Department of Chemical Engineering

Catalytic Partial Oxidation of Propylene for Acrolein Production

Sandra Anni Setyowati Wibawanta

This thesis is presented for the Degree of
Masters of Philosophy
of
Curtin University

March 2011

DECLARATION

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

Signature: …………………………

Date: ………………………....

ACKNOWLEDGEMENTS

DEDICATIONS

The mind of the prudent is ever getting knowledge,

and the ear of the wise is ever craving knowledge.

(Amsal 18:15)

For Dwi and Michael,
my beloved husband & son

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

BET   : Brunauer Emmett Teller

FID   : Flame Ionisation Detector

GC   : Gas Chromatography

HTC   : High Temperature Cement

G   : Glucose

TCD   : Thermal Conductivity Detector

XRD   : X-Ray Diffraction

ID   : Internal Diameter of tubular reactor (mm)

OD   : Outside Diameter of tubular (mm)

L   : Length of reactor (mm)

X   : conversion of propylene (%)

S_i : selectivity of product i

n_i : number of moles of component i (mol)

r_i : rate of ith product formation or reactant conversion ($mol.min^{-1}.g_{cat}^{-1}$)

C_i : concentration of ith component

k_i : rate constant of reaction

subscript i   : the ith component in the reaction

superscript α : reaction order of propylene

superscript β : reaction order of oxygen

CO_2 : carbon dioxides

CO : carbon monoxide

C_2H_4O : acetaldehyde

C_3H_6 : propylene (or propene)

C_3H_4O : acrolein

H_2 : oxygen

O_2 : oxygen

SUMMARY

The increase in acrolein demand globally and the dependency of Australia on overseas supplies for acrolein were two main reasons behind the collaboration of Department of Chemical Engineering with a local company to pioneer the acrolein production in Western Australia. Catalytic partial oxidation of propylene is the most common process for the acrolein production, in which the success is significantly contributed by the catalyst. The objective of this project was therefore to develop a high activity of catalyst with acrolein selectivity of 95% at reaction temperature not more than $350^{o}C$. As a fixed bed reactor is the most common reactor type for the acrolein production from propylene oxidation, therefore the catalyst has to be physically modified for the use accordingly.

The objective of this project has been successfully achieved by high performance of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst, which had 95% acrolein selectivity at reaction temperature of $350^{o}C$. The catalyst was prepared based on the precipitation technique, in which an amorphous or crystalline precipitate was formed. The wet solid was then converted to active catalyst by drying and calcinations. A tubular fixed bed reactor system connected to Gas Chromatography for online analyses was used for the catalyst screening test. The detected by-products of the reaction included carbon dioxides, carbon monoxide and acetaldehyde. The carbon balance for screening tests was within $\pm$ 6% error.

The catalyst was duplicated in several batches, including various sizes of production from 50 g to 1.5 kg of catalyst per batch and two methods of catalyst drying, i.e. manual by hot petroleum drying and by using spray drier. The reasonable consistency of activity variation of 10% within the data has verified the reproducibility of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst.

The $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst was even economically more attractive, as it has proven its feasibility and consistency in maintaining its high

activity and selectivity when using the propylene feedstock straight from the by-product of refinery without prior purification were verified.

A differential tubular quartz reactor was used for studying the rate of reaction and optimisation of parameter. It was observed that within the experimental conditions of 120ml.min^{-1} with variation of reactant concentrations within 3.33% - 13.33% for propylene and 3.75% - 15% for oxygen over reaction temperatures of 300 – 450°C, the combination of 5% propylene and 10% oxygen was the optimum reactant composition at 350°C (i.e. the temperature of optimum acrolein selectivity).

As the catalyst prepared by precipitation technique was in form of powder, therefore it had to be physically modified for application in the fixed bed reactor. Two final catalyst types were prepared and studied in this project: the coated catalyst spheres and the catalyst pellets. Both of the catalyst types have proven the feasibility to be used in the laboratory scale fixed bed in terms of the activity properties and the physical strength. Main parameters in coated catalyst preparation including the calcination temperatures of, the sizes of carrier, the types and compositions of binder as well as compositions of catalyst loading were studied. The coated catalyst with 25-30% $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst loading and 5% high temperature cement as binder on 3 mm alumina spheres that was calcined at 450°C for two hours, was the best performing coated catalyst spheres in terms of acceptable physical strength and acrolein yield. The catalyst pellets in this project were prepared by two methods: the pelletising and the extruding techniques. The catalyst pellets from both types of preparation techniques have proven to be catalytically active and physically stronger than the coated catalyst spheres. The catalyst pellets with low composition of binder (i.e. less than 11% for high temperature cement and 2% for glycol) have maintained high catalytic properties up to 90% acrolein selectivity at 330°C consistent with the catalyst pellets prepared without addition of binder. Therefore the innovative idea of using high temperature cement as an alternative to conventional binders (glucose and glycol) was also proven. Both of coated catalyst (25% catalyst loading and 5% high temperature cement) and catalyst pellets (with 5% high temperature) have been separately utilised in the Chemeq pilot plant to produce 100 g acrolein for eight hours operation.

CHAPTER 1

INTRODUCTION

Catalytic oxidation of hydrocarbons to produce valuable chemicals has been an object of many intense studies in many decades, not only because of its theoretical interest but also because of its practical and industrial importance. Oxidations have proven to yield many significant industrial products and to reduce environmental pollutants. Acrolein production from catalytic partial oxidation of propylene in particular was the focus of this research. The process has considerable economical and environmental advantages. The main feedstock, propylene, is abundantly available worldwide at reasonable price. It is a by-product in the oil refineries that is currently sent to waste through flaring. On the product stream, acrolein has widespread applications. It is well known as a very versatile intermediate of many important products of organic polymers, such as anti-microbial products and animal health care applications. The expansion of acrolein functions has significantly increased the demand of acrolein globally and locally in Australia.

Currently acrolein demand exceeds production capacity globally. Most of the acrolein producers are located in the United States, Germany, France and Japan (Ohara et al. 1985). Australia is dependent on overseas supplies. Acrolein itself is difficult to transport and store due to its characteristics that are volatile, toxic and flammable.

All the aforementioned facts were the reasons for Department of Chemical Engineering at Curtin University in cooperation with a local production company pioneered the development of the Australian acrolein production facility. The overall aims of this research were to provide valuable input into the feasibility to produce suitable catalyst for the first acrolein production in Australia.

Catalyst performance plays a significant role in the success of the acrolein production. Though the modern era of catalysts can offer up to 80% acrolein yield at

high propylene conversion (90-95%), the selective oxidation still proposes fascinating development possibilities (Ohara et al. 1985). Most of available high selectivity catalysts for acrolein production are used in commercial plant and are protected by copyright, thus not much information about these commercial catalysts are available in the open literature. The catalysts can be purchased from some well-known catalyst producers at exorbitant prices. However to fully taken control acrolein production, the catalyst must be produced independently in house. The catalyst has to meet the commercial standards of activity, selectivity and durability.

The overall aim of this project was, therefore, to develop an effective and efficient catalyst for partial oxidation of propylene to acrolein and then to utilise that catalyst for industrial applications. In order to achieve this objective, firstly lots of selective catalysts were prepared then compared with reference to the catalytic performance using screening tests. The targeted catalyst should have a minimum selectivity of 95% to acrolein. Finally, the catalyst (that is in original form of powder) was physically modified into a suitable form for the use in the industrial reactor.

This thesis consists of five chapters, in which the interconnection among the chapters is described in Figure 1.1. The present chapter (Chapter 1) presents the background of this project that leads to the opportunity for further research and the description of the overall structure of this thesis.

Chapter 2 presents literature review on the catalytic partial oxidation of propylene to acrolein. It begins with the description of the product acrolein and its applications. The history on acrolein production is then briefly mentioned, which is concluded that the catalytic selective oxidation of propylene was and still is the most effective process for acrolein production. Particular attention was given to the appropriate journal papers on the catalyst development, the reaction kinetics and the reactor types used in existing acrolein production plant as the applicable final form of catalyst was determined the type of reactor.

Kochloeft (2001) describe five steps in the catalyst design, i.e. catalyst preparation, catalyst screening, catalyst characterisation, catalyst reproducibility and catalyst particles' modification for industrial application. The first four steps are discussed in Chapter 3, whist the last step in Chapter 4. In this project the catalysts were prepared

using the precipitation technique and the catalytic performances were determined by screening tests using a tubular fixed bed reactor. The screening results were analysed using Gas Chromatograph and compared to each other in parallel with continuous preparation of improved catalyst characteristics until the catalyst of desired properties (i.e. 95% selectivity to acrolein at reaction temperature not more than $350^{o}C$) was found. The catalytic performance of best performance catalyst was further studied in terms of its reproducibility and the feasibility of using a typical propylene feedstock tapped directly from petroleum refineries without prior purification as the feedstock. Once its reliability was confirmed, the rate of reaction was investigated using a fixed bed reactor for the purpose of experimental optimisation.

The catalyst produced from precipitation method was in form of power; therefore it had to be physically modified to be appropriately used in the fixed bed reactor. Coating and pelletising techniques were particularly used in this project and discussed in Chapter 4.

Finally, Chapter 5 presents conclusions from the present study and provides recommendations for future work.

On overall this thesis illustrates a coherent study of catalyst development, which includes the discovery of high activity and selectivity catalyst for partial oxidation of propylene to acrolein and the modification of this catalyst in the practical use in a fixed bed reaction.

Chapter 1: Introduction
- Background
- Scopes & objectives
- Thesis structure

Chapter 2: Literature Review
- Review the previous studies on this topic
- Analyse the available techniques
- Identify the gaps leading to specific objectives of thesis

Chapter 4: Catalysts for Applications in Fixed Bed Reactor
- Describe the coating and pelletising technique for catalyst particles' modification
- Discuss the reliability of coated and pelletised catalysts in terms of catalytic performance and physical strength

Chapter 3: Catalyst Development for Partial Oxidation of Propylene to Acrolein
- Describe the catalyst preparation technique
- Describe the method of screening tests including the reactor set up and analysis technique
- Study the screening results in order to achieve the targeted catalyst (with minimum 95% selectivity to acrolein)
- Justify the reproducibility of the best performance catalyst in terms of physical, chemical and catalytic characteristics
- Discuss the catalytic performance of the best performance catalyst when using the impurity propylene feedstock tapped directly from petroleum refineries

Chapter 5: Conclusions and Recommendations
- Coherent with the overall aim
- Recommendations for future research

Figure 1.1:   Thesis presentation

CHAPTER 2

LITERATURE REVIEW

The purpose of this research was to study the catalytic partial oxidation of propylene to acrolein with emphasis on the catalyst development and the physical catalyst modification for application in the most commonly used reactor for acrolein production. The first step to achieve this objective was to review prior studies on the related topic and then to identify gaps for the improvement. The outline of this chapter is illustrated in Figure 2.1.

```
┌─────────────────────────────┐
│          Acrolein           │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│     How produce acrolein?   │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│    Heterogeneous catalysis  │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│     Catalyst development     │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│       Reaction kinetics      │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│   Production plant (reactor)  │
└─────────────────────────────┘
```
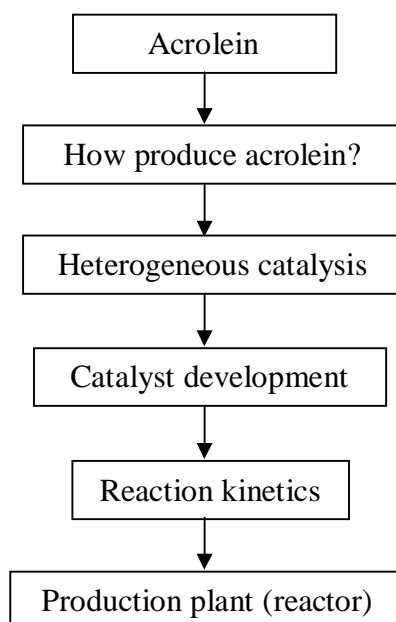
Figure 2.1:   The outline of literature review

As most developments in this area are of commercial interest, not many publications explicitly give details. However, based on the limited number of publications, it is necessary to examine the available information to establish a knowledge base for this study. This research focuses on the catalyst development for acrolein production,

thus the following issues have to be understood. Among available techniques on acrolein production, the catalytic partial oxidation of propylene was developed over 60 years ago (Ohara et al. 1985). Until today this production method is used for acrolein production at large scale by some international companies such as ARKEMA in France (Fauconet et al. 2006; Dubois 2008, 2009), BASF Aktiengesellschaft in Germany (Martan et al. 1990; Hefner et al. 1997; Petzoldt et al. 2007a, 2007b; Machhammer et al. 2008a, 2008b; Dieterle et al. 2006a, 2006b, 2006c), E.I. du Pont de Nemours and Company in Germany and Atofina in France (Contractor et al. 2002), Degussa Aktiengesellschaft in Germany (Arntz et al. 1982; Neher et al. 1995), Elf Atochem in France (Hecquet 2000), Nippon Shokubai Co. Ltd. in Japan (Tanimoto 2003), Union Carbide Chemicals and Plastics Technology Corporation in United States (Etzkorn & Harkreader 1993a, 1993b).

Propylene is a commercially attractive feedstock for acrolein production due to its abundant availability at reasonable price. Catalyst certainly plays important roles in the success of acrolein production. Therefore, the process pathway to achieve the goal of this project begins with the catalyst development to discover an effective catalyst of high conversion, selectivity and durability.

2.1 ACROLEIN

Acrolein is also known as propenal or acrylaldehyde. It is the simplest unsaturated aldehyde and its molecular structure is illustrated in Figure 2.2 below.
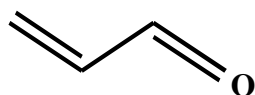
Figure 2.2:   The molecular structure of acrolein

2.1.1 PROPERTIES

Acrolein is a colourless, volatile, toxic and lacrimatory liquid with a powerful odour. The primary characteristic of acrolein is its high reactivity due to the conjugation of

carbonyl group and vinyl group. Therefore controlling this reactivity to give the desired derivative is the key to its usefulness. Commercially, acrolein is always stored in hydroquinone and acetic acid as inhibitors (Ohara et al. 1985).

Acrolein can be detected by its odour at levels above 0.35 ppm; the lowest lacrimatory level is 0.5 ppm (Ohara et al. 1985). The most frequently encountered hazards of acrolein are acute toxicity from inhalation and ocular irritation (Etzkorn et al. 1991). Its vapour causes strong eye and nasal irritation. Direct contact of eye or skin with liquid acrolein results in severe burns. As acrolein is classified as a dangerous, flammable and poisonous substance, its storage and transportation has to be done in accordance with international and regional regulations. Acrolein is readily flammable in air between 2.8% and 31.0% by volume (Ohara et al. 1985). Preferred fire-fighting agents are foam, powder (not alkaline), spray water and carbon dioxide. Due to its high toxicity and volatility, it is necessary to use a respirator in case of fire (Ohara et al. 1985).

Acrolein polymerises easily. While the addition of hydroquinone can prevent radical-initiated polymerisation, the addition of buffer solution (84% acetic acid, 8% hydroquinone, 8% anhydrous sodium acetate) can control further reaction by ionic contaminant (Ohara et al. 1985). Light, air, heat, or peroxides can also catalyse acrolein; therefore it should be stored in the dark under a blanket of nitrogen at temperature below $20^{o}C$ and should be used within three months. Acrolein should be transported in either stainless steel or aluminium 3003 containers (Etzkorn et al. 1991).

2.1.2 APPLICATIONS

Acrolein has wide applications. It is an important intermediate for many useful products, mainly for the production of D,L-methionine, which is an important animal feed supplement. Acrolein can be oxidised to produce acrylic acid, which is used to make acrylates. Other commercially important products derived from acrolein are glutaraldehyde, pyridines, tetrahydrobenzaldehydes, allyl alcohol, glycerol, butanedial, 1,4-butanediol, 1,3-propanediol, D,L-glyceraldehyde and acrolein polymers. These products are used for leather tanning, synthesis of

pharmaceuticals, flavours, fragrances, lubricants, textile treatment and many various syntheses (Ohara et al. 1985).

The direct use of acrolein is as an antimicrobial agent. It is used commercially as agent to control growth of microbes in process feed lines, such as controlling the rates of plugging and corrosion, and as micro biocide in oil fields (Ohara et al. 1985).

2.2 ACROLEIN PRODUCTION FROM CATALYTIC PARTIAL OXIDATION OF PROPYLENE

2.2.1 HISTORY

Acrolein was first commercialised in 1942 when Degussa produced acrolein based on the condensation of acetaldehyde and formaldehyde, catalysed by sodium silicate on silica supports at 300-320°C (Ohara et al. 1985). This technique prevailed until 1948 when Shell Chemical Company produced acrolein by oxidation of propylene over cuprous oxide catalyst (US patent 2,451,485 as cited in Ohara et al. 1985). The yield of this process was reported to be about 50% of the total input of propylene at propylene to oxygen ratio of one. Ever since, the improvement of techniques for acrolein production has focused on the development of selective catalyst systems for the oxidation of propylene. The partial oxidation of propylene to acrolein is illustrated in Equation 2.1.

$$CH_2 = CH - CH_3 + O_2 \xrightarrow{\text{catalyst}} CH_2 = CH - CHO + H_2O \qquad (2.1)$$

2.2.2 PROPYLENE FEEDSTOCK

Propylene is produced as a by-product in naphtha crackers process and petroleum refineries, and by the dehydrogenation of propane. In Australia, the majority of propylene is supplied from the first two mentioned processes. Local propylene producers include ICI at Botany, New South Wales (NSW); Hoechst at Altona,

Victoria; Shell at Clyde, NSW and at Gelong, Victoria; and BP at Kwinana, Western Australia (WA) (ACTED 1997).

Two potential sources of propylene in WA are from the BP Kwinana oil refinery and from LNG North West gas (ACTED 1997). The first alternative seems to be a better solution since it has existing infrastructure and markets, and thus promises lower construction, operating and transportation costs. In the BP refinery, propylene is produced from the cracking of LPG stream that contains approximately 65 to 70% propylene with the remainder being saturated propane, ethane and butane. The data from a feasibility study done by ACTED Consultant show that BP refinery at Kwinana produces 60,000 tonnes of propylene in 1997, which is projected to increase by between 5 and 20% per annum (ACTED 1997).

2.2.3 THERMODYNAMICS

In addition to acrolein, several by-products are produced in the oxidation of propylene. The principal by-products of this reaction are acrylic acid, acetaldehyde, acetic acid, carbon monoxide, and carbon dioxide. Small amounts of other aldehydes and acids are also formed. The thermodynamic parameters of the acrolein and primary by-products of propylene oxidation are listed in Table 2.1.

Table 2.1:   Thermodynamic parameters of primary products of propylene oxidation (Grasselli 1982)

Products	Reactions	$\Delta_r H^o_{298K}$ (kJ/mol)	$\Delta_r G^o_{700K}$ (kJ/mol)
Acrolein	$C_3H_{6(g)} + O_{2(g)} \rightarrow CH_2{=}CHCHO_{(g)} + H_2O_{(l)}$	- 340.80	-180.19
CO_2	$C_3H_{6(g)} + 4.5\ O_{2(g)} \rightarrow 3\ CO_{2(g)} + 3\ H_2O_{(l)}$	-2058.43	-1942.09
CO	$C_3H_{6(g)} + 3\ O_{2(g)} \rightarrow 3\ CO_{(g)} + 3\ H_2O_{(l)}$	-1209.48	-1276.77
Acrylic acid	$C_3H_{6(g)} + O_{2(g)} \rightarrow CH_2{=}CHCOOH_{(l)} + H_2O_{(l)}$	- 404.21	-550.23
Acetaldehyde	$C_3H_{6(g)} + 0.75\ O_{2(g)} \rightarrow 1.5\ CH_3CHO_{(l)}$	- 426.24	-338.80

Catalytic partial oxidation of propylene to acrolein is an exothermic reaction, which produces 340.8 kJ of heat per mole of reacted propylene. The Gibbs free energy for acrolein production indicates that the reaction will take place spontaneously once it is

initiated. However, the formations of side products, e.g. CO_2 and CO, are more thermodynamically favourable than the formation of acrolein. Therefore, the use of a high selectivity catalyst for this process is very important to favour the oxidation for the formation of acrolein.

2.2.4 THE CATALYSTS

An appropriate catalyst plays a vital role in the success of propylene oxidation to selectively produce the desired product, acrolein.

2.2.4.1 CATALYST SYSTEMS

Five most commonly used catalyst systems for acrolein productions are cuprous oxides, uranium antimony oxides, tin antimony oxides, bismuth molybdate oxides and multi-component bismuth molybdate based oxides (Farkas 1985).

A cuprous oxide was the catalyst used in the first acrolein production (Hearne & Adams 1948). In this system, the copper exists in three oxidation states (Cu metal, Cu^+ and Cu^{2+}) and is made up of a mixture of Cu-Cu_2O-CuO system. This system is very difficult to characterise since the catalyst undergoes significant changes in its bulk chemical composition, activity, and selectivity during the oxidation of propylene (Krenzke 1977). It is commonly accepted that for oxidation of propylene on copper oxide, the Cu_2O catalyst is selective for acrolein formation while the CuO catalyst leads to complete combustion (Wood et al. 1969; Tan et al. 1989; Hildenbrand & Lintz 1990; Reitz & Solomon 1998). Practically, the usefulness of this catalytic system as selective propylene oxidation is limited because it is difficult to maintain the oxidation state in the range where propylene is selectively converted to acrolein (Tan 1986).

There are two pure compounds found in the uranium antimony oxides. They are USb_3O_{10} and $USbO_5$ (Grasselli et al. 1970). Both phases are found to be catalytically active, but the USb_3O_{10} phase is more selective. The USb_3O_{10} phase has an orthorhombic structure, which consists of layers of metal and oxygen ions in alternate positioned to layers of only oxygen ions (Krenzke 1977; Tan 1986).

Tin antimony oxide catalysts have been developed not only for the oxidation of propylene to acrolein, but also for the ammoxidation of propylene to acrylonitrile and the oxidative dehydrogenation of butenes to buta-1,3-diene (Tan 1986). Tin antimonite is a mixture of SnO_2 and a solid solution of α-Sb_2O and β-Sb_2O_4. These individual components themselves had low activity and selectivity for the formation of acrolein from propylene but the combination created an effective catalyst for the related reaction (Belousev & Gershingorina 1971 as cited in Krenzke 1977). From the X-Ray diffraction analysis Goden et al. discovered that a mixture of SnO_2 and Sb solid solution played a significant role in the catalytic activity (Goden, McCain & Porter 1968 as cited in Krenzke 1977). They also noted very little change in the selectivity as the catalyst compositions varied over a wide range.

A much more selective binary catalyst system for propylene oxidation to acrolein is the bismuth molybdate oxides. In bismuth molybdate oxide systems, the catalytic properties of each compound were found to be poor. Bi_2O_3 was active, but yielded mostly carbon dioxide and water, while MoO_3 was fairly selective but had low activity. However, the combinations of bismuth molybdate oxides appeared to be remarkably active and selective catalyst as the bismuth oxide was responsible for the activation of a hydrocarbon molecule, the molybdate sub-lattices perform the nucleophilic addition of oxygen (Bielanski & Haber 1991). Superior catalytic properties especially were appeared with Bi/Mo composition between 2:3 and 2:1, in which three compounds exist: α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$ and γ-Bi_2MoO_6 (Krenzke 1977; Tan 1986; Bielanski & Haber 1991).

In comparison to binary catalyst systems, today's most efficient catalysts for partial oxidation of propylene to acrolein consist of multi-component metal oxides systems. In almost every multi-component catalyst system, bismuth molybdate serves as the main ingredient. Modern catalysts could produce up to 80% acrolein yield at high propylene conversion (90-95%) (Ohara et al. 1985). In commercial reactor, typical catalysts were applied at temperatures of 300-400°C, contact times of 1.5-3.5 seconds and propylene concentrations of 5-8 vol% of the feed gas at the inlet pressures of 150-250 kPa (Ohara et al. 1985).

