 X 10^{-5} mol/L standard solution is needed to obtain 50 mL 5.0 X 10^{-5} mol/L standard solution.

To dilute 5.0 X 10^{-5} mol/L standard solution to 50 mL 3.0 X 10^{-5} mol/L standard solution,

$M_i = 5.0 \text{ X } 10^{-5}$ mol/L

$M_f = 3.0 \text{ X } 10^{-5}$ mol/L

$V_f = 0.05$ L

Thus, $M_iV_i = M_fV_f \Rightarrow V_i = \dfrac{M_fV_f}{M_i} = \dfrac{3.0\times10^{-5}\,mol/L\times0.05L}{5.0\times10^{-5}\,mol/L} = 0.03L$, or 30 mL 5.0 X 10^{-5} mol/L standard solution is needed to obtain 50 mL 3.0 X 10^{-5} mol/L standard solution.

(e) Catalyst: 0.5 % Pt on titanium (IV) oxide

Concentration of formaldehyde in diluted 100 mL (mmol/L)	Concentration of formaldehyde in 5 mL (mmol/L)	mol CH2O	Percentage conversion (%)
0.005	0.1	0.0001	0.003949603
0.008	0.16	0.00016	0.006319365
0.014	0.28	0.00028	0.011058889
0.022	0.44	0.00044	0.017378253
0.011	0.22	0.00022	0.008689127
0.010	0.2	0.0002	0.007899206

(f) Catalyst: 1.1 % Pt on titanium (IV) oxide

Concentration of formaldehyde in diluted 100 mL (mmol/L)	Concentration of formaldehyde in 5 mL (mmol/L)	mol CH2O	Percentage conversion (%)
0.004	0.08	0.00008	0.003159682
0.006	0.12	0.00012	0.004739524
0.008	0.16	0.00016	0.006319365
0.010	0.2	0.0002	0.007899206
0.012	0.24	0.00024	0.009479047
0.015	0.3	0.0003	0.011848809

A7. Average rate of reaction calculation

The average methanol consumption is estimated from:

$$r_A = \frac{1}{V_r}\frac{N_A - N_{A0}}{t}$$

But since $N_B = N_{A0} - N_A$, the equation is simplified to:

$$-r_A = \frac{1}{V_r}\frac{N_B}{t}$$

where $V_r = 0.1$ L, and $N_B = 0.1\left(\frac{100M_{100}}{5}\right) = 2M_{100}$, where M_{100} is the concentration in the diluted 100 mL sample. Thus, the rate equation becomes:

$$-r_A = \frac{1}{0.1}\frac{2M_{100}}{t} = 20\frac{M_{100}}{t}$$

Sample calculation: For 0.1 % Pt on silicon dioxide, at t = 60 min, M_{100} = 0.006 mmol/L

$$-r_A = 20\frac{0.006\text{mmol/L}}{60\text{min}} \times \frac{1\text{min}}{60\text{s}} \times \frac{1\text{mol}}{1000\text{mmol}} = 1.6667 \times 10^{-9}\text{mol/L.s}$$

The rest are tabulated in Table 13, identical in Chapter 4: Result and Discussion.

Table 13: Average rate of reaction of formaldehyde synthesis with various catalysts

Catalyst	Average Rate of Reaction (mol/L.s)
0.1 % Pt on Silicon Dioxide	1.6667×10^{-9}
0.3 % Pt on Silicon Dioxide	2.9630×10^{-8}
0.1 % Pt on Titanium (IV) Oxide	4.4444×10^{-8}
0.3 % Pt on Titanium (IV) Oxide	4.4444×10^{-8}
0.5 % Pt on Titanium (IV) Oxide	1.2222×10^{-7}
1.1 % Pt on Titanium (IV) Oxide	4.1667×10^{-8}

A8. Activation Energy and Frequency Factor Determination

As an example, for methanol oxidation using 0.5 % Pt on titanium (IV) oxide at 30 ^{O}C:

The reaction rate is 4.7222 X 10^{-8} mol/L.s.

The methanol concentration is directly obtained from methanol density:

Density: 810.2 g/L, molar mass: 32 g/mol

$$810.2\frac{gCH_3OH}{L}\times\frac{1molCH_3OH}{32gCH_3OH}=25.31875mol/L$$

The oxygen gas (component B) concentration is estimated from Henry's Law, assuming ideal vapour-liquid equilibrium:

$$x_B H_B(T)=P$$

Where x_{air} : mole fraction of air in the liquid phase

$H_{air}(T)$: Henry's constant

P : Atmospheric pressure = 1 atm

The mole fraction of air is determined by dividing concentration of air by concentration of methanol:

$$x_B=\frac{C_B}{C_{air}+C_A}, C_A >> C_{air}$$

$$\therefore x_B \cong \frac{C_B}{C_A}$$

At 25 ^{O}C, the Henry's Law constant for oxygen gas, H_B (40 ^{O}C) = 5.35 X 10^4 atm