2.2.4.2 CATALYST PROMOTERS

Addition of some selective components in the catalyst-based ingredients can effectively improve the catalytic performance. These additives are often called promoters. They themselves may not be catalytically active but can increase the activity of catalysts. Promoters are added to these catalysts in amounts of only a few percent. Due to their remarkable influence on the activity, selectivity and stability of industrial catalysts, promoters have attracted great interest in catalysis research.

In general, there are four types of promoters (Hagen 1999). The first type is the structural promoter, which increases the selectivity by modifying the catalyst surface leading to a desired reaction pathway. The second promoter is the electronic promoter that can disperse in the active phase, and thus influences the electronic character of active phase and the chemical binding of the adsorbate. The third category is the textural promoter, which restrains the growth of catalyst particles by sintering to form larger, less active structures during the reaction. By its function, the textural promoter can prevent loss of active surface and increase the thermal stability of the catalyst. The last group is the catalyst-poison-resistant promoter that can protect the active phase against poisoning by impurities and may either be present in the starting materials or formed in the side reactions. The effects of promoters tend to overlap in practice. Therefore it is difficult to precisely define the function of each promoter. Based on the available literature, the functions of most frequently used promoters for bismuth molybdate based catalysts are reviewed.

Until today molybdate bismuth based multiple oxides catalysts have been used in the industry for acrolein production from propylene (Le et al. 2003; Bub et al. 2005; Petzoldt et al. 2007a, 2007b; Kang et al. 2009). Although the catalyst activity reaches very high level (Ohara et al. 1985), the improvement of this catalyst is still the main research topic of many researchers. Among the literature reviewed (Callahan et al. 1970; Batist et al. 1971; Daniel & Keulks 1973; LoJacono et al. 1975; Notermann et al. 1975; Krenze 1977; Grasselli 1985; Ohara et al. 1985; Matsuura et al. 1986; Qiu et al. 1989a, 1989b; Weng et al. 1992; Ponceblanc et al. 1993; Bemaichouba et al. 1995; Bettahar et al. 1996; Carrazan et al. 1996a, 1996b; Hagen 1999; Kaddouri et al. 1999; Chang 2001; Dieterle et al. 2001; Fansuri et al. 2003; Udalova et al. 2005;

Jo et al. 2007, 2009; Kang et al. 2009), the following components were the most commonly used as the catalyst additives in molybdate bismuth oxide based catalyst for acrolein production from oxidation of propylene: iron, cobalt or/and nickel, tungsten, potassium and phosphorous.

The Bi-Fe-Mo catalysts have been reported to be more active and stable than the Bi-Mo catalysts (Daniel & Keulks 1973; LoJacono et al. 1975). Iron could exist as binary systems either with molybdate as $Fe_2(MoO_4)_3$ and $FeMoO_4$, which both effectively performed the oxygen(s) and electron(s) transfers (Batist et al. 1971; Ponceblanc et al. 1993; Benaichouba et al. 1995; Udalova et al. 2005) or with bismuth as $BiFeO_3$ or $Bi_2Fe_4O_9$ (Annenkova et al. 1969 as cited in Lo Janoco et al. 1975). Iron also existed as ternary Bi-Fe-Mo system, $Bi_3FeMo_2O_{12}$ and $Bi_2Fe_2Mo_2O_{12}$, which created more active and stable catalysts (Daniel & Keulks 1973; Lo Jacono et al. 1975; Notermann et al. 1975).

Cobalt was proven to be the most active and selective component in the multi-component catalyst ($M_6Mo_{12}Bi_{0.5}Fe_2K_{0.4}O_x$) in the partial oxidation of propylene to acrolein when comparing the catalytic performance of $MMoO_4$ framework for M = Ni, Co, Mg, and Mn (Udalova et al. 2005). Cobalt molybdates work more effectively to improve the catalyst performance (increase the activity and selectivity to acrolein) with the existence of iron molybdates in the multiphase catalysts (Moro-Oka et al. 1990; Moro-Oka & Ueda 1994 as cited in Carrazan et al. 1996).

Tungsten oxides, either in the form of WO_2 or WO_3, could be used to remove water that may be formed in the reaction and absorbed on the active centres of the catalyst (Hagen 1999). Tungsten was discovered to be a good structural promoter, as it was found to have the ability to enhance and stabilise the formation of the Mo_5O_{14}-type mixed oxide (Dieterle et al. 2001). Weng et al. also proved that the addition of an oxide phase, such as MoO_3, SnO_2, or WO_3, improved the catalytic activity and selectivity of γ-Bi_2MoO_6 in the selective oxidation of propylene to acrolein or isobutene to methacrolein (Weng et al. 1990; Weng & Delmon 1992 as cited in Carrazan et al. 1996a & 1996b).

Potassium was used as a promoter in many catalytic reactions. Matsuura and colleagues (1986) showed that the addition of potassium in the form of KOH in the

CoMoO$_4$ based catalyst for oxidation of propylene significantly improved the acrolein selectivity due to the increase of acidic property. Findings by Ozkan et al. were also revealed that the alkali metals (Li, Na, K, or Cs) reduced the acidity of the catalysts, therefore promoted the olefin adsorption and product desorption (Ozkan et al 1990, 1992 as cited in Udalova et al. 2005). In the hydrogenation of CO and ammonia synthesis, potassium promoter also has proven to increase the reaction rate (Hagen 1999).

Phosphorous for partial oxidation of propylene to acrolein has been used since the first generation of catalyst, which developed by SOHIO in 1957 in the form of Bi$_9$PMo$_{12}$O$_{52}$ supported on SiO$_2$ (Ohara et al. 1985). Since then many scientists have reported the role of phosphorous in bismuth molybdate catalysts for selective oxidation of hydrocarbon. Qiu et al. (1989a & 1989b) reported that the phosphorous additive in the form of BiPO$_4$ improved the performance of ZnFe$_2$O$_4$ catalyst for butene dehydrogenation to butadiene. They found that BiPO$_4$ protected the catalysts against deactivation, which was then also proved by Weng and coworkers (1992). Kaddouri et al. (1999) studied the effect of phosphorous in Ni-Mo-Te-O catalyst for direct oxidation of propane to acrolein and acrylic acid and found that phosphorous increased the acidity of catalyst thus increased the conversion of propane. Chang et al. (2001) also reported that phosphorous additive increased the acidity of molybdate leading to promotion of O^{2-} as the product of O$_2$ dissociation. The increase in acidity of bismuth molybdate catalysts played an important role in enhancing the catalyst activity because the acid site was the place where the hydrocarbon species were absorbed by the catalyst. The acid sites then abstracted one hydrogen atom from the gaseous reactant to produce the allyl groups (in the case of propylene partial oxidation). This process was believed to be the rate-determining step in the partial oxidation of propylene to acrolein over the bismuth molybdate catalysts (Callahan et al. 1970; Krenze 1977; Grasselli 1985; Bettahar et al. 1996).

Fansuri et al. (2003) studied the effect of phosphorous on the catalyst activity and selectivity to acrolein based the α-Bi$_2$Mo$_3$O$_{12}$ catalyst. They found that although both BiPO$_4$ and MoO$_3$ on their own have very low activity toward the acrolein formation, they were able to improve the activity of the main catalysts (Bi$_2$Mo$_3$O$_{12}$ and Bi$_9$PMo$_{12}$O$_{52}$) (Fansuri et al. 2003). Some researchers believed that either MoO$_3$ or

BiPO$_4$ improved the catalyst activity by acting as an oxygen source for rapid re-oxidation of the active site (Cullis & Hucknall 1982; Qiu et al. 1989a, 1989b; Bielanski & Haber 1991).

Recently, the new way for molybdate bismuth multiple oxide catalysts by using the drying control chemical additives were discussed in a number of investigations (Jo et al. 2007, 2009; Kang et al. 2009). Some of the effective drying control chemicals for molybdate bismuth based catalyst are listed in the literature, such as glycerol, formanide, propionic acid, ethylene glycol). It was reported that the drying control chemical additive did not change the crystallite phases of the molybdate bismuth based catalyst but the sizes of the crystallite reduced significantly by the use of this additives. As consequences, the catalytic activity was increased. Propionic acid was stated as the important drying control additive (Jo et al. 2007) because in addition to the increase of the catalyst surface area, it offered more advantage such as reducing the amount of Bronsted type acidic sites so that the acrolein selectivity would increase.

2.2.4.3 CATALYST SUPPORTS

Typical catalyst supports are inert porous solids, such as SiO$_2$, Al$_2$O$_3$, MgO, TiO$_2$, ZrO$_2$, aluminosilicates, zeolites, activated carbon, and ceramics. The choice of catalyst support should depend on the numerous physical and chemical aspects of the support material and the arrangement of the metal atoms in the pore structure of the support (Hagen 1999).

Addition of such micro spheres could also provide strength and attrition resistance to the catalysts (Etzkorn & Harkreader 1993a, 1993b). Desikan and co-workers (1995) studied the effect of loading and support of SiO$_2$, Al$_2$O$_3$ and TiO$_2$ onto molybdenum oxide catalysts for propylene oxidation. The results indicated that the order of affinity of the supports for molybdenum oxide was SiO$_2$<Al$_2$O$_3$<TiO$_2$ and the interactions of the supports with molybdenum oxide were an acid base in nature.

2.2.4.4 CATALYST PREPARATION TECHNIQUES

Various techniques for catalyst preparations are available. They include precipitated catalysts, impregnated catalysts, skeletal catalysts, zeolites, fused and molten catalysts. Among many available techniques, precipitation was believed to be the most appropriate method for catalyst preparation in the present project. It is a flexible and simple method, thus relatively not difficult and not expensive to set up.

In the production of precipitated catalysts, an amorphous or crystalline precipitate or gel was formed, which was later carefully washed to remove foreign ions (Farkas 1985). The wet solid was then transformed to the finished catalyst by drying, calcination and activation (Farkas 1985).

2.3 KINETICS OF PROPYLENE OXIDATION TO ACROLEIN

One of the earlier kinetic studies of propylene oxidation was done by Adams et al. (Adams & Jennings 1963, 1964a; Adams et. al. 1964b) using an integral tubular fixed bed reactor at reaction temperature of 460°C and atmospheric pressure. It was found that the propylene oxidation was first order of propylene and independent of oxygen. The carbon dioxide, acetaldehyde and formaldehyde were observed to be formed via both parallel and consecutive reactions.

A similar result (first order of propylene and zero order of oxygen) was found by Gel'bshtein et al. (1965), who investigated the propylene oxidation over supported β-phase bismuth molybdate catalyst at 410-500°C using an external recycle reactor. Acetaldehyde and formaldehyde were detected together with acrolein and carbon dioxide. Though the external recirculating reactor was capable of being operated isothermally, having large dead space volume might cause the gas phase homogeneous reaction to occur in the non-catalytic zone of the reactor system.

Keulks, Rosyneck and Daniel (1971) did a series of studies on kinetics and mechanisms of propylene oxidation over various bismuth molybdate catalysts. By means of an integral reactor, they discovered that the oxidation of propylene to

acrolein was a first order dependency of propylene and independent of oxygen over temperature 400-460°C with an activation energy of 100-140 kJ/mol. Acetaldehyde, formaldehyde, ethylene, carbon monoxide and carbon dioxide were formed in a consecutive pathway via acrolein or its surface species precursor when excess oxygen was present.

Using a differential reactor at atmospheric pressure over temperature ranges of 325-475°C Keulks together with Krenzke and Lo did a more intense kinetic study of propylene oxidation. Several well-characterised selective oxidation catalysts were used in those experiments: α-Bi$_2$O$_3$.3MoO$_3$, γ-Bi$_2$O$_3$.MoO$_3$ and Bi$_3$FeMo$_2$O$_{12}$ (Krenzke & Keulks 1980) and FeSbO$_4$ (Keulks & Lo 1986). They found that the kinetics of acrolein and carbon dioxide formation were varied with temperature. As the temperature increased, the reaction order of propylene increased from zero to one, and that of oxygen decreased from one to zero. The Arrhenius plots for bismuth molybdate catalysts had a break at temperature around 400°C. The apparent activation energies were found to vary from 62 to 75 kJ/mol for higher temperatures range and from 180 to 222 kJ/mol at lower temperatures. The changes in the kinetic parameters were explained in terms of the coupled kinetics of catalyst reduction and reoxidation.

Uda and Lin (Uda et al. 1980) found similar results. They investigated the kinetic parameters of reduction and reoxidation of γ-Bi$_2$O$_3$.MoO$_3$ over temperature range of 350-420°C using temperature programmed reoxidation (TPR) and microbalance techniques. It was found that the reduction step was first order in propylene and the reoxidation was 0.6 orders in oxygen. The activation energy for the reduction of propylene was found to be 59 kJ/mol. The Arrhenius plot for reoxidation showed a break at 400°C, at which the activation energy at lower temperatures was 184 kJ/mol. The catalyst reoxidation process also appeared to be related to the rate-determining step for propylene oxidation to acrolein at temperatures below 400°C.

Joshi and Chanda (1978) also supported the redox mechanism. During the oxidation of propylene on bismuth molybdate using a differential fixed bed reactor in the temperature range of 406-475°C, they found that acrolein was the main product and

carbon dioxide was the only by-product. From the product distribution patterns, they proposed a parallel-reaction scheme for the formation of acrolein and carbon dioxide.

The first order in propylene was also reported by Kremenic and Nieto et al. (Kremenic et al. 1987; Nieto et al. 1988). Using a Pyrex glass tubular reactor, the kinetic was studied over a $Mo_4Pr_{0.5}Bi_{0.5}O_x$ on SiO_2 supported catalyst at temperatures of 320-380°C based on the differential method. The apparent order of reaction with respect to oxygen was relatively low and decreased from 0.4 to 0.1 as the temperature increased over the range from 320°C to 380°C. These findings were reasonably consistent with those of Keulks and co-workers (Uda et al. 1980; Krenzke & Keulks 1980) and with the adsorption results i.e. the bonding of oxygen to the catalyst surface was significantly stronger than that of propylene. Based on the Arrhenius plots, the apparent activation energy was calculated to be 117 kJ/mol. The experimental data was also fitted to several models widely used for catalytic reactions such as Langmuir-Hinshelwood, Eley-Rideal, Mars-van Krevelen redox and the stationary state of adsorption. The least squares method was used as the base to find the best-fit of the experimental data to those kinetic models. The combination of the best-fit models and the information on adsorption of propylene and oxygen on the Mo-Pr-Bi catalyst led them to the conclusion that the reaction was best described by the Mars-van Krevelen mechanisms.

Using statistical procedures for model discrimination and parameter estimation to design and analyse experiments, Tan et al. (1988) studied the oxidation of propylene over a silica-supported bismuth molybdate catalys. A differential bed reactor was used to conduct the initial-rate study of kinetics at near atmospheric pressure and at three temperatures between 350-390°C. The experimental data was fitted to a total of seven models: three models based on the stationary state of adsorption models (with $k_d = 0$ and n =1 for first model; $k_d = 0$ and n = ½ for second model; and n = 1 for third model); three models based on the Langmuir-Hinshelwood models (competitive adsorption with n = 1 for forth model; noncompetitive adsorption with n = 1 and n = ½ for fifth and sixth model respectively); and the seventh model was the stationary state of adsorption model, with same assumptions as the first model ($k_d = 0$ and n =1) in addition to the assumption that propylene was adsorbed on the catalyst surface and the adsorbed propylene then reacts with catalyst oxygen. The competences of seven

fitted models were evaluated through two-stage procedures. Based on 5% "lack of fit" test and the precision of the models when fitted to the Arrhenius-van't Hoff plots, only the second and seventh model passed. In order to decide which of these models was the best, Tan et al. established two criteria. The first criterion was based on the mean squares of residuals from the fitted model. The model that gave the smaller mean square was considered to be the better model. The second criterion was based on the concept of parsimony of parameters. If both models fit the data equally well, the model with smaller number of parameters was preferred. The steady-state model with half order oxygen concentration dependence (second model) was considered to be the best model to describe the oxidation of propylene over silica supported bismuth molybdate catalyst.

An isothermal oxidation of propylene over a multi-component bismuth molybdate oxide catalyst was done using a laboratory catalytic wall reactor over temperatures 330-430°C at atmospheric pressure (Redlingshofer et al. 2002, 2003). They also supported the redox mechanism for explaining their experimental kinetic data. At temperatures below 360°C, the catalyst reoxidation was the rate-determining step, with increasing oxygen content speeding up the acrolein formation. At higher temperatures, the effect of oxygen concentration on acrolein formation was reduced considerably and the catalyst reduction by propylene seemed to be the rate-determining step. The Arrhenius plot had a break at 360°C and the apparent activation energy was found to be 120 and 41 kJ/mol for the lower and higher temperature range respectively.

More recent kinetic study was done by Fansuri (2005) using quartz reactor that was proven to be inert for oxidation of propylene over reaction temperature of 300-450°C. The catalysts in use were characterised α, β and γ bismuth molybdate. Generally the apparent order of reaction with respect to propylene (m) and oxygen (n) over these three catalysts were varied over the reaction temperature range: α-$Bi_2Mo_3O_{12}$ has m = 0.6 to 0, n = 0.6 to 1 and Ea = 100 kJ/mol; β-$Bi_2Mo_2O_9$ has m = 0 to 0.9, n = 0.2 $\pm$ 0.1 and Ea = 173 kJ/mol; and γ-Bi_2MoO_6 has m = 0.6 to 0.9, n = 0.3 to 0 and Ea = 98 kJ/mol. In addition to the acrolein formation, Fansuri also determined the kinetic parameters of side products (acetaldehyde and carbon

dioxide) and suggested that carbon dioxide was produced from further oxidation of acrolein and acetaldehyde.

Table 2.2: Summary of kinetic and mechanism studies that were derived from experimental data

Authors	Catalyst	Reactor	Temp. (^{o}C)	Reaction orders of power rate law ($r_A = k.C_P^{\alpha}.C_O^{\beta}$)		Proposed mechanism model	Activation energy, Ea (kJ/mol)
				α	β		
Adams et al. (1963, 1964a, 1964b)	Unspecified	Integral reactor	460	1	0	The authors not specifically proposed any mechanism, however since the kinetics were first order of propylene and zero order of oxygen. It also can be explained as Redox mechanism.	-
Gel'bshtein et al. (1965)	β - Bismuth molybdate	External recycle reactor	410-500	1	0		-
Keulks et al. (1971)	Bismuth molybdate	Integral reactor	400-460	1	0		100-140
Krenzke et al. (1977, 1980)	α - Bismuth molybdate	Differential reactor	325-475	Changing (0→1)	0	Redox	T>410: 54 T<410: 205
	γ - Bismuth molybdate			Changing (0→1)	Changing (0.4→0)		T>419: 63 T<419: 180
	Bi$_3$FeMo$_2$O$_{12}$			Changing (0.2→1)	Changing (1→0)		T>379: 63 T<379: 201
Keulks & Lo (1986)	FeSbO$_4$			Changing (0.4→0.8)	Changing (0.4→0.3)		82
Uda et al. (1980)	γ - Bismuth molybdate	TPR (Temp Program Reoxidation)	350-420	1	0.6	Redox	T>400: 59 T<400: 184

Table 2.2 cont.: Summary of kinetic and mechanism studies that were derived from experimental data

Authors	Catalysts	Reactors	Temp. (°C)	Reaction orders of power rate law ($r_A = k.C_P^{\alpha}.C_O^{\beta}$)		Proposed mechanism models	Activation energy, Ea (kJ/mol)
				α	β		
Joshi & Chanda (1978)	Bismuth molybdate	Differential reactor	406-475	-	-	Redox for parallel rx of acrolein & CO_2 formation	-
Kremenic (1987)	$Mo_4Pr_{0.5}Br_{0.5}O_x$ on SiO_2	Differential reactor	320-380	Changing (0.9→0.98)	Changing (0.1→0.39)	Redox and stationary state of adsorption	117
Tan et al. (1988)	Bismuth molybdate on SiO_2	Differential reactor	350-390	Changing	Changing	Stationary state of adsorption	92
Redlingshöfer et al. (2002, 2003)	Multi-component bismuth molybdate	Catalytic wall reactor	330-430	Changing (0→1)	Changing (0.86→0)	Redox	T>360: 41 T<360: 120
Fansuri (2005)	α - Bismuth molybdate	Differential reactor	300-450	Changing (0.6→0)	Changing (0.6→1)	Redox	100
	β – Bismuth molybdate			Changing (0→0.9)	Changing (0.2 ± 0.1)		173
	γ - Bismuth molybdate			Changing (0.6→0.9)	Changing (0.3→0)		98

Two most common methods for kinetic analysis were differential method (Fansuri 2005; Krenzke & Keulks 1980; Keulks & Lo 1986; Joshi & Chanda 1978; Kremenic et al. 1987; Nieto et al. 1988; Tan et al. 1988) and integral method (Adams et al. 1963, 1964a, 1964b; Keulks, Rosyneck & Daniel 1971). The differential and integral reactors are similar in construction but differ in the methods of analysing the data. Both of them can be categorised as packed bed reactor.

The criterion for a reactor being differential is that the conversion of the reactants in the bed is extremely small so the change in concentration through the bed is negligible. Consequently, the reactant concentration through the reactor is essentially constant and approximately equal to the inlet concentration. Therefore, the reactor is believed to be gradientless and the reaction rate is considered spatially uniform within the bed (Fogler 1999). If the catalyst under study is a high conversion catalyst then having a low conversion reactor can be achieved either by having a very small amount of catalyst that usually arranged in the form of a thin wafer or disk, or diluting the catalyst bed with inert solids. However, having a low conversion of reactants can cause difficulty in the sampling and analysis.

The integral method uses a trial-and-error procedure to find the reaction order. The procedure can be tedious: (1) guess the reaction order; (2) integrate the relevant differential equation; (3) if the assumed order is correct, then the plot of the concentration versus time (that derived from integration in step 2) should be linear; otherwise (4) if the plot is not linear, then repeat step 1 until a linear plot is obtained, which means the assumption of reaction order is right.

2.4   ACROLEIN PRODUCTION PLANT

A typical process flow sheet for acrolein production by propylene oxidation is shown in Figure 2.3. It is a general version of the process employed by Degussa in Germany and Sohio in USA (as cited in Ohara et al. 1985) as well as Atochem in France (Etzkorn et al. 1991).
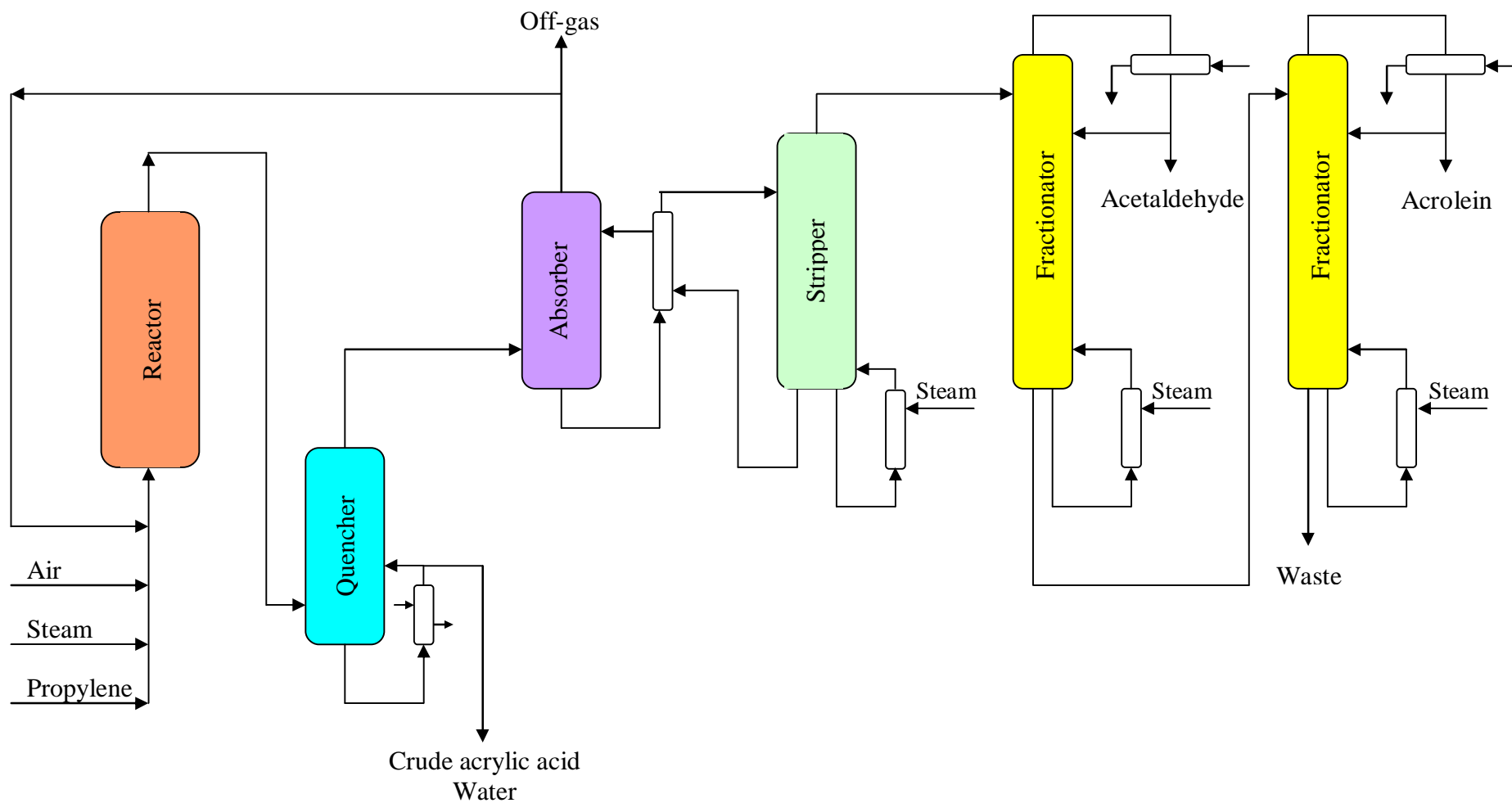
Figure 2.3:   Typical process flow sheet for acrolein production by propylene oxidation (Ohara et al. 1985)

At the beginning of the process, propylene, steam (or inert gas) and air (or oxygen) were mixed in a pipeline before being fed to a stainless steel reactor. The reactor could either be a fixed or a fluidised bed, which was usually operated at 300–400°C and at inlet pressure of 150-250kPa (Ohara et al. 1985). Molten salt was usually used for temperature control. Depending on the performance of the catalyst used in the reactor, the conversion rate of propylene could achieve up to 95%, in which 90% of the initial propylene was converted to acrolein. However, there were some complete oxidations of the propylene to carbon dioxides and water, as well as the formation of acrylic acid, acetic acid, acetaldehyde and other possible minor products. The exit stream of reactor was passed to a quench tower in which the acrylic acid was condensed and absorbed in a water-based stream. In this way, acrylic acid might be recovered from the aqueous product stream if desired.

The gas exiting from the quench tower was then fed into an absorber where an aqueous solution of acrolein was obtained by absorbing the gas in cold water. However part of the off-gas from the absorber contained non-condensable components, such as un-reacted propylene, carbon oxides, oxygen and nitrogen. These non-condensable gases were purged as waste gas after it passed through a combustion system.

The aqueous solution of acrolein was sent to a stripper (also called a desorption column or an exchanger), where it was stripped to give crude acrolein. The crude acrolein consisted of low boiling point compounds, which were mainly acrolein and acetaldehyde. The bottom stream from this column was cooled and recycled as an absorbent.

The crude acrolein stream was then distilled into the first fractionator to remove acetaldehyde as tops. The bottoms went to another fractionator in which the acrolein itself was taken as the overhead product. The product typically was up to 98% pure acrolein, with the remaining consisting of water and trace acetaldehyde (Ohara et al. 1985). The bottoms of this last fractionator comprised higher boiling compounds, which were discarded. In order to minimise polymerisation, the whole system was stabilised by hydroquinone (Ohara et al. 1985). Pipelines and apparatus were constructed preferably of stainless steel.

Gas chromatography with a thermal conductivity detector could be utilised to determine the impurities in acrolein (Ohara et al. 1985; Etzkorn et al. 1991). Hydroquinone could be determined either colorimetrically by using Millon's reagent to form a yellow complex (Ohara et al. 1985) or spectrophotometrically at 292 nm in methanol after a sample was evaporated to dryness to remove the interference of acrolein (Etzkorn et al. 1991). A typical specification for commercial acrolein is listed in Table 2.3.

Table 2.3:   Commercial specifications for acrolein (Ohara et al. 1985; Etzkorn et al. 1991)

Requirements	Value (weight %)	
	Data from Ohara (1985)	Data from Etzkorn (1991)
Purity of acrolein	95 – 97	Min. 95.5
Other carbonyl compound	Acetaldehyde max. 0.3	Max. 1.5
Hydroquinone	Max. 0.2	0.1 – 1.25
Water	Max. 3.0	Max. 3.0

2.4.1 THE REACTOR

A packed bed (also called fixed bed) reactor is the most commonly used reactor not only for the general heterogeneous catalysis (Farkas 1985) but also for the catalytic propylene oxidation to acrolein. This reactor also has difficulties with temperature control, thus it requires extra attention to ensure uniform temperature along the reactor and to avoid hot spots, especially when the reaction is exothermic. When operating this reactor in the differential method, precautions must be taken so that the reactants not bypass or channel through the packed catalyst but instead flow uniformly across the catalyst bed. However, a packed bed reactor gives the highest conversion per weight of catalyst of any catalytic reactor. In addition, it is relatively easy and inexpensive to construct, to operate, to maintain and to scale up. It is even more practical, due to its suitability to any types of catalysts (powder, pellets, spheres, etc.). Therefore, it is an attractive choice for industrial catalysed reactor if the catalyst is non-decaying.

Among of companies using the fixed bed reactor for acrolein production are BASF Aktiengesellschaft (Dieterle et al. 2001, 2005, 2006a, 2006b, 2006c, 2007a, 2007b, 2009; Machhammer et al. 2008b; Klanner et al. 2008; Petzoldt et al. 2007a, 2007b, 2008; Olbert et al. 2007; Arnold et al. 2002; Zehner et al. 2002), Degussa (Arntz et al. 1982), China America Technology Corporation (2010), Mitsubishi Chemical Corporation in Japan (Ogawa et al. 2009; Jinno et al. 2009; Yada et al. 2008) and Mitsubishi Rayon Co. Ltd. (Watanabe et al. 2007).

In addition to the aforementioned research, laboratory size fixed bed reactors were also used in many experimental studies of the kinetic and catalytic performance of propylene oxidation to acrolein (Adams et al. 1963, 1964a, 1964b; Gel'bshtein et al. 1965; Keulks 1971; Schall 1973; Krenzke 1977, 1980a, 1980b; Joshi & Chanda 1978; Pichat et al. 1979; Keulks & Lo 1986; Kremenic et al. 1987; Brückman et al. 1988; Tan et al. 1988; Baerns et al. 1997; Teng & Kobayashi 1998; Sinev et al. 2000; Lin 2000; Vitry 2004).

Another type of catalytic reactor in common use is the fluidised bed (Fogler 1999). The advantages are similar to that of CSTR. It offers good temperature control and good mixing and therefore has uniform concentration and temperature throughout the reactor. In operation it is easy to facilitate catalyst replacement or regeneration. However, a fluidised bed reactor is expensive to construct and is difficult to design, as it cannot be modelled as either a CSTR or PFR due to particle loss in the cyclone and other factors. Fluidised bed is used for catalytic partial oxidation of propylene to acrolein in production scale by E.I. du Pont de Nemours and Company in Germany and Atofina in France (Contractor et al. 2002) and in the laboratory scale researches by Patience & Mills (1994), Leib et al. (1996), Aliev et al. (2004) and Feng et al. (2008).

However, in the case of reaction systems with significant catalyst decay, neither fixed bed nor CSTR is suitable. Currently two types of industrial reactors are available to accommodate this special arrangement, i.e. the moving bed and straight through transport reactor. These reactors are assembled to accommodate the continual regeneration and/or replacement of the catalyst. This convenience, however, is offset by a complicated reactor design and high construction cost.

2.4.2 FORMING THE CATALYST PARTICLES TO SUIT THE REACTOR

The size and shape of catalyst particles depend on the nature of the reaction, the phase of reactants, and the types of the reactor used (Farkas 1985). As mentioned before, two types of reactors are commonly used for catalytic gaseous reaction: fluidised bed and fixed bed reactors. The fluidised bed reactor requires small particle catalysts (0.05-0.25 mm) that are microspherical and are usually obtained by spray drying of a solution or slurry (Farkas 1985).

On the other hand, the size of catalyst particles in fixed bed reactor depends on the tolerable pressure drops, consequently the resistance of the catalyst charge to gas flow. As the catalyst produced from precipitation method is in the form of powder, it has to be further modified to suit the use in fixed bed. Various methods are available to form the catalyst powder into other shapes, such as spheres, and cylindrical pellets. The use of binders can improve the mechanical strength of the formed catalyst particles.

Catalyst spheres can be prepared on a titled rotating pan into which the catalyst powder containing a binder is fed. The angle of the tilt and the speed of rotation control the size of the spheres formed. Another method of production of spherical particles is tumbling short extruded cylinder catalysts in a rotating drum until spherical forms are obtained.

Cylindrical pellets can be produced either by extrusion or by pelletising (tableting). Extruded pellets are obtained by feeding pastes of fine catalyst powders into ring-roll or auger-type extruders (Farkas 1985). In the ring-roll method, the catalyst mixture is fed to a rotating cylinder drilled with numerous holes of a given size. Inside the cylinder one or more compression rolls press the mix through the holes while the outside of the cylinder a knife removes the extrudate. In the auger extruder, a screw presses a perforated die through the mix and a rotating knife cuts off the extrudate to form pellets. Extrusion generally produces low density, high porosity pellets containing superficial macropores (Farkas 1985).

Catalyst tablets are commonly produced automatically using a tableting machine of the same type as that used pharmaceutical industry. It is important to have a dry, fine

catalyst powder of uniform particle size in order to have uniform filling of the dies in the tableting machine. Solid lubricants, e.g. graphite, talcum powder, paraffin, wax, stearic acid, can be added into the catalyst powder to improve flow characteristics, i.e. to reduce friction between the particles and the formed aggregates. Tableting produces strong pellets of high mechanical strength that are suitable for tall reactors but unsuitable for reactions in which diffusion limitation affects selectivity (Farkas 1985).

Catalysts are exposed to diverse physical strength during transportation, charging to the reactor and operation. Therefore in addition to their catalytic properties, the usefulness of catalysts is also significantly determined by its physical properties. For example, the crushed strength or the hardness test can be used to examine the strength of catalysts under static condition. In addition, tests for impact strength and resistance against abrasion or attrition can be carried out under dynamic conditions.

2.5 Conclusions on Literature Review

Until today, the catalytic partial oxidation of propylene is still the applied process to produce acrolein in the industry. The most important part of this process is the used heterogeneous catalyst. After molybdate bismuth oxide was found by Shell Chemical Company in 1948, this multiple oxide is still the basic component in the currently used catalyst for acrolein production from propylene of most processes around the world (Arnold et al. 2002; China America Technology Corporation 2010; Dieterle et al. 2009, 2007a 2007b; Jinno et al. 2009; Kang et al. 2008, 2009; Klanner et al. 2008; Machhammer et al. 2008b; Ogawa et al. 2009; Olbert et al. 2007; Petzoldt et al. 2007a, 2007b, 2008; Yada et al. 2008; Watanabe et al. 2007; Zehner et al. 2002).

The catalyst activity and selectivity have improved significantly by addition of the promoters and improvement of the preparation techniques. The precipitation technique is the most common technique for molybdate bismuth multiple oxide preparation, not only in the laboratory for research purpose but also in the industry for acrolein production at large scale (Brazdil et al. 1980; Kishimoto & Matsunami 2004; Yunoki & Tanimoto 2005; Kang et al. 2008, 2009).

A fixed bed reactor is the most common used reactor type for acrolein production from propylene oxidation (BASF Aktiengesellschaft (Dieterle et al. 2009, 2007a, 2007b, 2006a, 2006b, 2006c, 2005, 2001; Machhammer et al. 2008b; Klanner et al. 2008; Petzoldt et al. 2007a, 2007b, 2008; Olbert et al. 2007; Arnold et al. 2002; Zehner et al. 2002); Degussa (Arntz et al. 1982); China America Technology Corporation (2010); Mitsubishi Chemical Corporation in Japan (Ogawa et al. 2009; Jinno et al. 2009; Yada et al. 2008); and Mitsubishi Rayon Co. Ltd. (Watanabe et al. 2007)). The catalyst produced by the precipitation method is in the form of powder, and therefore has to be physically modified for the use in the fixed bed reactor. Currently the molybdate bismuth multiple oxides catalyst is used in the form of sphere or cylinder that are produced by using coating, extruding or pelletising techniques.

Both the kinetic and the mechanisms of the formation of acrolein from propylene over the molybdate bismuth multiple oxides catalysts are reported intensively in the literatures. Unfortunately the reported results are not agreed each other. It is necessary to note that the reported results come from difference research groups using different process parameters such as contact time, feed composition, temperature and pressure. Moreover, the properties of the used catalyst such as chemical composition, surface area, crystalline size and structure were not identical for all research experiments.

It is important to obtain a series of reliable and reproducible data since the reaction kinetics will be derived based on those data and ultimately the reactor will be designed based on the kinetic rate equation. For these reasons an appropriate type of laboratory reactor and method of rate analysis should be carefully chosen. A fixed bed reactor is selected for this system since it is relatively easy and inexpensive to design, to operate, to maintain and to scale-up in addition to its flexibility to use various types of catalysts. Having a low conversion reactor means the reactor is gradientless in temperature, pressure and concentration; therefore the kinetic parameters can be simply determined from method of initial rate. In spite of its conveniences, precautions should be taken to minimise the channelling problem and errors from sampling and analysis of low conversion system.

All the literature considered in this review has revealed a good understanding of the partial oxidation of propylene to form acrolein and resulted in the outline and objectives of this project.

CHAPTER 3

CATALYST DEVELOPMENT FOR PARTIAL OXIDATION OF PROPYLENE TO ACROLEIN

The objective of catalyst development in this project was to develop a catalyst for partial oxidation of propylene with selectivity of 95% to acrolein at reaction temperature not more than 350°C. The pathway to achieve the objective is illustrated in Figure 3.1.
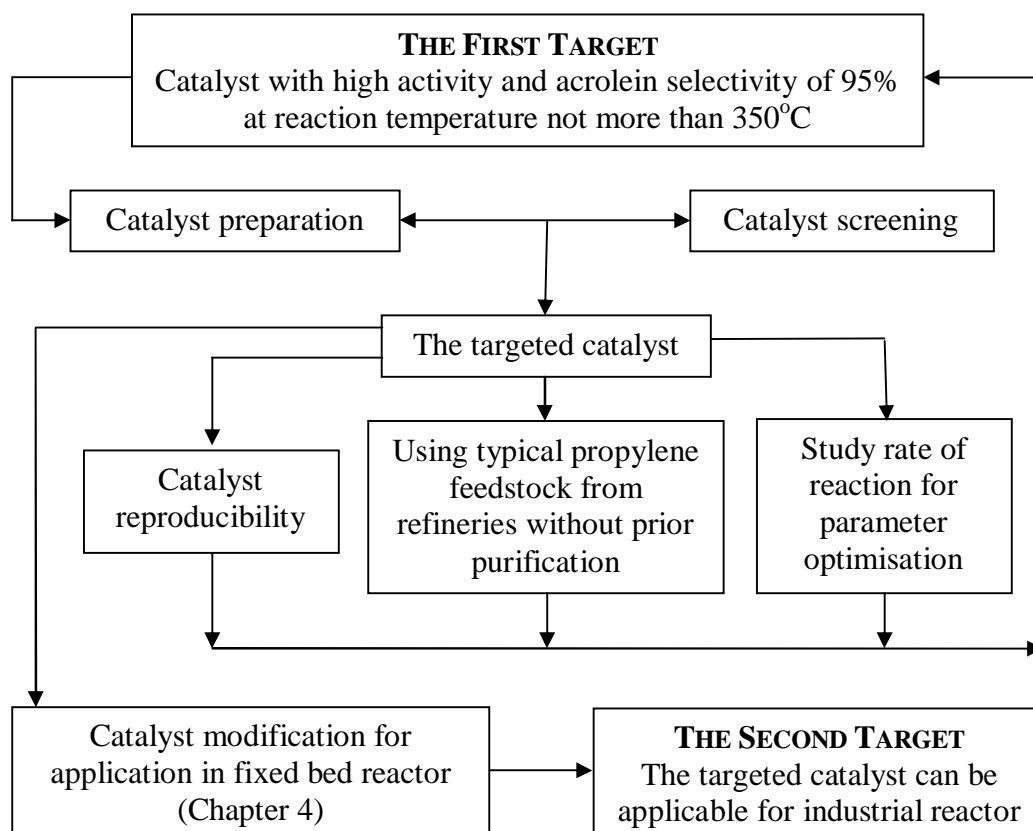
Figure 3.1:   Pathway to achieve the objective of this project

3.1 EXPERIMENTAL TECHNIQUES

3.1.1 CATALYST PREPARATION

The precipitation method was selected for catalyst preparation in this research because of its simplicity and flexibility. It gives flexibility to introduce various promoters easily and to accommodate variations in the composition of each component without difficulty. Therefore the role of each component can be studied in order to achieve the target level of activity and selectivity. As discussed in the literature review (Chapter 2), the development of molybdate bismuth catalyst in this project was limited to the additions of six catalyst promoters, i.e. iron, cobalt, tungsten, potassium, silicium and phosphorus.

Catalyst preparation using the precipitation method was selected also due to its ability to use various support materials, such as silica, which could improve the strength and attrition resistant of the produced catalyst (Bergna 1987; Hagen 1999). The catalyst preparation using precipitation procedure at relatively low temperature (450°C) made it cost effective in comparison to other techniques such as fused catalysts or solid-state reactions. It also signified good reproducibility of catalysts at any scales from laboratory scale to full plant operation. The final form of catalyst prepared based the precipitation method was powder, which gave flexibility for further modification to other shapes by various techniques, such as coating, pelletising and extruding.

In precipitation technique, initially an amorphous or crystalline precipitate was formed and carefully washed to remove the foreign ions. The wet solid was then converted to catalyst by drying, forming, calcination, and activation.

There were three key parameters in precipitation operations. The first one was the precipitation temperature, as it might control the precipitate properties, such as crystal sizes and surface areas. Nitrates, carbonates, and ammonium compounds are typical components used in the precipitation method for catalyst preparation because they can be decomposed easily to oxides during calcination. In order to optimise the catalyst production, the precipitation was carried out at a temperature of 70°C although room temperature proved sufficient in other instances.

The second important parameter was the drying condition, as it affected the specific area and the pore structure of the catalysts. If the catalyst is required to be coated onto inert carrier, then introducing silica support is necessary to improve its stability (Bergna 1987; Hagen 1999). For silica-supported catalyst, the optimum drying temperature is about 170°C. This temperature allows water to be vaporised at sufficient rate in order to produce the desired texture. For small-scale catalyst production (less than 250 g of catalyst powder), hot petroleum drying using kerosene was used as a substitute for a spray drier.

The third key parameter is the calcination process as it controlled the activation of the final catalysts. In this step the nitrate, carbonate, and ammonium ions are removed and the catalyst precursor is transformed to the active oxides. Then the metal oxides are converted into a multi layer that was anchored to the support. The calcination step generated the final catalyst with the creation of very small crystals of the catalyst components. All catalysts used in this study were calcined at 450°C for 8 hours in air.

Steps in catalyst preparation are schematically described in Figure 3.2. The procedure for catalyst preparation consists of three main parts: (1) preparation of catalyst powder, (2) activation of catalyst powder and (3) modification of catalyst powder into either spheres or pellets.

The catalysts prepared in this research were in the form of oxides, which is the most common used type of catalysts in modern industry (Haber 1985). The oxidised catalysts are widely used in both redox and acid-based reactions due to their ability in the exchange of electrons and in the exchange of protons or oxide ions, as well as their effectiveness as catalyst carriers for active metal (Haber 1985).

The ingredient specifications of catalyst preparation are presented in Table 3.1. Most of catalyst ingredients were in the form of nitrates and ammonium, as they are decomposed easily to oxides during calcination. Distilled water was used as the solvent for the precipitation process because the solubility of most metal salts in water is much higher than that in organic solvents.

Among many catalysts prepared, only ten catalysts were presented and discussed in the thesis. The recipes of these catalysts are listed in Table 3.2.
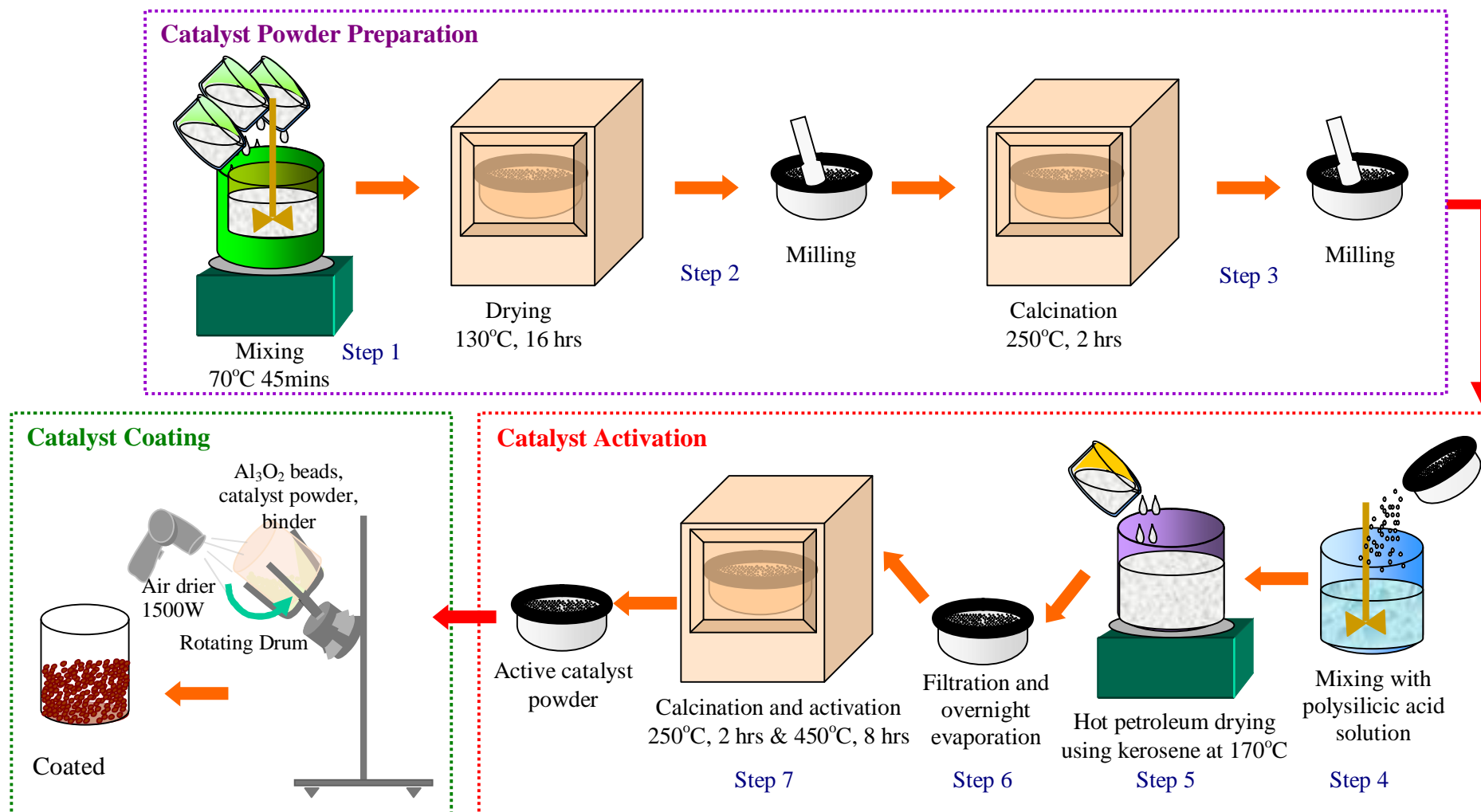
Figure 3.2: A schematic procedure of (coated) catalyst preparation