$$\text{Henrys Law}: H_B(40^O C)\frac{C_B}{C_A}=1atm$$

$$H_B(25\ ^{O}C)\times\frac{C_B}{25.31875mol/L}=1atm$$

$$\therefore C_B=\frac{25.31875}{5.35\times10^4}mol/L=0.0005mol/L$$

Thus, the rate constant k, at T = 25 ^{O}C = 298 K

$$k=\frac{-r_A}{C_A C_B^{0.75}}=\frac{4.7222\times10^{-8}\ mol/L.s}{(25.31875mol/L)(0.0005mol/L)^{0.75}}=5.81281\times10^{-7}(mol/L)^{-0.75}s^{-1}$$

$$\ln k=-14.35803240$$

Similarly, the other rate constants and their natural logarithm are obtained through the prescribed algorithm. The rate of reactions, reaction temperatures, Henry's Law constants, oxygen gas concentration in liquid phase, rate constants and their respective natural logarithm are tabulated in Table 16.

From Figure 18, the activation energy E, is given by:

$$\begin{aligned}\frac{E}{R} &= 4112.9, \\ E &= 4112.9 \times 8.314\,\mathrm{J/mol} \\ &= 34194.65\,\mathrm{J/mol}\end{aligned}$$

The pre-exponential/frequency factor, k_o: $k_o = e^{-1.3381} = 0.2623\,(\mathrm{mol/L})^{-0.75}\mathrm{s}^{-1}$

A9. Dispersion Degree and Metal Surface Area Calculation

The Metal Surface Are is calculated using equation:

$$A_{sam} = Ln_{ads}F_s a_{met} \times 10^{-23}$$

Where A_{sam} : Metal surface area, m^2/g

L : 6.02 X 10^{23} metal atom/mol

F_s : Adsorption Stoichiometry, in this experiment is 2

a_{met} : square section of a metal atom, $Å^2$/metal atom

n_{ads} : amount of gas adsorbed, μmol/g

For example, according to TPR report for 0.3 % Pt on titanium (IV) oxide,

$n_{ads} = 23.02872$ μmol/g

The metal surface area is calculated as:

$$A_{sam} = Ln_{ads}F_s a_{met} \times 10^{-23}$$
$$= 23.02872\times10^{-6} mol/g \times 6.02\times10^{23} metalatom/mol \times 2 \times 8.2\times10^{-20} m^2 \times 10^{-23}$$
$$= 2.27358\times10^{-23} m^2/g$$

The dispersion degree is obtained by equation:

$$D_{met} = \left(\frac{n_{ads}F_s M_{met} \times 10}{X_{met}}\right)$$

Where D_{met} : Metal dispersion, number of absorbing metal atoms contained in the catalysts

X_{met} : metal %

M_{met} : metal molecular weight

For example, according to TPR experiment, for 0.3 % Pt on titanium (IV) oxide,

$n_{ads} = 23.02872$ μmol/g

The platinum dispersion is calculated as

$$D_{met} = \left(\frac{23.02872\times10^{-6} mol/g \times 2 \times 10 \times 195.09 g/mol}{0.3}\right) \times 100\% = 299.51\%$$

A10. TPR EXPERIMENT REPORT

D/R/O 1100 **ThermoFinnigan**

dard Data Report

Nr.:170

ıta 2\Rinaldi\TPR 0.3% Pt on TiO2_800_120505.110

\snizam

ıperature 28°C Atmospheric Pressure 1000hPa

ple

Rinaldi Sample-Code: 0

% Pt on TiO2 Customer-Code: 0

l 79 g Support: Titanium dioxide

Metals: 0

n:

reatment

: 0.3% Pt on TiO2 Info:

nent: TPDRO 1100 MS with Ser.Nr.20022897 on Right Oven

12/2005 at 11:16:33 AM finished 1:03:48 PM

	With Gas	Flow [ccm/min]	Start at T [°C]	Ramp[°C/min]	Stop at T [°C]	Hold for [min]
g	Nitrogen	20	Off			10
	Nitrogen	20	Off	20	110	20
	Off					
	Off					
	Off					

treatment with Oven Off

/R/O

lame: TPR 0.3% Pt on TiO2 Info:

ment: TPDRO 1100 MS with Ser.Nr.20022897 on Right Oven

/12/2005 at 1:31:39 PM finished 3:56:43 PM

as	Flow [ccm/min]	Start at T [°C]	Ramp°C/min	Stop at T [°C]	Hold for [min]	
n 5.42% in Nitrogen		20	Off	20	800	120