Table 3.1:   Chemical specification for catalyst preparation

Chemical name	Structure	Supplier	Catalogue no.	Lot no.	Phase	Purity (%)	Mol. Wt. (g.mol^{-1})
Ammonium Molybdate Tetrahydrate	$(NH_4)_6Mo_7O_{21}.4H_2O$	Sigma	A-7302	118H0283	Solid	81.4	1235.9
Bismuth (III) Nitrate Pentahydrate	$Bi(NO_3)_3.5H_2O$	Aldrich	24,859-2	10820PR	Solid	98	485.07
Iron (III) Nitrate Nonahydrate	$Fe(NO_3)_3.9H_2O$	Aldrich	21,682-8	05222JU	Solid	98+	404
Cobalt (II) Nitrate Hexahydrate	$Co(NO_3)_2.6H_2O$	Aldrich	23,037-5	12824PS	Solid	98	291.03
Tungsten (VI) Oxide	WO_3	Aldrich	23,278-5	07120MS	Solid	99+	231.85
Potassium Hydroxide	KOH	Sigma	P-1767	39H0105	Solid	86	56.11
LUDOX® HS-40 Colloidal Silica	SiO_2	Aldrich	42,081-6	05119EU	Liquid	40	1.30 g/ml
Orthophosphoric Acid	H_3PO_4	Rowe	20,624.295	110YR	Liquid	85+	1.69 g/ml
Silica, fumed for preparation of polysilicic acid (catalyst support)	SiO_2	Aldrich	38,126-8	11030JR	Solid	99.8	60.09
Pentaerythritol for pore former	$C_5H_{12}O_4$	Fluka	76,640	405975/1	Solid	97	136.15
D-(+)-Glucose Dextrose or Corn Sugar for coating or pelletising	$C_{16}H_{12}O_6$	Sigma	G-8270	58H0128	Solid	99.5	180.2
Extra-strength High Alumina Castable for coating or pelletising	CAST 15 ES	Matthews	RC1550		Solid	40% SiO_2, 53% Al_2O_3, 0.9% Fe_2O_3	

Table 3.2: Catalyst recipes

Catalyst formula	Chemicals (unit of quantity)							
	Ammonium Molybdate Tetrahydrate (g)	Bismuth (III) Nitrate Pentahydrate (g)	Iron (III) Nitrate Nonahydrate (g)	Cobalt (II) Nitrate Hexahydrate (g)	Tungsten (VI) Oxide (g)	Potassium Hydroxide (ml)	Colloidal Silica (g)	Phosphoric Acid (ml)
$Mo_{12}Bi_{1.5}Fe_{0.8}O_x$	12.75	4.38	1.95	-	-	-	-	-
$Mo_{12}Bi_{1.5}K_{0.06}Si_{1.4}O_x$	25.41	8.73	-	-	-	3	2.61	-
$Mo_{12}Bi_{1.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	25.40	8.49	-	-	1.57	3	2.61	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}K_{0.06}Si_{1.4}O_x$	12.75	4.38	2.03	6.09	-	1.5	1.28	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.4}K_{0.06}Si_{1.4}O_x$	12.71	3.18	2.02	6.07	0.62	1.5	1.30	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	12.78	4.27	2.03	6.08	0.78	1.5	1.28	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{2.4}K_{0.06}Si_{1.4}O_x$	15.78	5.42	2.41	7.59	4.14	2	1.57	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.12}Si_{1.4}O_x$	25.42	8.73	4.08	12.14	1.42	6	2.56	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.18}Si_{1.4}O_x$	14.20	4.88	2.17	6.83	0.93	5	1.41	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$	38.19	12.68	6.08	18.26	2.39	3	3.66	0.8

The preparation procedures of all catalysts were similar. The step by step $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst preparation and its activation, as illustrated in Figure 3.1 steps 1–7, were as follows:

Step 1: Preparation and Mixing of Solutions

1.1 The following solutions were prepared in separate beakers:

Solution 1: 18.2552 g of $Co(NO_3)_2.6H_2O$ was dissolved completely in 5 ml distilled water.

Solution 2: 6.0750 g of $Fe(NO_3)_3.9H_2O$ was dissolved completely in 2 ml distilled water.

Solution 3: 12.6808 g of $Bi(NO_3)_3.5H_2O$ was dissolved in 5 ml distilled water, and 0.8 ml of H_3PO_4 (85 wt%) was added to the solution.

Solution 4: 3.6500 g of SiO_2 (40 wt%) was mixed with 2.7 ml KOH solution (0.24mol/l).

1.2 On the porcelain bowl that was placed on a warm sand bath of 70^oC, 38.1916 g of $(NH_3)_6Mo_7O_{21}.4H_2O$ was dissolved with 20 ml distilled water.

1.3 After Ammonium Molybdate Tetrahydrate was dissolved in water completely, 2.3854 g of WO_3 was added and mixed for 10 minutes.

1.4 Solution 1, 2, 3 and 4 were dropped slowly into the precipitation container and mixed for 45 minutes until a homogeneous mixture was formed. These mixing procedures were all carried out at 70^oC. The pH value of this final mixture was 1.

Step 2: Drying

The mixture was put into an air oven at 130^oC for 16 hours to obtain a solid precursor cake. The colour of the precursor cake was not homogeneous, black on the surface and dark green in interior. The precursor cake was milled until it formed homogeneous powder.

Step 3: Calcination at 250^oC

The powder was then calcined at 250^oC in air for 2 hours. 61.0600 g of the final solid precursor was obtained. Again the solid precursor was milled to ensure the uniformity of the powder.

Step 4: Mixing with polysilicic acid solution

The powder was mixed with 86 ml of polysilicic acid solution (5 wt% SiO_2) to form the active component solution.

Step 5: Hot petroleum drying using kerosene at 170^oC

The solution was dropped slowly into 300 ml of hot kerosene at 170^oC. In order to maintain the same condition of drying, the kerosene should be at temperature of 170^oC $\pm$ 10^oC.

Step 6: Filtration and overnight evaporation

After the solution was cooled down to room temperature, the catalyst precursor was filtered and left overnight in air allowing kerosene to evaporate.

Step 7: Calcination at 250^oC and activation at 450^oC

The catalyst precursor was calcined at 250^oC for two hours then at 450^oC for eight hours in air. Finally, the active catalyst powder was obtained and ready to use.

3.1.2 CATALYTIC SCREENING TEST

3.1.2.1 REACTOR SYSTEM

An overall schematic of reactor system used in this work is illustrated in Figure 3.3. This reactor arrangement accommodated both the online sampling to the GC and the manual sampling by syringe. Two pressure gauges were installed in the inlet and outlet of the reactor to allow for the measurement of the pressure differential across the reactor and to ensure a constant pressure of the standard gas for GC calibration. Overall, this arrangement enabled the operators to maintain the same pressure of samples being injected into the GC sample loop.
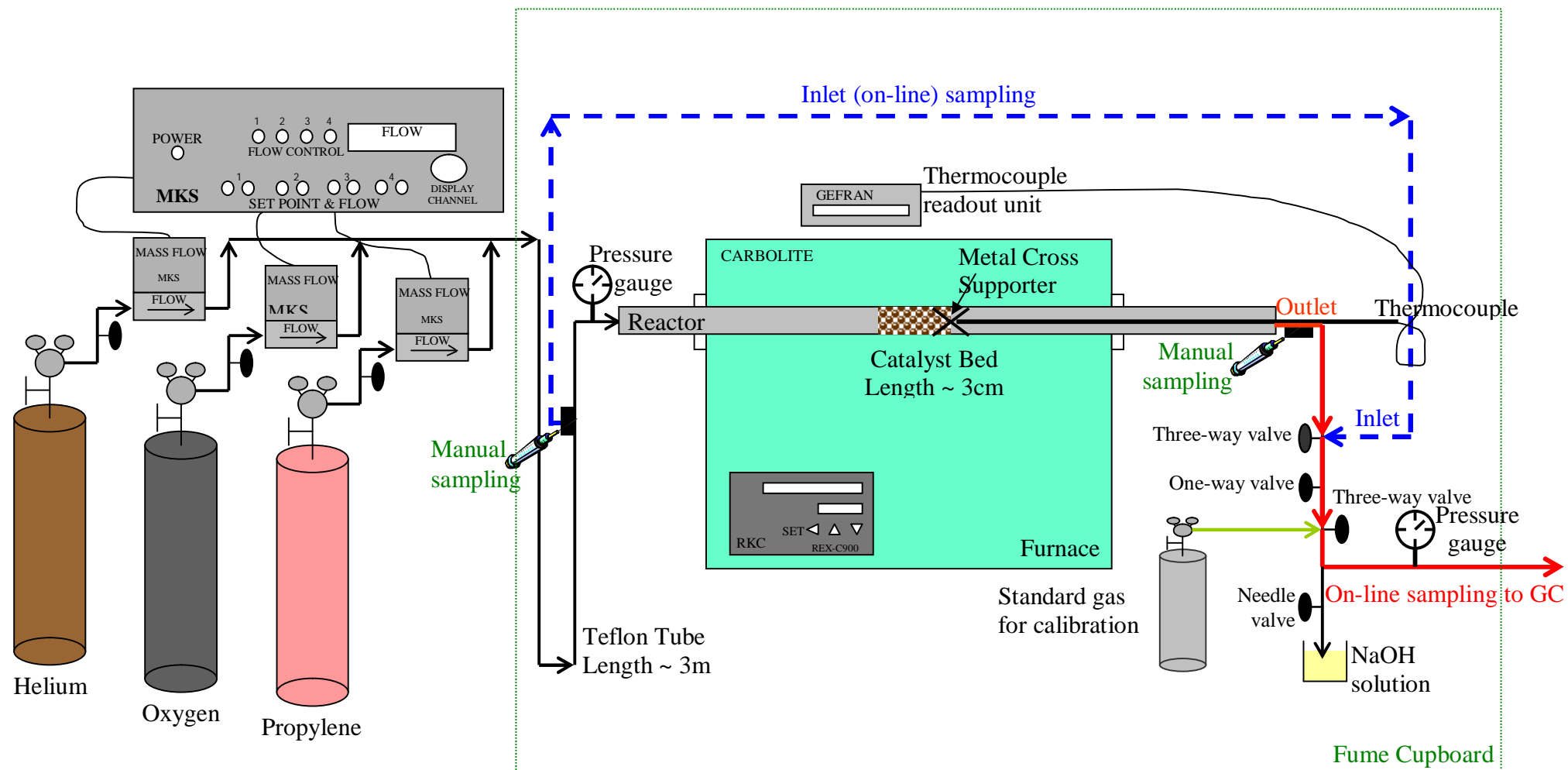
Figure 3.3:   An overall schematic of the reactor system for screening tests

The inlet gases of reactor consisted of high purity oxygen and polymer grade propylene as the reactants and high purity helium as the diluent gas. All gases were purchased from BOC Australia and used without prior purification. The flow rates of these gases were controlled by the MKS mass flow controllers (models 1159B and 1179A). The output signals of these flow controllers were displayed and controlled by a four-channels MKS readout unit model 247C. The mass flow controllers were calibrated using a Hewlett Packard soap film flow meter and a digital mini-Bulk Calibrator® Model M-5. A calibration was performed fortnightly in addition to the daily spot check. During the experiment, the mass flow controllers showed an accuracy of ± 3% for full-scale calibration and a repeatability of ± 0.5% at the same reading on the readout unit.

The mixture of gas reactants was flown through a 3 m Teflon tube before entering the inlet of reactor to ensure that the reactants were mixed thoroughly. A reactor was positioned in the centre of a Carbolite^{TM} tubular furnace type CFM 1. The furnace was installed with an RKC temperature controller (model REX-C900) and a K-type thermocouple to control and monitor the temperature of the furnace. There were two types of reactor used in this project: a stainless steel reactor for catalyst screening tests (Figure 3.4) and a quartz reactor for study rate of reaction (Figure 3.5). This quartz reactor was the same reactor used by Fansuri (2005) for conducting kinetic study of partial oxidation of propylene to acrolein over α, β and γ-bismuth molybdate by Fansuri (2005).
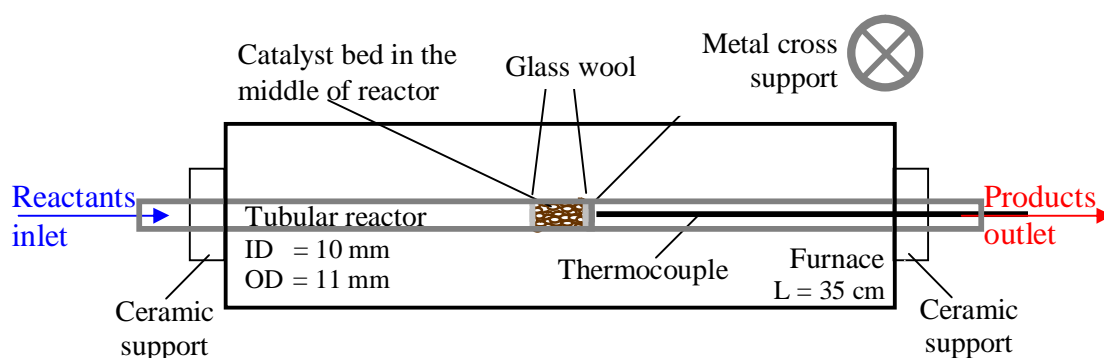
Figure 3.4:   The horizontal stainless steel reactor for the catalyst screening tests

The reactor for screening tests (Figure 3.5) was constructed from stainless steel tube with 10 mm in internal diameter and 1 mm in wall thickness. A thin cross-shaped

support made from the same material was welded in the middle of the reactor to avoid movement of the catalyst caused by gas flow. The catalyst bed was placed in the middle of the reactor and held in place by glass wool pads at both ends.
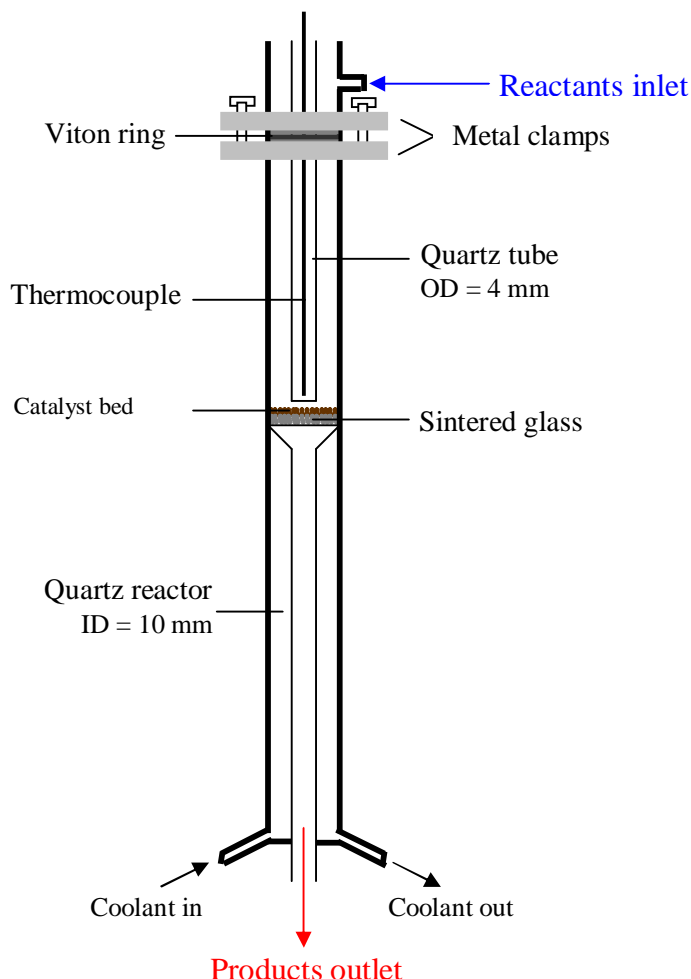
Figure 3.5:   A schematic of catalyst bed in the vertical quartz reactor

The quartz reactor (Figure 3.5) consisted of two parts, which were tightly coupled by metal clamps. The upper part consisted of a quartz tube for thermocouple insertion and as an inlet for reactant gases. The bottom segment consisted of a sintered glass tube that was used to support the catalyst located at the middle of the tube. At the end of the tube, a 2 mm inner diameter quartz tube was installed to reduce the residence time and consequently to minimise gas phase reactions in the post-catalytic zone (Krenzke 1977; Krenzke and Keulks 1980). The reactor was enclosed with a condensing shell to minimise further oxidation of the products.

Inside the reactor, a J-type thermocouple that was connected to the temperature read-out unit from Gefran, was installed near to the catalyst bed. By this positioned

thermocouple in the reactor, the temperature of the gas mixture (or the reaction) could be observed and found to be within $\pm 3^{\circ}C$ of the targeted temperature of the furnace throughout all experiments. Once the temperature reached its steady state, the temperature in the catalytic zone did not vary by more than $\pm 1^{\circ}C$ throughout the experiments and thus it validated the assumption of isothermal reactor.

The valve arrangement for the gas sampling is illustrated in Figure 3.6. The use of three-way valve allowed the samples to be taken either from the inlet or outlet of reactor or from standard gas cylinder for daily calibration. A needle valve was also installed on the outlet stream to adjust the pressure of the gas line connected to the GC.
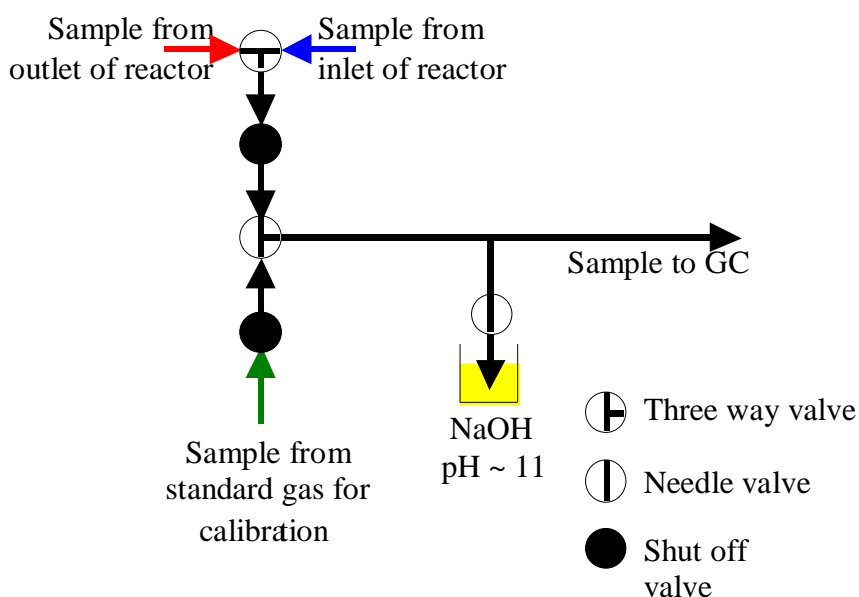
Figure 3.6:   Valve arrangement for the sampling system in the screening test reactor

The outlet of the reactor was divided into two streams. One stream was connected to the GC for the online analyses. Another stream was flown through a scrubber that contained a caustic soda solution of pH 11 so that the produced acrolein could be converted to poly-acrolein and therefore prevented the escape of acrolein to the atmosphere. The entire reactor system was located in a fume cupboard as further precaution against the escape of toxic or flammable gases into the laboratory.

The instrumentation, fittings and the operating procedure for stainless steel and quartz reactors were similar. All tubing was made from 3 mm (1/8") Teflon tubing. Stainless steel Swagelok connectors were used for all tubing connections except that

flexible silicon tubing was used for connection between the Teflon tubing and the quartz reactor. The use of silicon tubing for quartz reactor had made the reactor sensitive to the gas leakage; therefore the stainless steel reactor was more suitable for the catalyst screening tests that used more catalysts, therefore created a higher pressure.

Before any catalytic runs were started, an examination was made to justify the temperature limits at which non-catalytic or blank reaction became significant. The gas phase reaction of propylene oxidation were investigated by performing blank tests with a mixture of reactants containing 5% propylene, 10% oxygen, and 85% helium at 120 ml.min^{-1} over temperature range of 300-460°C. It was found that in the stainless steel reactor (Figure 3.4) the propylene starts to convert to carbon oxides at temperature of 360°C (Figure 3.7).
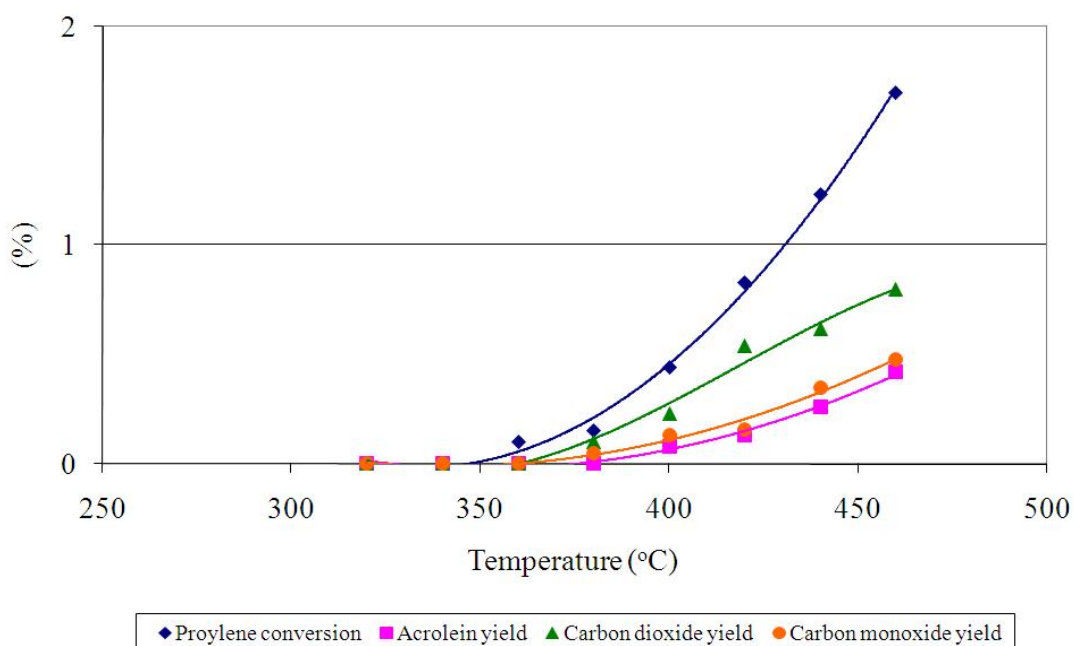
Figure 3.7:   Spontaneous oxidation of propylene in the stainless steel reactor

The formation of carbon oxides might be due to the formation of iron oxides inside the stainless steel reactor wall as the result of high temperature condition and the availability of gas phase oxygen to oxidise metallic iron on the stainless steel into iron oxides (Fansuri 2005). The formation of iron oxides from the oxidation of catalyst for hydrocarbon over temperatures between 300-460°C was also reported by Golunski and Walker (2000).

Tan (1986) also observed the spontaneous oxidation of propylene at temperature above 400°C in a stainless steel reactor. However it was reported that no blank reaction happened during the partial oxidation of propylene to acrolein up to temperature of 475°C using a quartz reactor (Keulks et al. 1971; Uda et al. 1980; Krenzke & Keulks 1980; Keulks & Lo 1986). Therefore, a quartz reactor (Figure 3.5) was used for study the rate of reaction. The blank tests detected no gas phase reaction in the quartz reactor over the experimental conditions (temperature of 300-460°C at total flow rate of 120ml.min^{-1}). Our results on the gas phase reaction in both reactors were consistent with previous findings (Golunski and Walker 2000; Tan 1986; Keulks et al. 1971; Uda et al. 1980; Krenzke and Keulks 1980; Keulks and Lo 1986).

3.1.2.2 GAS CHROMATOGRAPH AS THE ANALYSIS INSTRUMENT

A Varian GC (STAR 3400CX) was used to analyse the gas composition of the inlet reactant and outlet product streams. The GC is equipped with a gas sample loop, two packed columns and two detectors. A sample loop was used to ensure a constant volume of gas sample was injected for every gas analysis.

Two packed columns, which were made from stainless steel with length of 4 ft (1.2 m) and diameter of 1/8″ (3 mm) and packed with 80-100 mesh range of either Porapak N and Molecular Sieve 13X, were installed for separation of samples. A Porapak N column was used to separate the slow-eluting gases such as carbon dioxide and hydrocarbons (propylene, acetaldehyde, and acrolein). Whilst a Molecular Sieve (MS) 13X separated the fast-eluting gases such as oxygen, nitrogen, and carbon monoxide.

The effluent from these columns was directed through a non-destructive Thermal Conductivity Detector (TCD) that was in series with a Flame Ionisation Detector (FID). Two 6-port valves controlled the sample injection and the column switching automatically. The configuration of the valves, columns, and detectors is illustrated in Figure 3.8. High purity helium with flow rate of 30 ml.min^{-1} was used as the carrier gas, whilst high purity hydrogen of 30 ml.min^{-1} and industrial air of 300 ml.min^{-1} were required to operate the FID. In addition, the air was also used to control the pneumatic valves. All gases were supplied by BOC and used without prior purification.
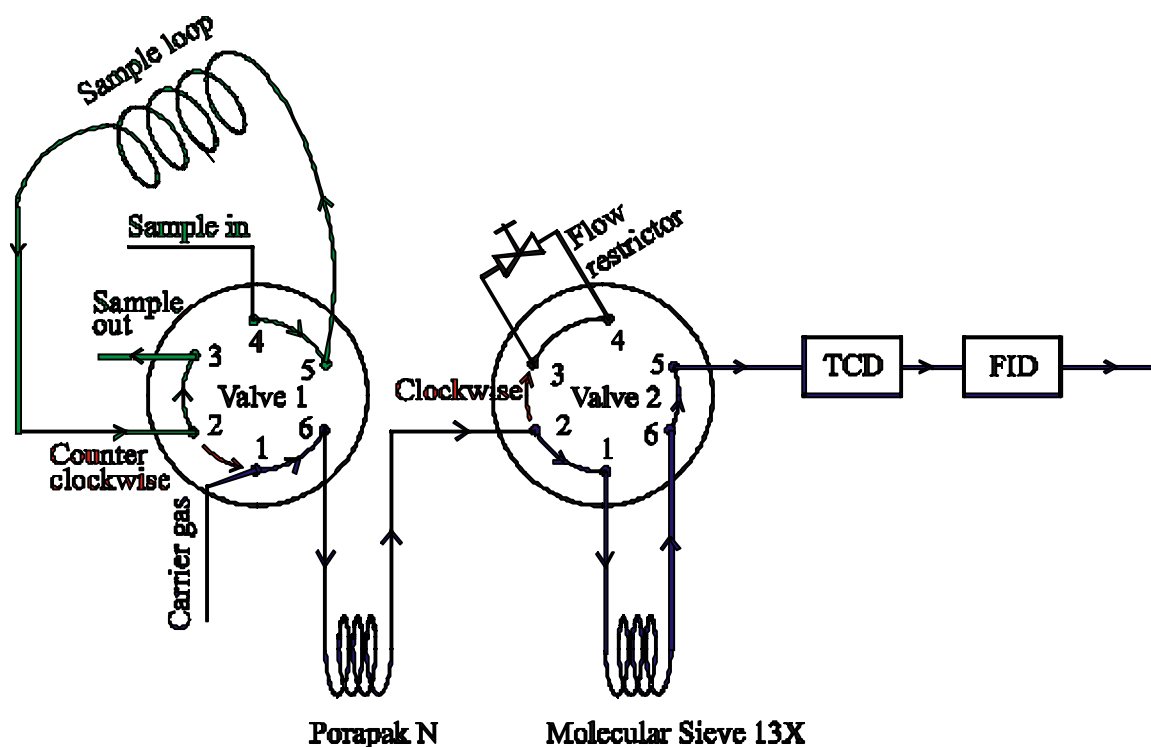
Figure 3.8:   Configuration of GC valves, columns and detectors
This is the configuration at the fill position and the columns run in series. Valve 1 turns counter clockwise to inject the sample from the loop onto the column. Valve 2 turns clockwise to bypass the MS column, with the flow restrictor offering equivalent resistance to the MS column.

Having a suitable GC method of analysis that can detect all possible components in the reaction within an appropriate composition range is of prime importance. The GC analysis method was controlled through the STAR software, which programmed the temperatures of the GC columns, injector, detectors, auxiliaries and the functioning of the GC valves and detectors (FID and TCD). The temperature of the GC columns was programmed initially to start $110^{o}C$ and maintained at this temperature for 5.5 minutes. Then a heating rate of $20^{o}C$ per minute was applied to a temperature of $170^{o}C$, which was then maintained for 8 minutes. Meanwhile, the temperatures of the injector, detectors, and auxiliaries were kept constant.

Using the GC switching column method (Figure 3.9), all components in the system were separated in 15 minutes of total analysis time. The retention times of the components were detected by separately injected: 1) a diluted mixture of standard Micromat-14 gas and propylene (which the chromatogram is shown in Figure 3.10),

and 2) a diluted mixture of acrolein and acetaldehyde (which the chromatogram is shown in Figure 3.11).

At 0.10 minutes, open the Poparak N and Molecular Sieve 13X

CO_2 CO N_2 O_2
C_3H_4O C_2H_4O C_3H_6 → PN → MS → TCD — FID →

At 1.13 minutes, open the Poparak N but bypass the Molecular Sieve 13X

CO_2

C_3H_4O C_2H_4O C_3H_6 → PN → TCD — FID → CO_2 at 1.49 min

CO N_2 O_2

At 1.90 minutes, open the Poparak N and Molecular Sieve 13X

C_3H_4O C_2H_4O C_3H_6 → PN → MS → TCD — FID → O_2 at 2.20 min
N_2 at 2.28 min
CO at 2.56 min

CO N_2 O_2

At 3.20 minutes, open the Poparak N but bypass the Molecular Sieve 13X

C_3H_4O C_2H_4O C_3H_6

→ PN → TCD — FID → C_3H_6 4.54 min
C_2H_4O 8.87 min
C_3H_4O 13.30 min
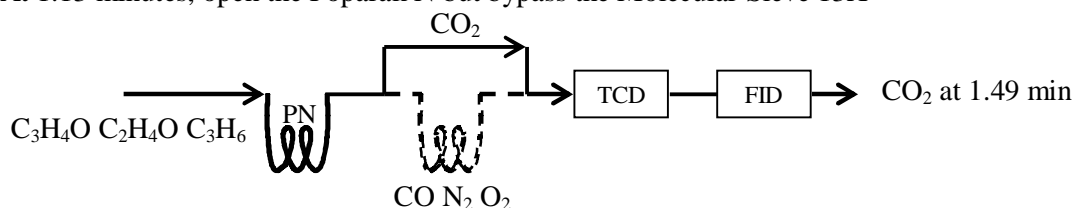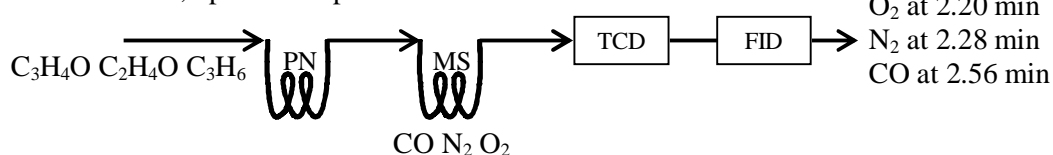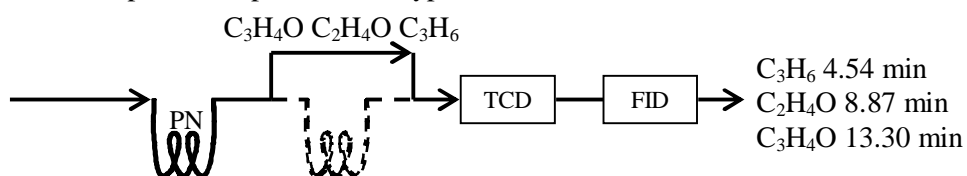
Figure 3.9:   GC program for the columns switching

A standard Micromat-14 gas of Matheson Tri-Gas containing 5% CO_2, 5% CO, 5% O_2, 5% N_2, 4% CH_4, and 4% H_2, balanced with helium, was used to identify the retention times and to do the quantitative calibrations of CO_2, CO, O_2, and N_2. The propylene for calibration was the polymer grade propylene from BOC Gases, which was also used as the reactant of this reaction.
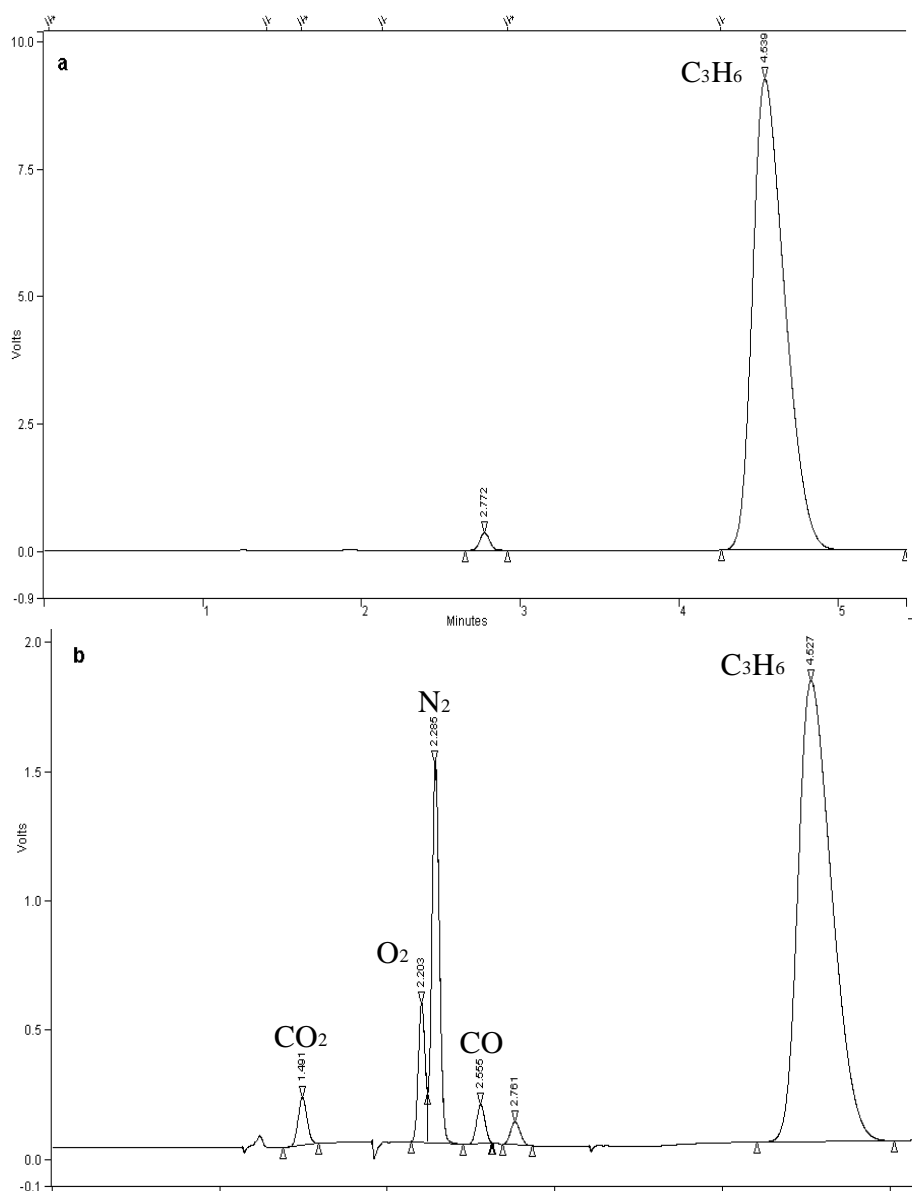
Figure 3.10: Chromatograms of a diluted mixture of standard Micromat-14 gas (CO$_2$, O$_2$, N$_2$, CO, and CH$_4$) and C$_3$H$_6$, which were detected by a) FID and b) TCD

Chromatograms in Figure 3.9 show the separation of each gas. It was noted that the N$_2$ peak was approximately three times higher than the O$_2$, which indicated a typical composition of air peak since the sample was diluted with air. The gas and propylene were mixed together in a Teflon plastic bag and diluted with helium to reduce the concentration to an acceptable concentration limit of the GC system.

The acrolein and acetaldehyde sample for calibrations were supplied by Sigma-Aldrich. Both of them were in the form of liquid, which had purity of 90% for

acrolein and 99.9% for acetaldehyde. Since the acrolein and acetaldehyde products of the process were in gas phase, the liquid samples for calibration were vaporised in the sealed glass bottle before they are injected into the GC. Figure 3.11 presents a typical chromatogram of a mixture of acetaldehyde and acrolein in vapour phase when diluted with air.
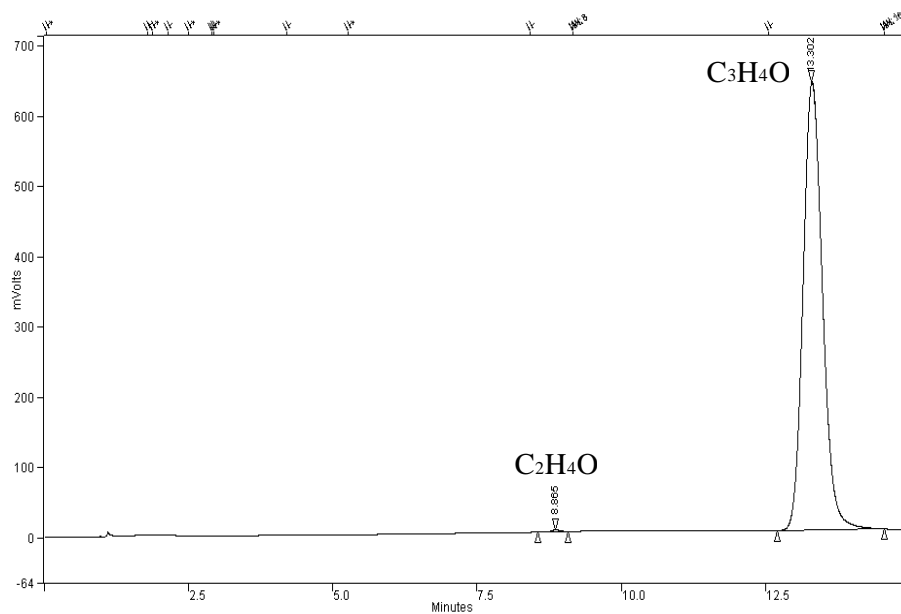
Figure 3.11: Chromatogram of a diluted gas sample of acetaldehyde and acrolein, which was detected by FID

Daily spot checks were performed at the beginning and at the end of experiments in addition to the fortnightly calibrations. When the daily spot check shifted more than ± 1%, a calibration was performed. During the whole period of experiment, the calibration curves were found to drift less than ± 3%. A GC recalibration was also repeated after either regeneration of columns, changing the flow rate of GC carrier gas, or modification of GC analysis method. Column regeneration was performed periodically to achieve better gas separation and to remove any possible impurities from the GC columns. In addition, the regular leak checking was performed to ensure reliable operation. The Varian leaks detector (type: LD228) was used to check the leaks around the fittings and connections in GC.

Linearity test (Bromly & Roga 1980) was performed in order to justify the performance of GC detectors. The detector is legitimate if it shows a linear plot of Equation 3.1.

$$R = a\,c^b \tag{3.1}$$

Where: R   = response

c = concentration of sample

a, b   = constants

The range of c for which b is 1 is referred to as linear or dynamic range of the detector. In the case of the FID, the end of this range usually indicates the inability of the electrical field to collect the high concentration of ions efficiently (Bromly & Roga 1980). This effect is termed as detector overload, which should be avoided to achieve accurate FID response. Most researchers used the assumption of b = 1 for the range within the lower limit of detection and detector overload (Bromly & Roga 1980). As detector overload is approached, the b value varies from one, sometimes exceeding unity for a certain concentration range before ultimately falling below one. Figure 3.12 shows the linearity plots of FID and TCD when analysed two independent gaseous samples contained of 10% and 20% propylene in the 167.67 µL sample loop. From the plots, the b values = 1 ± 0.05, which could be said to be quite linear.
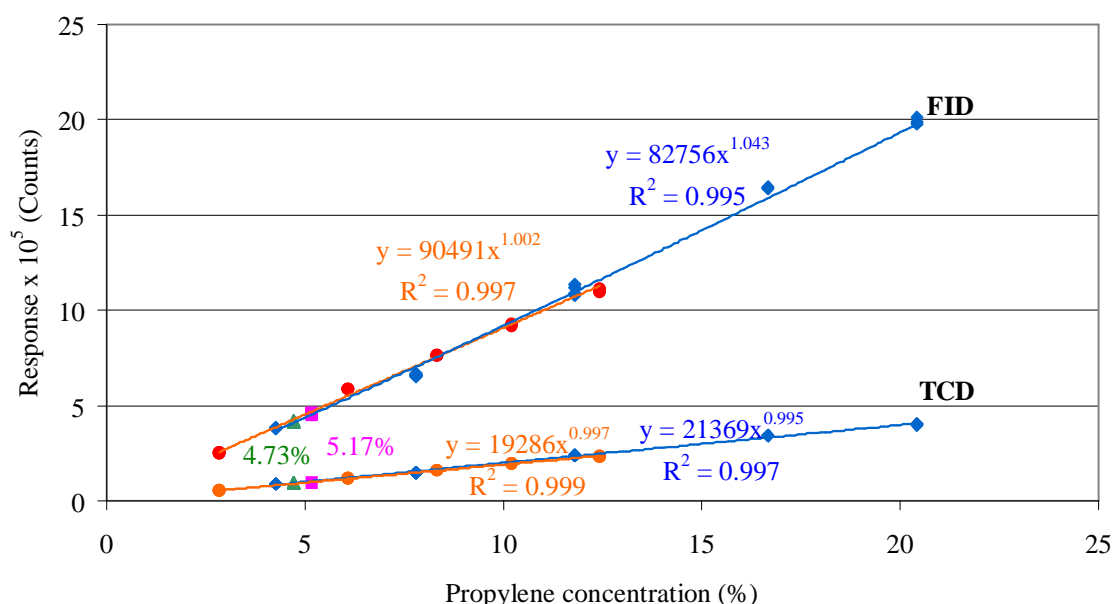
Figure 3.12: Detectors' linearity tests in the 167.67 µL sample loop using samples of 10% and 20% propylene. Parameter of FID: attenuation 8 and range 10. Parameters of TCD: attenuation 8, range 0.5, and filament was on at 280°C.

3.1.2.3 SCREENING PROCEDURE

A catalyst bed (approximately 5 ml) was placed in the middle of a stainless steel tube as a fixed bed reactor (Figure 3.4). The arrangement of the reactor system is described in Section 3.1.2.1. Prior to obtain the true data for catalyst activity, the catalysts were pre-aged by passing through the reactant gas comprising of 5% propylene, 10% oxygen, and 85% helium at 400°C for eight hours or until the catalyst activity became steady. The technique for catalyst screening has to be representative, efficient, and adequately sensitive to observe any distinctions between various catalyst samples.

The catalyst screenings were carried out at the inlet flow rate of 120 ml.min^{-1} containing 5% propylene, 10% oxygen, and 85% helium by volume over 300-450°C with 30°C step. This temperature range was selected based on the preliminary screening results, indicating that below 300°C the conversion of propylene was negligible and above 450°C side products were significantly produced.

At least three samples were taken at each temperature. The samplings were done at least five minutes after the thermocouple at the outlet of catalyst bed showed a constant temperature, which indicated that the reaction has taken place at steady state condition. The analysis of reactants and products was carried out by on-lined gas chromatography (Varian GC STAR 3400CX) as explains in Section 3.1.2.2.

The catalytic activity is defined as the moles of propylene converted per moles feed (Equation 3.2). The selectivity was measured as moles of propylene converted to a particular product per moles of propylene consumed (Equation 3.3). The catalyst activity and selectivity were measured based on the number of carbon atom as the propylene oxidation can also produce smaller molecules such as carbon dioxide and carbon monoxide.

$$X = \left[1 - \frac{n_{C_3H_6 \ outlet}}{n_{C_3H_6 \ inlet}}\right] \times 100\%$$

$$(3.4)$$

$$S_i = \left[\frac{n_{i \ outlet}}{n_{C_3H_6 \ inlet} - n_{C_3H_6 \ outlet}}\right] \times 100\%$$

$$(3.5)$$

Where: $\quad$ X $\quad$ = conversion of propylene (%)

$\qquad\qquad$ Si $\quad$ = selectivity of product i (can be C_3H_4O, C_2H_4O, CO_2, or CO)

n_i = number of moles of component i (mol)

3.2 SCREENING TEST RESULTS

All catalyst screening tests were conducted at total flow rate of 120 ml.min^{-1} that consisted of 5% propylene, 10% oxygen and 85% helium over temperatures 300$^-$450°C. The temperature range was chosen based on the knowledge that below 300°C the conversion of propylene over the catalysts was negligible and above 450°C, side products were significantly produced. The summary of the screening results at optimum acrolein yield and at reaction temperature of 350°C are presented in Tables 3.3 and 3.4 respectively.

Table 3.3: Catalytic screening test results at maximum acrolein yield over temperature of 300-450°C

Catalyst formula	Reaction condition and screening result at maximum acrolein yield						
	Temperature (^{o}C)	Propylene conversion ($\%.g_{cat}^{-1}$)	Acrolein yield ($\%.g_{cat}^{-1}$)	Acrolein selectivity (%)	Acetaldehyde selectivity (%)	CO_2 selectivity (%)	CO selectivity (%)
$Mo_{12}Bi_{1.5}Fe_{0.8}O_x$	448	2	6	75	10	8	8
$Mo_{12}Bi_{1.5}K_{0.06}Si_{1.4}O_x$	-	-	-	-	-	-	-
$Mo_{12}Bi_{1.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	-	-	-	-	-	-	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}K_{0.06}Si_{1.4}O_x$	359	17	11	67	9	10	13
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.4}K_{0.06}Si_{1.4}O_x$	358	20	15	78	8	7	8
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	385	20	17	81	9	11	9
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{2.4}K_{0.06}Si_{1.4}O_x$	389	19	13	69	11	9	12
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.12}Si_{1.4}O_x$	391	16	13	80	7	13	8
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.18}Si_{1.4}O_x$	391	13	11	80	7	11	8
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$	357	25	24	95	4	4	6

Table 3.4:   Summary of screening test results at reaction temperature of 350°C

Catalyst formula	Screening result at temperature of 350°C						
	Temperature (^{o}C)	Propylene conversion (%)	Acrolein yield (%)	Acrolein selectivity (%)	Acetaldehyde selectivity (%)	CO$_2$ selectivity (%)	CO selectivity (%)
$Mo_{12}Bi_{1.5}Fe_{0.8}O_x$	350	2	2	89	4	0	5
$Mo_{12}Bi_{1.5}K_{0.06}Si_{1.4}O_x$	350	1	-	-	-	-	-
$Mo_{12}Bi_{1.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	350	2	-	-	-	-	-
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}K_{0.06}Si_{1.4}O_x$	350	16	11	68	10	8	14
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.4}K_{0.06}Si_{1.4}O_x$	350	19	15	77	8	7	7
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	350	19	16	84	6	9	7
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{2.4}K_{0.06}Si_{1.4}O_x$	350	15	11	74	8	8	10
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.12}Si_{1.4}O_x$	350	13	11	87	7	9	6
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.18}Si_{1.4}O_x$	350	11	10	88	6	7	6
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$	350	24	23	95	4	4	6

The screening results, which were summarised in Tables 3.3 and 3.4, concluded the following points. Additions of catalyst promoters have improved the catalytic performance of the catalysts. From the screening results of first four catalysts in the tables ($Mo_{12}Bi_{1.5}Fe_{0.8}O_x$, $Mo_{12}Bi_{1.5}K_{0.06}Si_{1.4}O_x$, $Mo_{12}Bi_{1.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ and $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}K_{0.06}Si_{1.4}O_x$), it can be said that iron in molybdate bismuth catalyst was significant element for acrolein formation as no acrolein was detectable in the catalysts without iron element ($Mo_{12}Bi_{1.5}K_{0.06}Si_{1.4}O_x$, $Mo_{12}Bi_{1.5}W_{0.6}K_{0.06}Si_{1.4}O_x$) within the experiment conditions of catalyst screening.