ults

;as adsorbed: 23.02872 µmol/g

eline

0167 min 25.48218 mV. Stop at 144.9000 min -33.46761 mV

bration

ration Factor: 1.035267 *10e-7 mmol/mVs

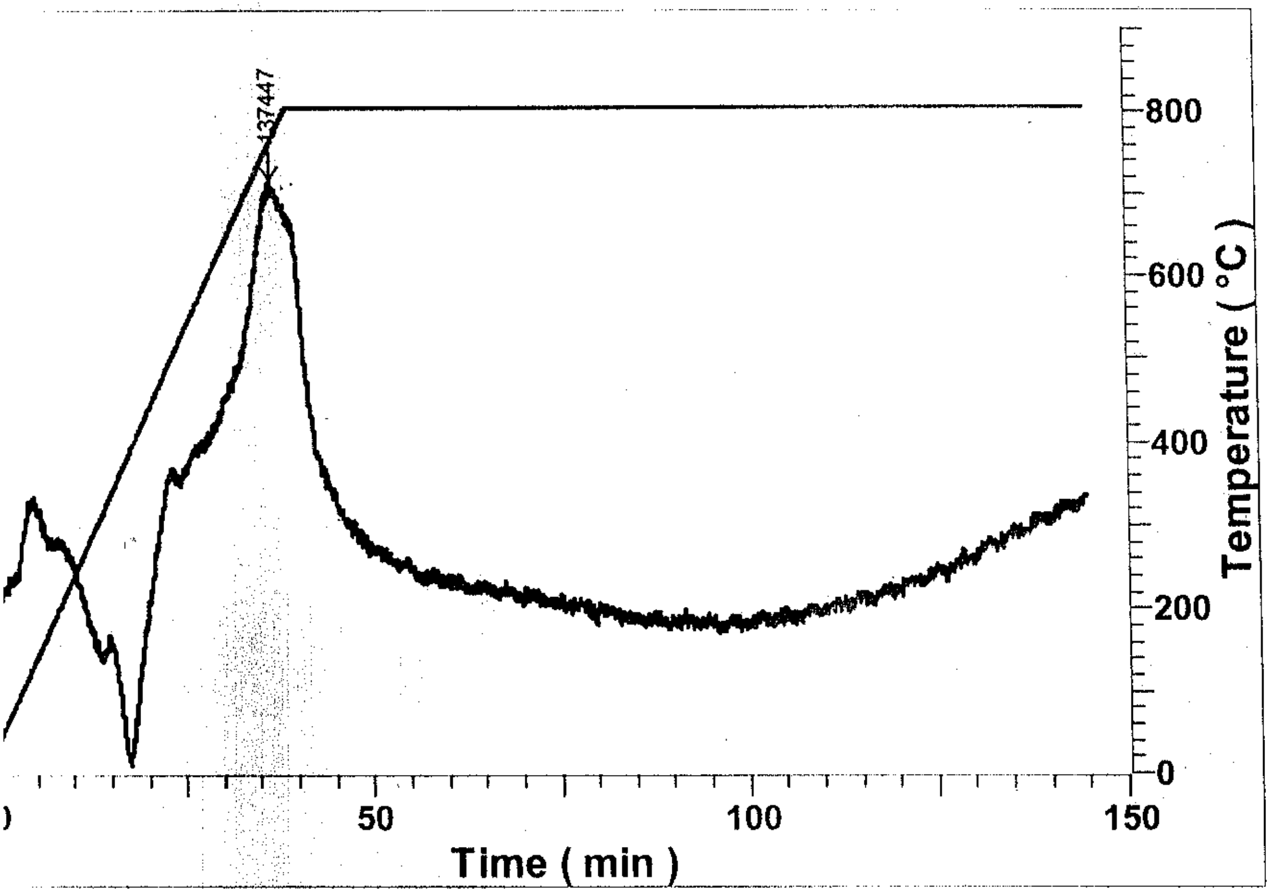
ks

rt [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[µmol/g]	[%]
l67	144.9000	36.7667	760	137447.10	23.02872	100.00

natogram Report

:\\Rinaldi\\TPR 0.3% Pt on TiO2_800_120505.110

/O



)/R/O 1100 **ThermoFinnigan**

ard Data Report

Ir.:169

2\Rinaldi\TPR 0.5% Pt on TiO2_800_110505.110
lready Pretreatment
nizam
erature 28°C

Atmospheric Pressure 1000hPa

)le

naldi
Pt on TiO2
3 g

Sample-Code: 0
Customer-Code: 0
Support: Titanium dioxide
Metals: 0

eatment

.5% Pt on TiO2

Info:

nt: TPDRO 1100 MS with Ser.Nr.20022897 on Right Oven
/2005 at 11:43:15 AM finished 4:15:45 PM

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp [°C/min]	Stop at T [°C]	Hold for [min]
Nitrogen	20	Off			10
Nitrogen	20	Off	20	110	20
Off					
Off					
Off					

eatment with Oven Off

R/O

ne: TPR 0.5 % Pt on TiO2

Info:

nt: TPDRO 1100 MS with Ser.Nr.20022897 on Right Oven
1/2005 at 5:11:13 PM finished 7:51:57 PM

	Flow [ccm/min]	Start at T [°C]	Ramp °C/min	Stop at T [°C]	Hold for [min]	
5.42% in Nitrogen		20	Off	20	800	120

lts

adsorbed: 13.91068 µmol/g

line

67 min 13.52946 mV. Stop at 160.5667 min 24.36320 mV

ration

tion Factor: 1.035267 *10e-7 mmol/mVs

s

[min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[µmol/g]	[%]
7	67.1500	36.3167	753	82676.64	13.91068	100.00

matogram Report

ı 2\\Rinaldi\\TPR 0.5% Pt on TiO2_800_110505.110

R/O