The composition of tungsten (WO_3) in the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_wK_{0.06}Si_{1.4}O_x$ catalyst (with w = 0, 0.4, 0.6 and 2.4) was studied. The comparable screening results were indicated that the catalyst with w = 0.4 has the lowest optimum temperature (Table 3.3) and the highest conversion of initial propylene (Figure 3.14). However slightly increase in tungsten composition from w = 0.4 to 0.6 had improved the selectivity to acrolein significantly (Figure 3.15). The $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_wK_{0.06}Si_{1.4}O_x$ catalyst therefore was the best performance catalyst among four catalysts (with w = 0, 0.4, 0.6 and 2.4) as it yielded the most acrolein over the temperature range of 330-450°C (Figure 3.15).
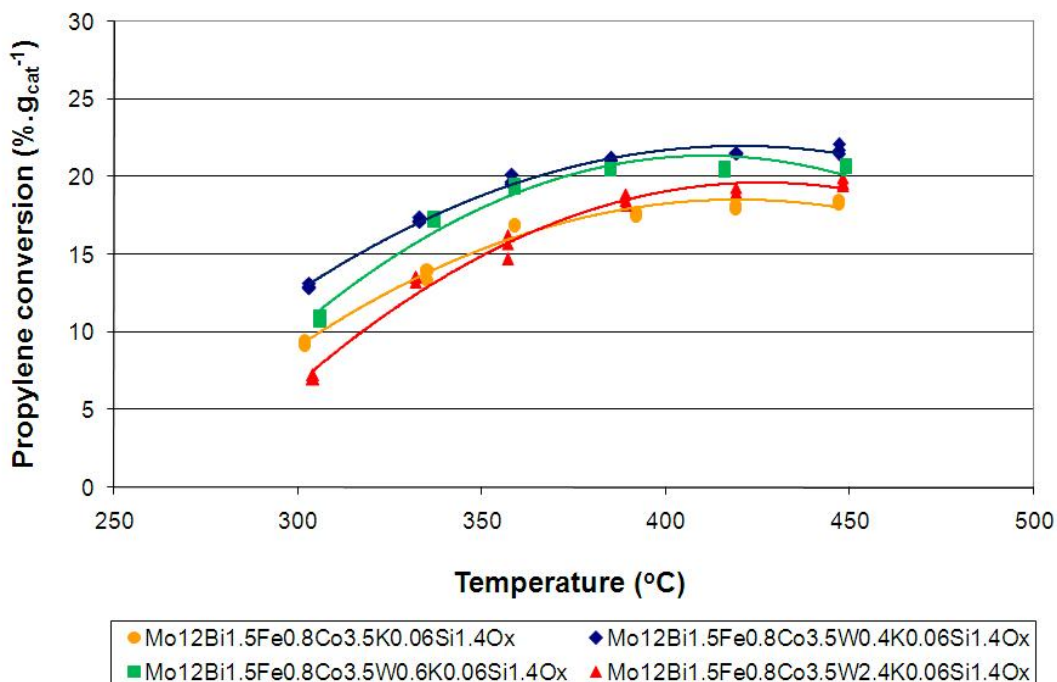
Figure 3.13: Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_wK_{0.06}Si_{1.4}O_x$ catalyst in terms of propylene conversion
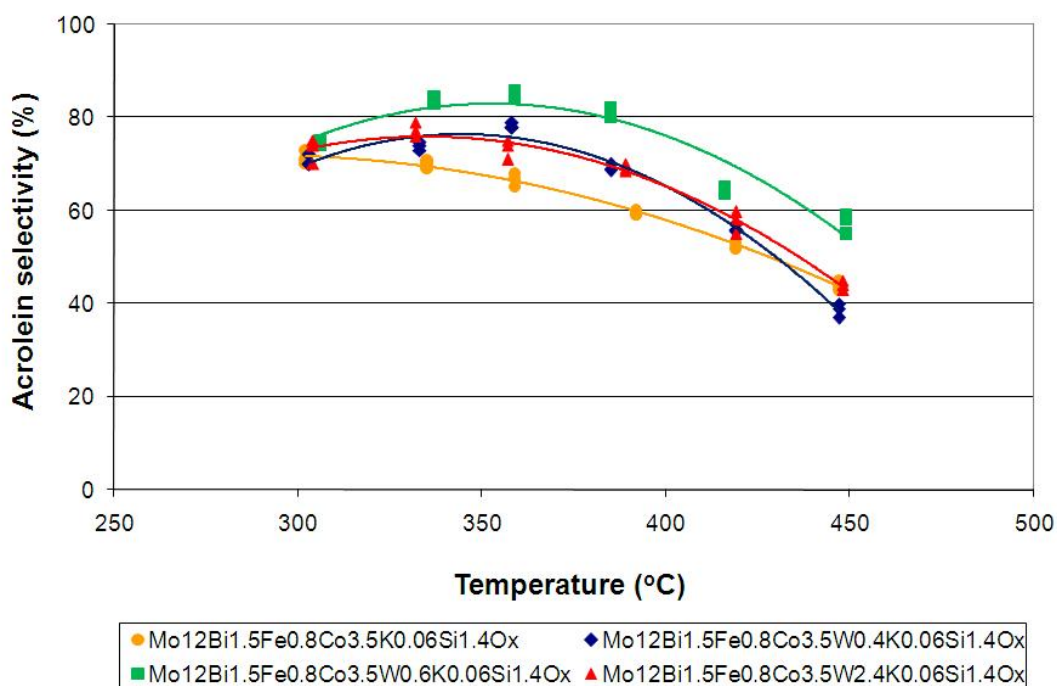
Figure 3.14: Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_wK_{0.06}Si_{1.4}O_x$ catalyst in terms of acrolein selectivity
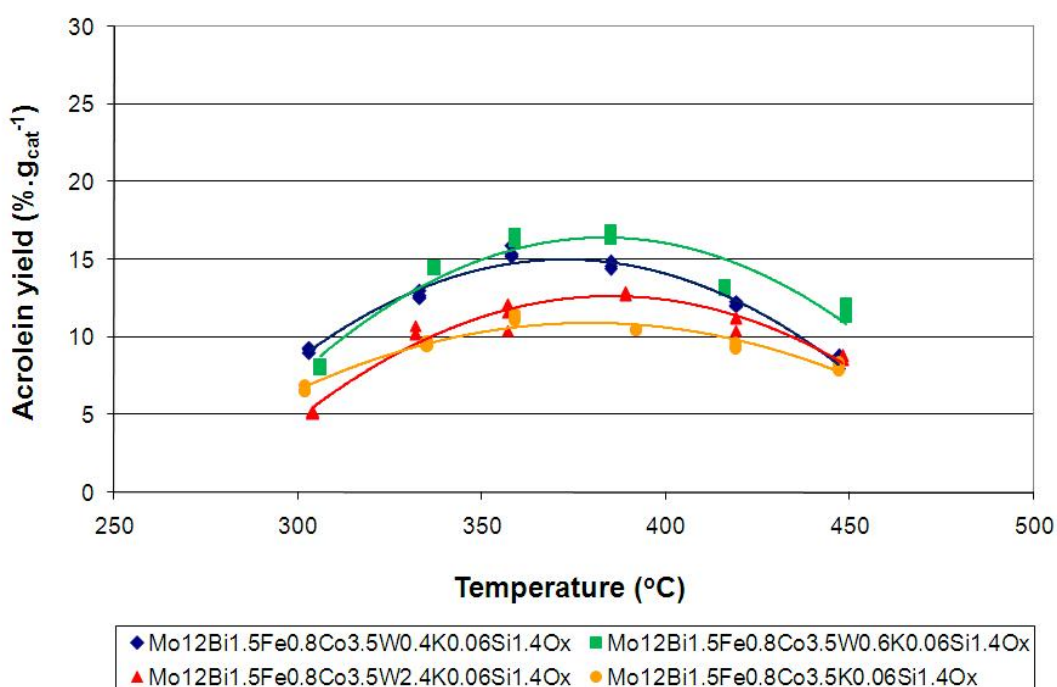
Figure 3.15: Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_wK_{0.06}Si_{1.4}O_x$ catalyst in terms of acrolein yield

The observation on the variation of tungsten composition in the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_wK_{0.06}Si_{1.4}O_x$ catalyst (for w = 0.4, 0.6 and 2.4) indicated that small addition of tungsten had certainly improved the catalytic performance of catalyst however the excess would decreased the catalytic performance of catalyst. This finding was consistent with previous studies by Weng et al. (Weng, Sham, Doumain, Ruiz & Delmon 1990; Weng & Delmon 1992 as cited in (Carrazan et al. 1996a)) who proved that the addition of an oxide phase, such as MoO_3, SnO_2, or WO_3, improved the catalytic activity and selectivity of γ-Bi_2MoO_6 in the selective oxidation of propylene to acrolein or isobutene to methacrolein.

As tungsten oxides, WO_3, have similar function as the MoO_3 as both of them are group VI transition metals, the finding by Udalova et al. (2005) can be also used to support our screening results on the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_wK_{0.06}Si_{1.4}O_x$ catalyst, where w = 2.4 had the least acrolein yield (Figure 3.16). When studying the effect of Mo content in a $Mo_aBi_{0.75}Fe_3Co_8O_x$ catalyst with a = 9-15, Udalova and co-workers found that a high catalytic performance was shown by Mo_{11} - Mo_{13} system and the highest selectivity was observed for the Mo_{12} system. However the acrolein yield was fallen significantly for the $Mo_aBi_{0.75}Fe_3Co_8O_x$ catalyst with a > 13. Therefore they concluded that though a small amount of MoO_3 increased the catalytic performance, the excess of MoO_3 behaved the opposite.

The effect on variation of the potassium composition was investigated in the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_kSi_{1.4}O_x$ catalyst, where k = 0.06, 0.12 and 0.18. The screening results of these catalysts are plotted in Figures 3.17-3.19.
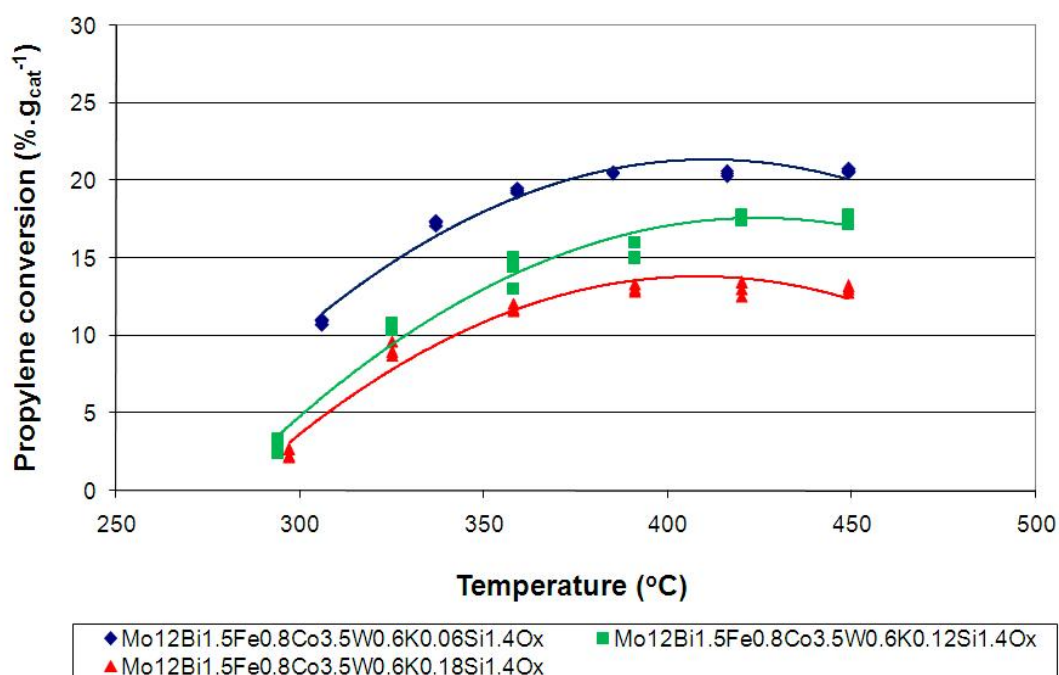
Figure 3.16:   Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_kSi_{1.4}O_x$ catalyst in terms of propylene conversion
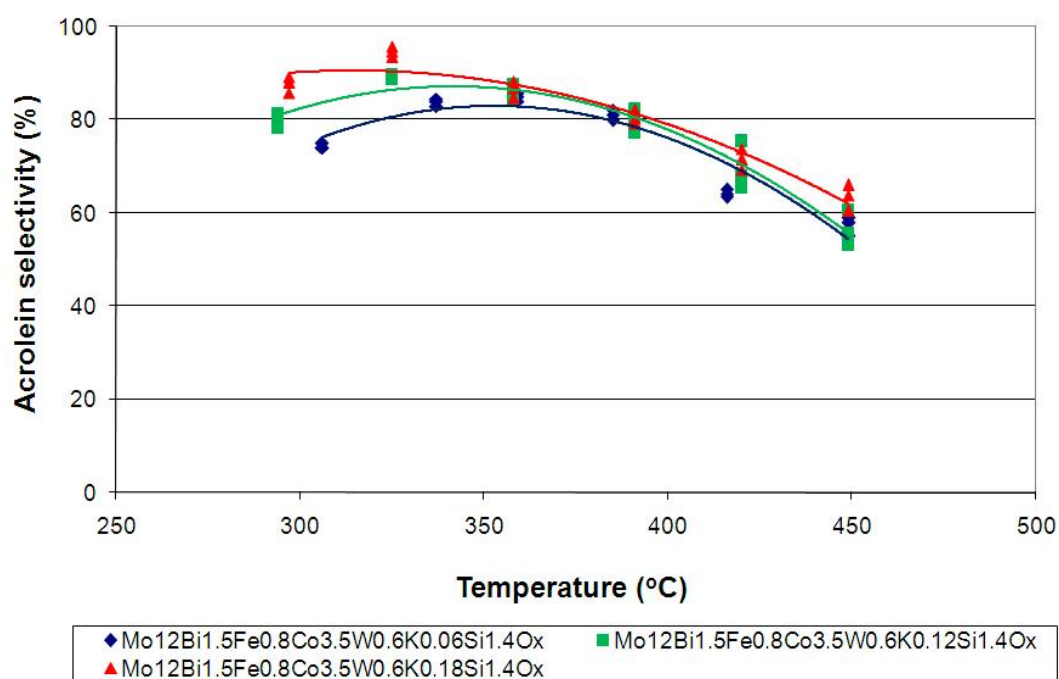
Figure 3.17:   Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_kSi_{1.4}O_x$ catalyst in terms of acrolein selectivity
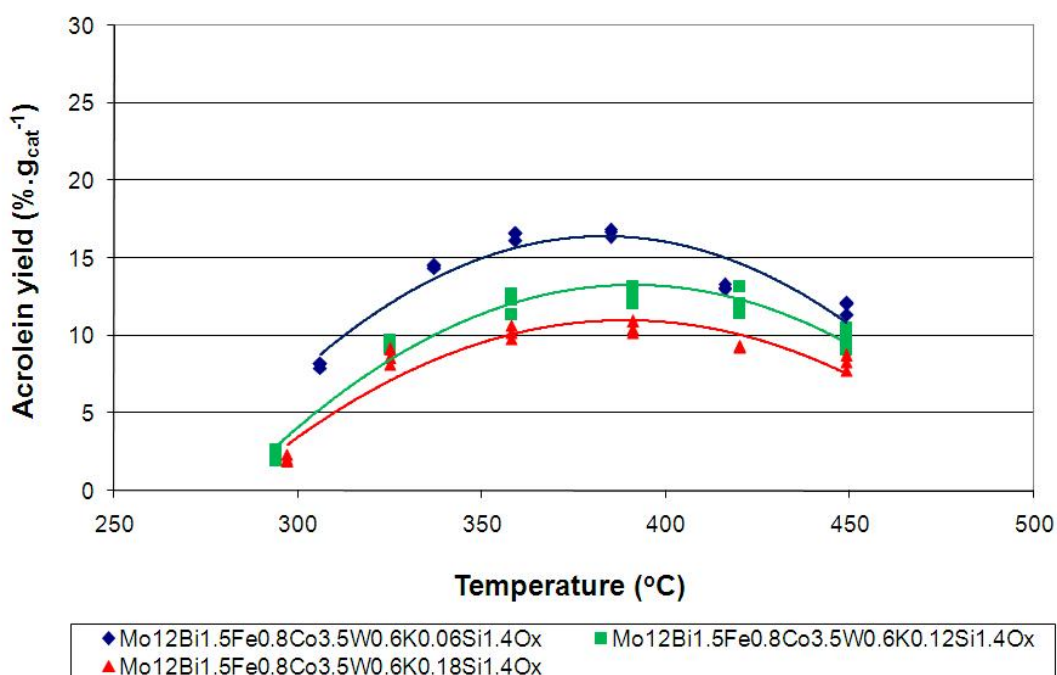
Figure 3.18: Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_kSi_{1.4}O_x$ catalyst in terms of acrolein yield

An increase in potassium content in catalysts indicated the decrease in activity of the catalysts to convert the initial propylene (Figure 3.17) but slightly increase the selectivity to acrolein (Figure 3.19). This finding was consistent with previous studies by Matsuura et al. (1986), Ozkan et al. (Ozkan, Smith & Driscoll 1990; Ozkan, Driscoll, Zhang & Ault 1992 as cited in (Udalova et al. 2005)), Martin-Aranda et al. (1995), Ermini et al. (Ermini, Finocchio, Sechi, Busca & Rossigni 2000 as cited in (Buyevskaya & Baerns 2002)) and Udalova (2005).

Matsuura and colleagues (1986) showed that the addition of potassium in the form of KOH in the $CoMoO_4$ based catalyst for oxidation of propylene significantly improved the acrolein selectivity due to the decrease of acidic property.

Ozkan et al. also revealed that the alkali metals (Li, Na, K, or Cs) reduced the acidity of the catalysts, therefore promoted the olefin adsorption and product desorption (Ozkan, Smith & Driscoll 1990; Ozkan, Driscoll, Zhang & Ault 1992 as cited in (Udalova et al. 2005)). The high yield of propylene oxidation over Mo/K catalysts supported on Si/Ti mixed oxides were partly explained by the effect of potassium, which forms a tetrahedral K-Mo matrix (Watson & Ozkan 2000 as cited in (Buyevskaya & Baerns 2002)).

In the study of alkali metal promoters over the α and β-phases of $NiMoO_4$ catalysts for selective oxidation of butane, Martin-Aranda et al. (1995) observed that the alkali metal additions caused the decrease in the catalyst activity that was due the decrease of the surface area, and at the same time caused the increase in selectivity of partial oxidation because of the change of basicity level of catalysts. The higher basicity and the amount of promoter ion, the higher is the selectivity. They also observed that the added alkali metals were deposited only on the catalyst surface and did not affect the bulk structure. Therefore the additions of alkali metals often did not result in the formation of any new phases (Martin-Aranda et al. 1995; Udalova et al. 2005).

A study of the potassium addition in the alumina-supported vanadia catalyst for selective oxidation of propylene by Ermini et al. indicated the K-doping poisons the acid sites of the catalyst support. Therefore it resulted in the loss activity at the same time of the increase of selectivity (Ermini, Finocchio, Sechi, Busca & Rossigni 2000 as cited in (Buyevskaya & Baerns 2002)).

Udalova and colleagues (2005) studied the addition of potassium in the multi-component catalysts $Co_8Mo_{12}Bi_{0.75}Fe_3K_yO_x$ (y = 0-0.8) for selective oxidation of propylene to acrolein. They found the potassium promoter altered the redox and acid-base properties of catalysts and as the potassium content was increased, the catalyst lost activity but maintaining relatively high selectivity.

The study on the variation of both tungsten and potassium content in this project concluded that the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ catalyst resulted in the highest acrolein yield, i.e. 17% acrolein per gram of catalyst at temperature of 385°C (Table 3.3). Therefore the aforementioned catalyst was then used as the based catalyst for the addition of phosphorous. The $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$, which was the best performance catalyst, achieved the targeted performance i.e. 95% acrolein selectivity at temperature not more than 350°C. Figures 3.20-3.22 describes the addition of catalyst promoters certainly improved the catalytic performance. The best performance catalyst, $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$, at 350°C could convert 24% of the initial propylene per gram of catalyst at which 95% was converted to acrolein. This catalyst has superior high selectivity to acrolein (80-95%) at reaction temperature within 300-400°C (Figure 3.20).
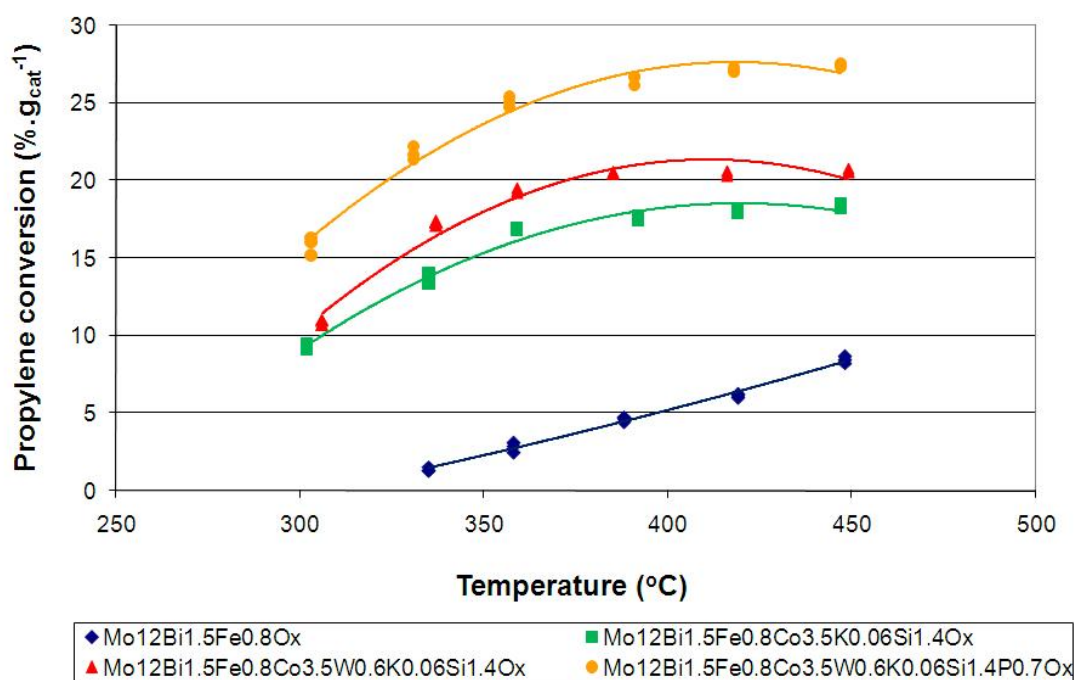
Figure 3.19:　Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{0-3.5}W_{0-0.6}K_{0-0.06}Si_{0-1.4}P_{0-0.7}O_x$ catalyst in terms of propylene conversion
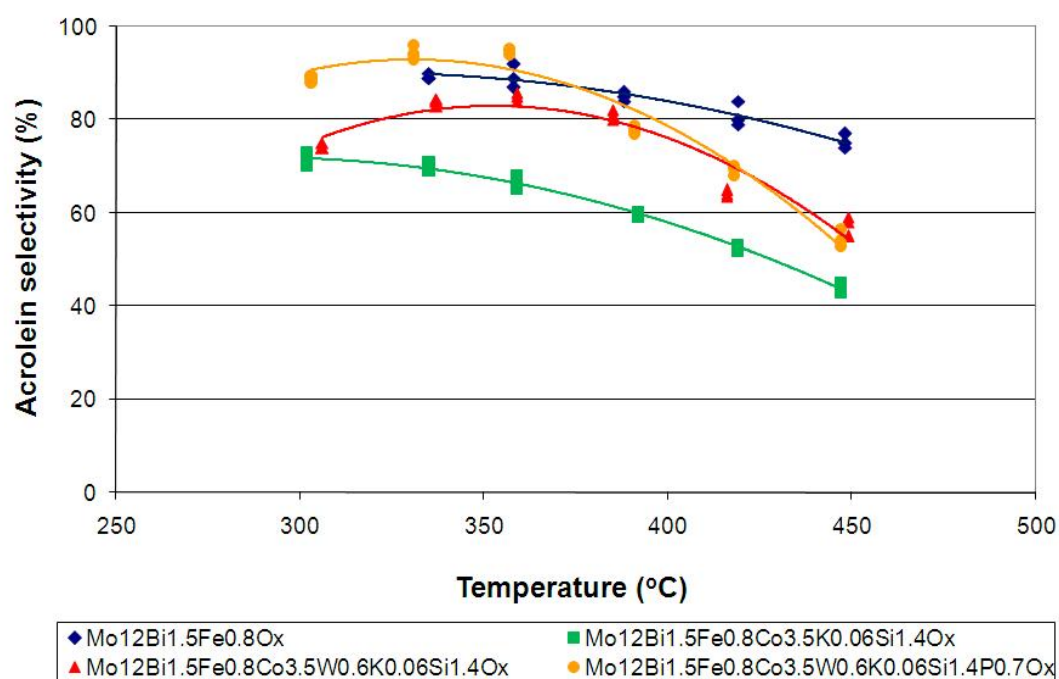
Figure 3.20:　Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{0-3.5}W_{0-0.6}K_{0-0.06}Si_{0-1.4}P_{0-0.7}O_x$ catalyst in terms of acrolein selectivity
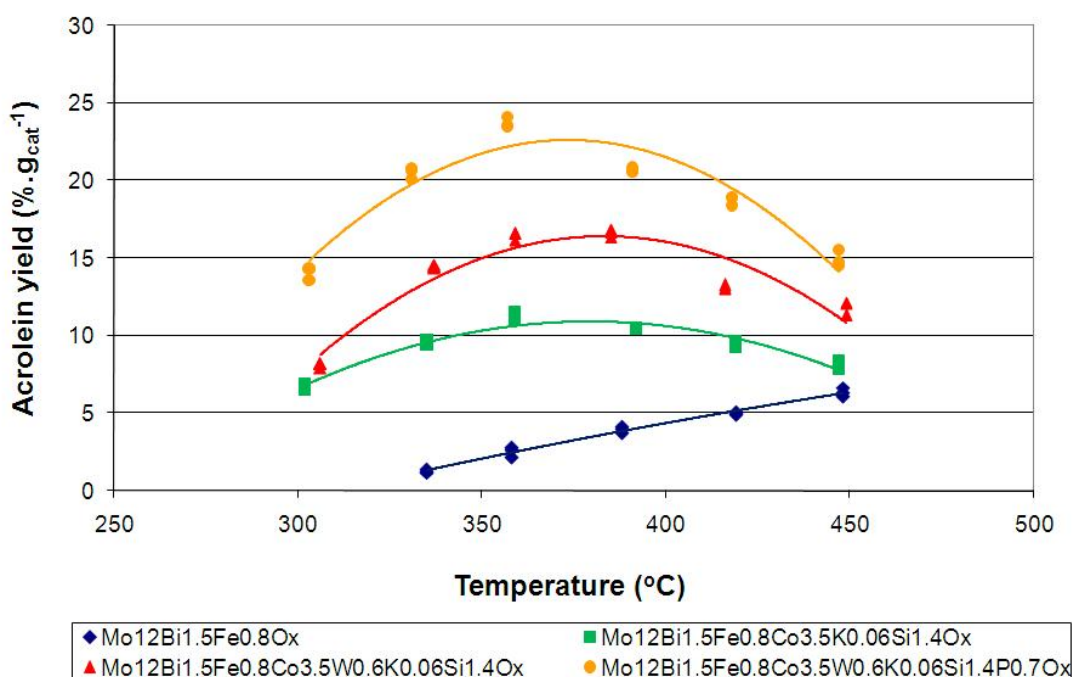
Figure 3.21: Screening results of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{0-3.5}W_{0-0.6}K_{0-0.06}Si_{0-1.4}P_{0-0.7}O_x$ catalyst in terms of acrolein yield

The main structural phases of catalysts, which observed use Siemens X-Ray Diffraction (XRD) type D-500 are tabulated in Table 3.5.

Table 3.5: Structural phases detected in catalysts by XRD analysis

Catalyst formula	Major phases
$Mo_{12}Bi_{1.5}Fe_{0.8}O_x$	MoO_3, BiO_3, α-$Bi_2Mo_3O_{12}$, $Fe(MoO_4)_3$
$Mo_{12}Bi_{1.5}K_{0.06}Si_{1.4}O_x$	MoO_3, BiO_3, KMo_4O_6
$Mo_{12}Bi_{1.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	MoO_3, BiO_3, WO_3, $Bi_{38}Mo_7O_{78}$
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}K_{0.06}Si_{1.4}O_x$	MoO_3, BiO_3, Bi_2O_3, α-$Bi_2Mo_3O_{12}$, $CoMoO_4$
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.4}K_{0.06}Si_{1.4}O_x$	MoO_3, BiO_3, WO_3, α-$Bi_2Mo_3O_{12}$, $CoMoO_4$
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	MoO_3, BiO_3, WO_3, α-$Bi_2Mo_3O_{12}$, $CoMoO_4$
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{2.4}K_{0.06}Si_{1.4}O_x$	MoO_3, BiO_3, WO_3, α-$Bi_2Mo_3O_{12}$, $CoMoO_4$
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.12}Si_{1.4}O_x$	MoO_3, BiO_3, WO_3, α-$Bi_2Mo_3O_{12}$, $CoMoO_4$
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.18}Si_{1.4}O_x$	MoO_3, BiO_3, α-$Bi_2Mo_3O_{12}$, $CoMoO_4$
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$	MoO_3, BiO_3, WO_3, α-$Bi_2Mo_3O_{12}$, $CoMoO_4$, $FeMoO_4$, $Fe(MoO_4)_3$, $Bi_3FeMo_2O_{12}$, $MoOPO_4$, $Bi_9PMo_{12}O_{52}$

Bismuth is an important component in the molybdate-based catalysts for selective oxidation of propylene. Here bismuth component presented as BiO_3 and Bi_2O_3 also in binary system as α-$Bi_2Mo_3O_{12}$, $Bi_{38}Mo_7O_{78}$ and in ternary system as $Bi_3FeMo_2O_{12}$, $Bi_9PMo_{12}O_{52}$. Bismuth free catalyst in fact has a very low selectivity to acrolein (Udalova et al. 2005).

Table 3.5 indicates that the XRD of catalysts contained tungsten element showed the presence of WO_3 phases. As WO_3 is also group VI transition metal, therefore it have similar function as the MoO_3 i.e. improves the activity and selectivity of the catalyst in selective oxidation of propylene to acrolein (Weng, Sham, Doumain, Ruiz & Delmon 1990; Weng & Delmon 1992 as cited in (Carrazan et al. 1996a)).

The existence of bismuth molybdate oxide catalysts as the α, β, and γ-phases are very selective to acrolein (Udalova et al. 2005). Among ten catalysts listed in Table 3.5 only the $Mo_{12}Bi_{1.5}K_{0.06}Si_{1.4}O_x$ and $Mo_{12}Bi_{1.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ catalysts did not contain α -$Bi_2Mo_3O_{12}$. Therefore the absence of α -$Bi_2Mo_3O_{12}$ can be used to explain why the screening results of these two catalysts did not indicate any acrolein yield formation over the experimental conditions at 300-450°C (Table 3.3).

Catalysts with cobalt element showed the presence of $CoMoO_4$ in the XRD pattern. Multi-component catalysts with an $MMoO_4$ framework (M = Co, Ni, Mg or Mn) were the very active in the partial oxidation of propylene and $CoMoO_4$ was the most active and selective framework to facilitate the acrolein formation (Udalova et al. 2005). Therefore the catalysts in Table 3.3 with cobalt had reasonably high activity and selectivity toward acrolein up to 80%.

Moro-Oka et al. believed that cobalt molybdates worked more effectively to improve the catalyst performance with the existence of iron molybdates in the multiphase catalysts. The addition of iron in the cobalt molybdate, which was used for the support of bismuth molybdate catalyst, increased the catalytic activity and/or selectivity to acrolein (Moro-Oka, He & Ueda 1990; Moro-Oka & Ueda 1994 as cited in (Carrazan et al. 1996a)).

Iron can exist as binary systems either with molybdate as $Fe_2(MoO_4)_3$ and $FeMoO_4$, which both effectively perform the oxygen(s) and electron(s) transfers (Ponceblanc et al. 1993; Benaichouba et al. 1995; Udalova et al. 2005) or with bismuth as $BiFeO_3$ or $Bi_2Fe_4O_9$ (Annenkova, Alkhazov & Belen'kii 1969 as cited in (LoJacono et al. 1975)). Iron also exists as ternary Bi-Fe-Mo system as $Bi_3FeMo_2O_{12}$ and

$Bi_2Fe_2Mo_2O_{12}$, which could create more active and stable catalysts (Daniel & Keulks 1973; LoJacono et al. 1975; Notermann et al. 1975).

The abovementioned finding in two previously paragraphs could be used as an explanation on the high activity and selectivity of the best performing catalyst, $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$, as it contained $FeMoO_4$, $Fe(MoO_4)_3$ and $Bi_3FeMo_2O_{12}$ phases in the presence of $CoMoO_4$ framework. High catalytic performance of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$ catalyst (95% acrolein selectivity at $350^{o}C$) was also contributed by the presence $Bi_9PMo_{12}O_{52}$, which was believed to be active and selective for partial oxidation of propylene since the discovery by SOHIO in 1975 (Ohara et al. 1985) until now (Fansuri et al. 2003). Many scientists believe that the presence of phosphorous increases the acidity of catalyst therefore increase the conversion of hydrocarbon (Kaddouri et al. 1999, Chang et al. 2001).

3.3 CATALYST REPRODUCIBILITY

As the targeted catalyst, $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ was reproduced in many batches. The screening results of five batches of this catalyst (including the original one) are presented here. The amounts of chemicals used for preparation of these catalysts are listed in Table 3.6 together with the experimental conditions for the screening test.

It should be noted that the catalyst production for the forth batch was about four times larger than the original production. For production of such size, a jacket stainless steel reactor of 15 cm diameter and 20 cm height with a four-blade impeller was designed for the precipitator. The reactor was warmed and kept at $60^{o}C$ using a water bath. It was verified that the scale up procedure and instrument was capable to produce catalyst of repeatable catalytic excellence.

Table 3.6:   Chemical quantities for reproduction of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst and experimental condition for screening test

Quantity of chemicals required for the catalyst reproduction					
Chemical name (unit measurement)	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Ammonium Molybdate Tetrahydrate (g)	38.19	190.95	190.95	723.05	38.17
Bismuth (III) Nitrate Pentahydrate (g)	12.68	63.41	63.41	240.10	12.63
Iron (III) Nitrate Nonahydrate (g)	6.08	30.38	30.38	115.38	6.05
Cobalt (II) Nitrate Hexahydrate (g)	18.26	91.31	91.34	345.70	18.27
Tungsten (VI) Oxide (g)	2.39	11.93	11.93	39.00	2.39
Potassium Hydroxide (0.24mol/l) (ml)	2.70	13.50	13.50	51.00	2.70
LUDOX^R HS-40 Colloidal Silica (40 wt%) (g)	3.65	18.25	18.25	69.10	3.70
Phosphoric Acid (85 wt%) (ml)	0.80	4.00	4.00	15.00	0.80
Final catalyst powder produced (g)	61.06	239	234	1150	59.24
Catalyst bed specification and experimental conditions for screening test					
Catalyst bed: Volume (ml)	5	5	5	5	5
Weight (g)	3.60	3.89	4.06	4.40	4.31
Reaction pressure (atm)	1	1	1	1	1
Reaction temperature (^{o}C)	300-450	300-450	300-450	300-450	300-450
Total flow rate (ml/min)	120	120	120	120	120
Gas composition (vol%): Propylene	5	5	5	5	5
Oxygen	10	10	10	10	10
Helium	85	85	85	85	85

The screening test results for five batches of catalyst are plotted in Figures 3.23-3.27, and the discrepancies within the data are tabulated in Table 3.7
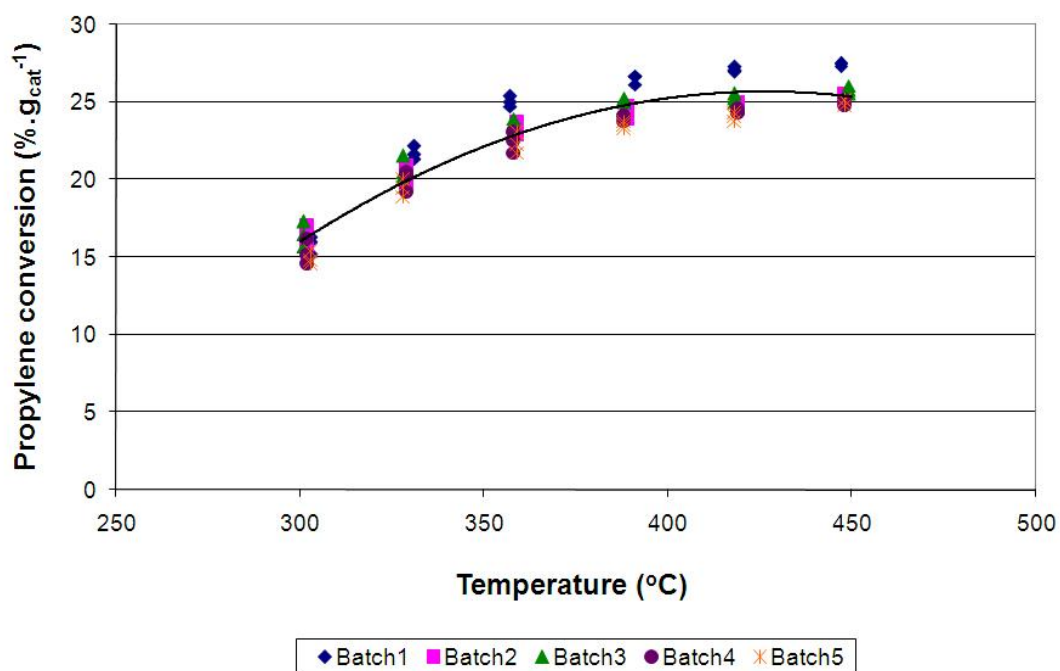
Figure 3.22:   Screening results of five batches of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst in terms of propylene conversion
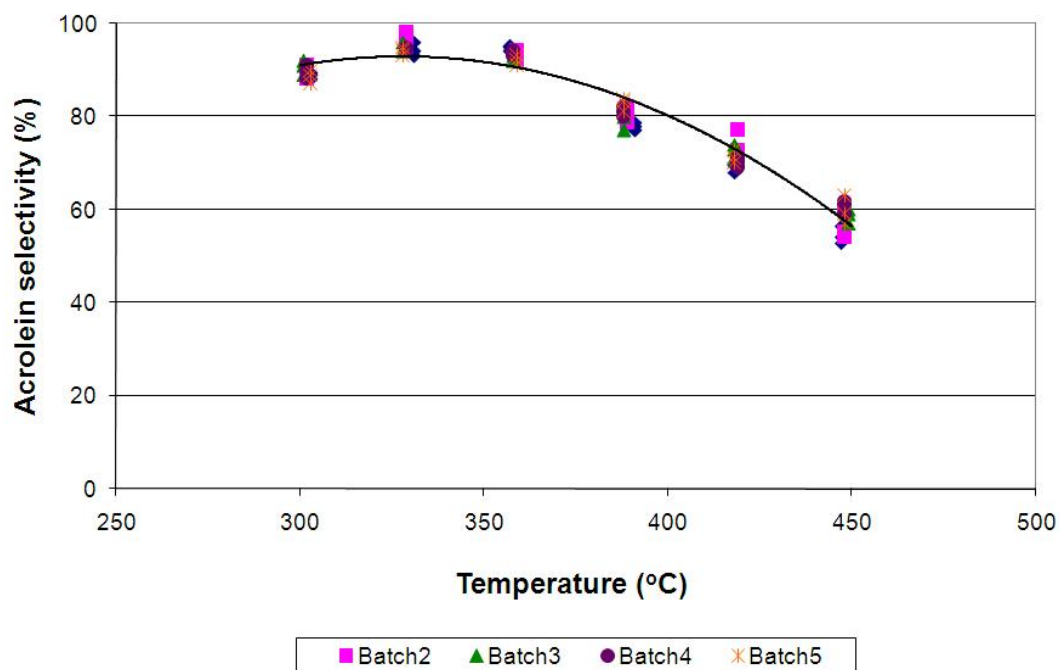
Figure 3.23:   Screening results of five batches of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst in terms of acrolein selectivity
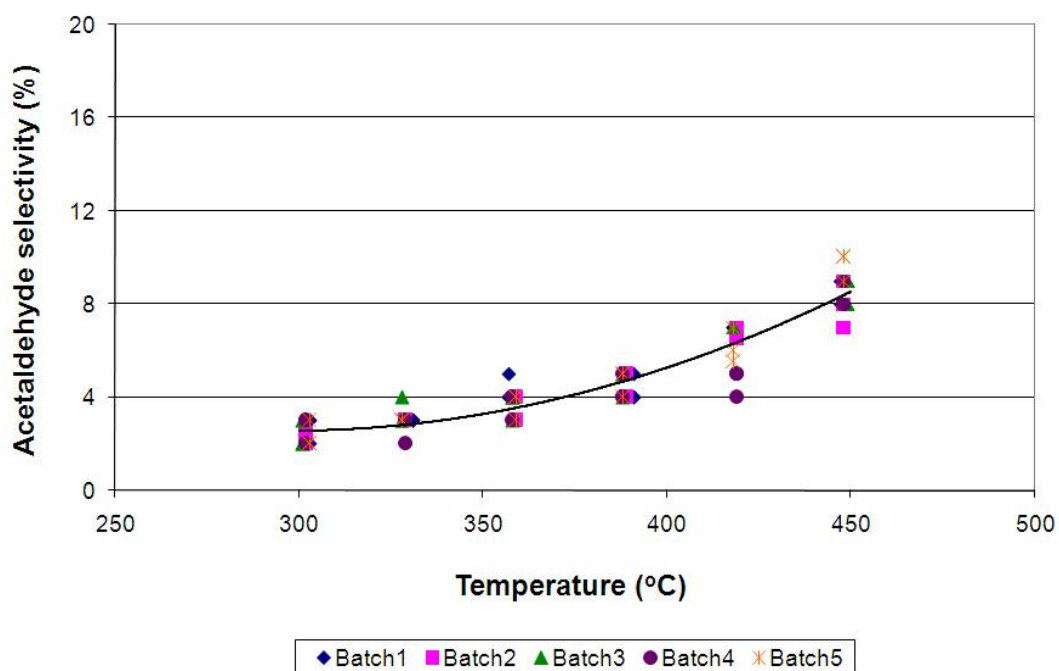
Figure 3.24:   Screening results of five batches of
Mo$_{12}$Bi$_{1.5}$Fe$_{0.8}$Co$_{3.5}$Si$_{1.4}$K$_{0.04}$W$_{0.6}$P$_{0.7}$O$_x$ catalyst in terms of
acetaldehyde selectivity
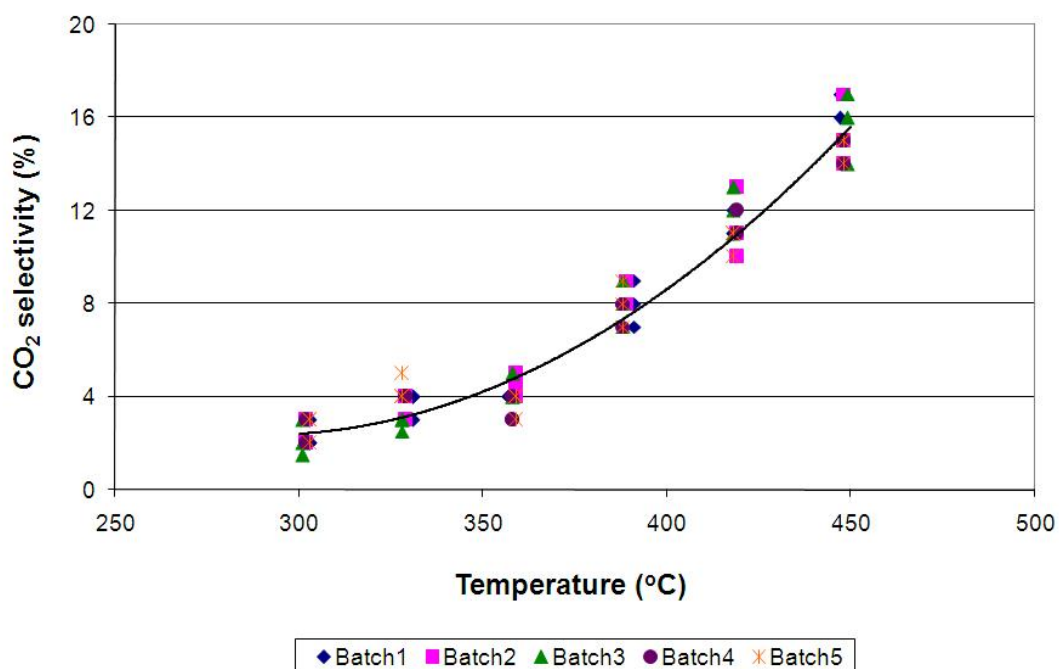
Figure 3.25:   Screening results of five batches of
Mo$_{12}$Bi$_{1.5}$Fe$_{0.8}$Co$_{3.5}$Si$_{1.4}$K$_{0.04}$W$_{0.6}$P$_{0.7}$O$_x$ catalyst in terms of carbon
dioxide selectivity
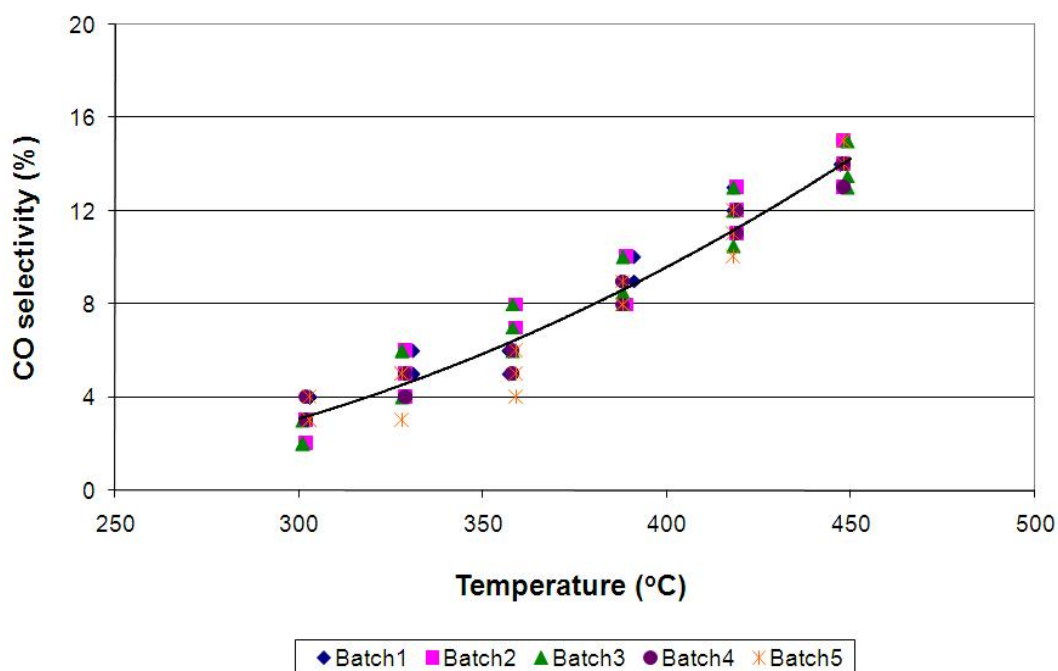
Figure 3.26: Screening results of five batches of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst in terms of carbon monoxide selectivity

Table 3.7: Percentage difference in screening results of five batches of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst

Temperature (^{o}C)	Difference in screening results between five batches (%)				
	Propylene conversion	Selectivity			
		Acrolein	Acetaldehyde	CO_2	CO
300	10	3	23	37	36
330	9	3	33	35	38
360	9	2	32	26	34
390	8	5	12	13	12
420	9	8	14	15	15
450	7	9	15	10	7

At the same reaction temperature, the difference in propylene conversion and selectivity to acrolein were within 10% over 300-450°C. The difference in production of by-products (acetaldehyde and carbon oxides) could be explained in two temperature range with reference of 360°C. At higher temperature range than 360°C, the difference in percentage selectivities of by-product was within 15% at the

same reaction temperature. However at lower temperature range, the difference reached 38%. The limitation of GC in analysis low concentration products might also contribute in high fluctuation of screening data.

In conclusion, the screening data showed that procedure of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst preparation was repeatable and reliable within 10% discrepancy in terms of conversion of initial propylene feed and selectivity to targeted product (acrolein).

3.4 EFFECT OF USING TYPICAL PROPYLENE FEEDSTOCK FROM THE REFINERY BY-PRODUCT WITHOUT PRIOR PURIFICATION AS FEED GAS

Experiencing difficulty in securing a supply of pure propylene during this project had become the main reason behind the preliminary investigation of using lower purity propylene feedstock as the feed gas. Typical propylene feedstock, which is abundantly available from the by-product refineries, consists of 66% propene, 30% propane and 4% other hydrocarbon components. If the selected catalyst $(Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x)$ proves having consistent catalytic performance when using lower purity propylene as the feed gas, then it would have been economically attractive as the typical propylene feedstock from the by-product of refineries can be used without prior purification.

Table 3.8 presents the catalyst specification and the experiment conditions used for study the effect of typical propylene feedstock from refineries over the selected catalyst. The results are plotted in Figures 3.28-3.32.

Table 3.8:   Catalyst specification and experimental condition for study the effect of typical propylene feedstock from refineries as feed gas

Catalyst specification		
Catalyst	$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$	
Type	Powder	
Weight	4.465 g	
Volume	5 ml	
Experimental condition	Test condition set 1 & set 2	
Total gas flow	120 ml/min	
Feedstock Propylene Propane & other impurities Oxygen Helium	99% C_3H_6 4.8% - 9.9% 85.3%	66% C_3H_6 4.8% 2.5% 9.9% 82.8%
Pressure	1 atm	
Temperature	250-450°C	
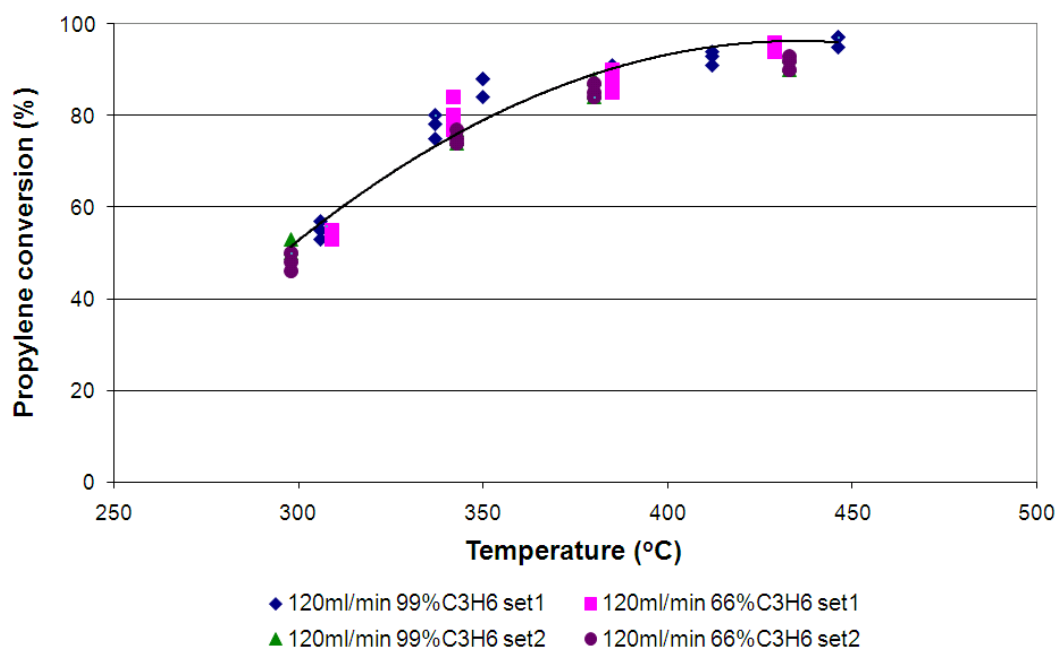
Figure 3.27:   Effect of using typical propylene feedstock from refinery by-product as the feed gas over $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst on propylene conversion
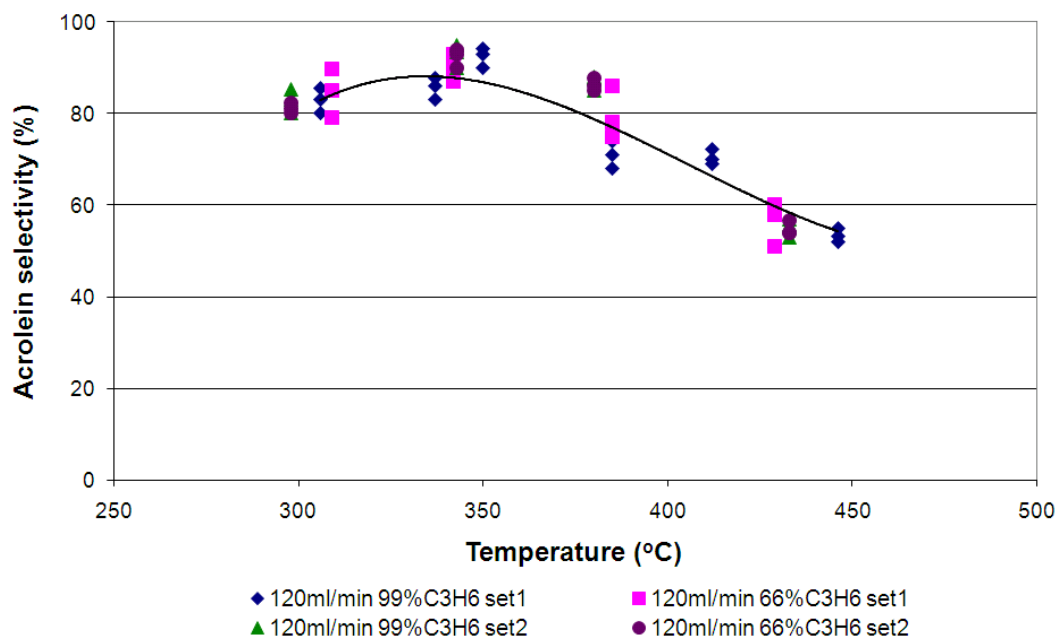
Figure 3.28:   Effect of using typical propylene feedstock from refinery by-product as the feed gas over $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst on acrolein selectivity
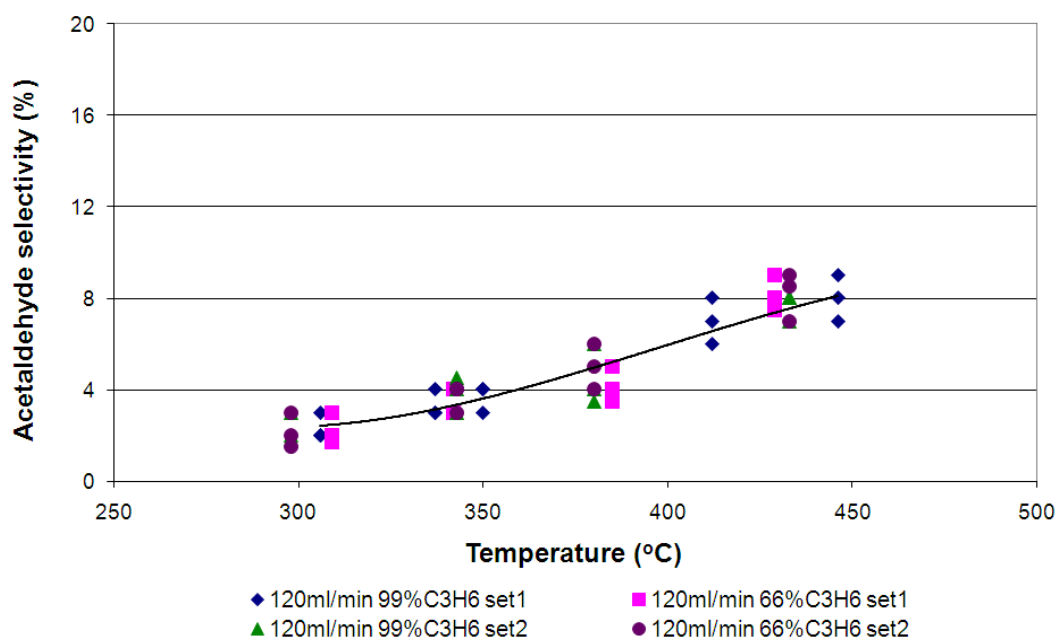
Figure 3.29:   Effect of using typical propylene feedstock from refinery by-product as the feed gas over $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst on acetaldehyde selectivity
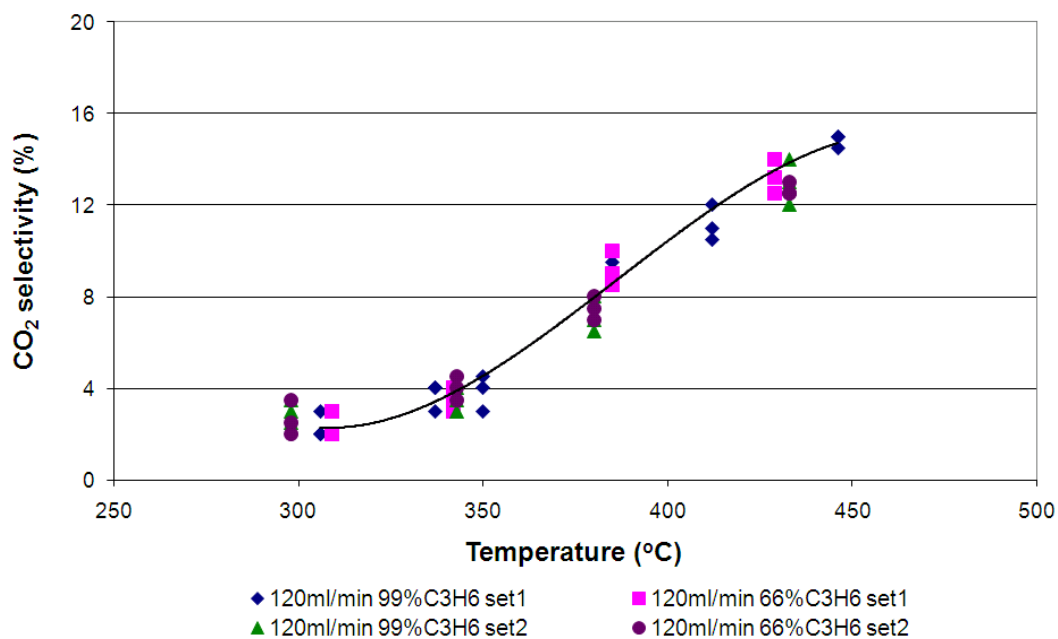
Figure 3.30:   Effect of using typical propylene feedstock from refinery by-product as the feed gas over $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst on carbon dioxide selectivity
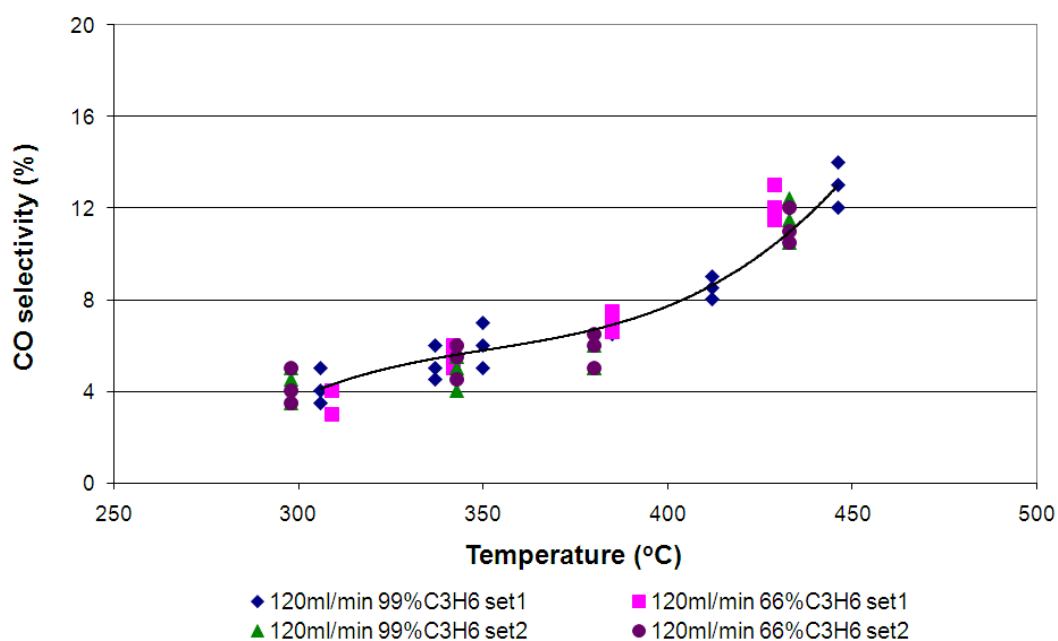
Figure 3.31:   Effect of using typical propylene feedstock from refinery by-product as the feed gas over $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst on carbon monoxide selectivity

There were no significant effects observed using the propylene feedstock with up to 34% impurity content as the feed gas over the selected $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.4}K_{0.04}W_{0.6}P_{0.7}O_x$ catalyst. All components detected as a result of catalytic oxidation of 66% propylene feedstock were also detected in that of high purity propylene.

The screening results in terms of two most important catalytic properties (the conversion of initial propylene and the selectivity to acrolein) indicated $\pm$ 5% relative error. However the results in terms of selectivity to detected by-products (acetaldehyde, carbon dioxide and carbon monoxide) showed up to $\pm$ 20% relative error at temperature lower than $350^{\circ}C$. Relatively high fluctuations for the by-product selectivities were mainly due to GC analysis error at very low concentration of side products.

3.5 RATE OF REACTION USING DIFFERENTIAL REACTOR

Study of rate of reaction for experimental parameter optimization was carried out in a 1 cm in diameter of tubular quartz reactor (Figure 3.4), which was operated based on differential method. The differential method was selected so that the data can be further utilised as preliminary input in study of reaction kinetics. However the differential reactor has two limitations, i.e. the channelling problem and the difficulty in sampling and analysis. The channelling problem may be anticipated by using a transparent inert reactor that can withstand high temperatures such as quartz. Using a transparent type of reactor enables the operator to observe the catalyst bed, then to ensure that the bed is in good arrangement and the reactants can pass through the bed uniformly. The inaccuracy in sampling and analysis for a low conversion system can be minimised by connecting the reactor system online to the GC that has an appropriate sample loop installed and performing regular calibrations.

In order to obtain reliable data using a differential, plug flow reactor model, several criteria have to be satisfied. First, the diameter of the tube has to be at least ten times larger than the diameter of the catalyst particles to perform a uniform gas flow (Larsen 2003). Second, the size of the catalyst charge has to be kept small to

minimise the possibility of developing temperature gradients in the catalyst bed. Third, the conversion level must be kept sufficiently low so that differential rate data can be obtained directly.

To satisfy the above criteria, the rate reaction study over temperature range of 300-450°C was carried out a total flow rate of 120 ml.min^{-1} in a quartz reactor and only 0.09 g of the selected catalyst powder, $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}Si_{1.3}K_{0.04}W_{0.6}P_{0.7}O_x$, was used in order to maintain a conversion level below 10%. The BET surface area of this catalyst was 21 m^2.g^{-1}. Prior to experiments, the catalysts were lined-out for several hours to ensure a steady-state reaction was reached before any data was taken. Periodically activity checks were done during experiment to determine if any deactivation had occurred. It was also important to ensure that no gas phase reaction between propylene and oxygen as well as no condensation of gases were happened during the study. The method of data analysis was similar to the screening tests (Section 3.1.2) using GC as the analysis instrument. At least three data were taken at each experiment conditions.

Table 3.9: Concentrations of reactants used in study of the rate of reaction for optimisation reaction parameters

Molar ratio of C_3H_6 to O_2	% Volume		
	C_3H_6	O_2	He
Determination of optimum concentration of oxygen			
1.0:0.75	5.00%	3.75%	91.25%
1.0:1.0	5.00%	5.00%	90.00%
1.0:1.5	5.00%	7.50%	87.50%
1.0:2.0	5.00%	10.00%	85.00%
1.0:2.5	5.00%	12.50%	82.50%
1.0:3.0	5.00%	15.00%	80.00%
Determination of optimum concentration of propylene			
1.0:3.0	3.33%	10.00%	86.67%
1.2:3.0	4.00%	10.00%	86.00%
1.5:3.0	5.00%	10.00%	85.00%
2.0:3.0	6.67%	10.00%	83.33%
3.0:3.0	10.00%	10.00%	80.00%
4.0:3.0	13.33%	10.00%	76.67%
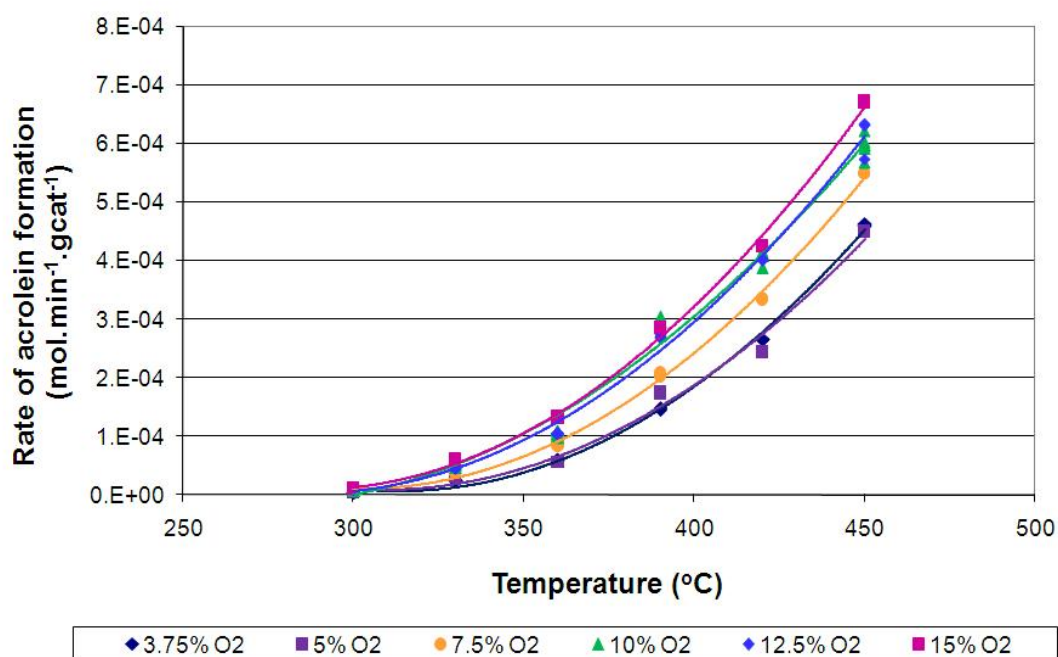
Figure 3.32: Rate of acrolein formation at constant propylene composition of 5% at 120ml.min^{-1} total flow rate over the Mo$_{12}$Bi$_{1.5}$Fe$_{0.8}$Co$_{3.5}$W$_{0.6}$K$_{0.04}$Si$_{1.4}$P$_{0.7}$O$_x$ catalyst
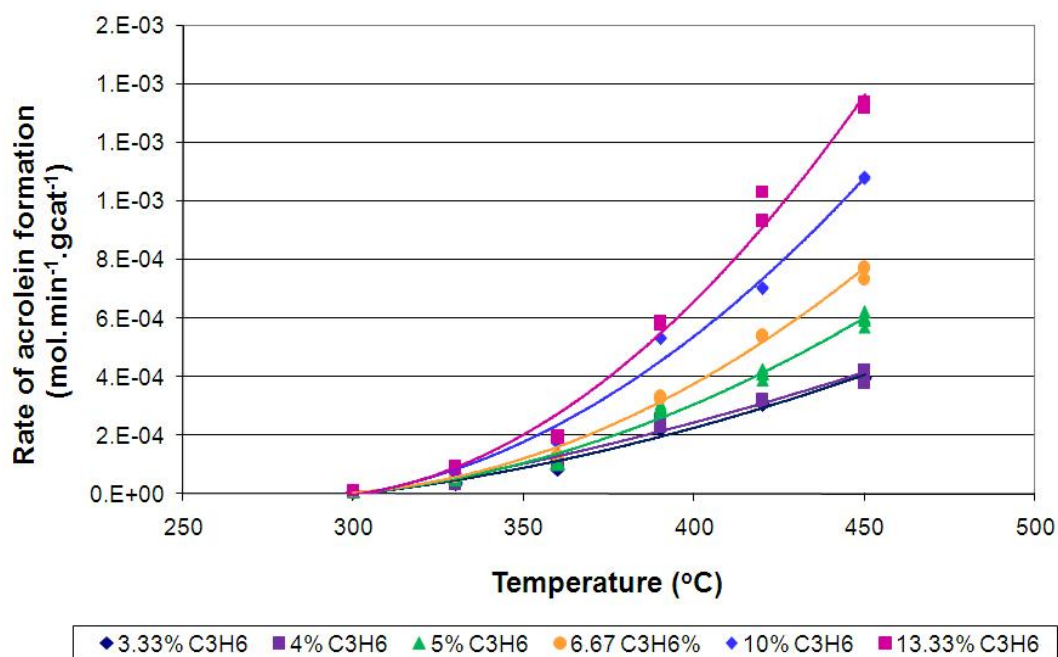
Figure 3.33: Rate of acrolein formation at constant oxygen concentration of 10% at 120ml.min^{-1} total flow rate over the Mo$_{12}$Bi$_{1.5}$Fe$_{0.8}$Co$_{3.5}$W$_{0.6}$K$_{0.04}$Si$_{1.4}$P$_{0.7}$O$_x$ catalyst

As can be observed in Figure 3.33, the trends of acrolein formation rate at constant propylene concentration (i.e. 5% at total flow rate of 120ml.min^{-1}) significantly improved when increased the oxygen compositions from 5% to 10%. However, no noteworthy improvement in acrolein formation was observed when the oxygen composition increased up to 15%. Therefore, 10% could be said as the optimum parameter for oxygen concentration.

At constant 10% oxygen, the increase in propylene concentrations was generally increased the acrolein formation (Figure 3.34). However at temperature less than 360°C, the increase in propylene concentration from 5% to 13.3% was not significant. As reaction temperature of 350°C was of particular interest, the data for formation of acrolein and other products at this temperature are summarised in Table 3.10.

Table 3.10:   Rate of reaction at reaction temperature of 350°C at 120ml.min^{-1} and constant oxygen composition of 10%

Propylene (%)	Average rate of reaction (mol.min^{-1}.g$_{cat}^{-1}$)			
	Acrolein	CO_2	CO	Acetaldehyde
3.33%	6.76×10^{-5}	1.04×10^{-5}	3.12×10^{-6}	5.14×10^{-7}
4.00%	8.18×10^{-5}	1.17×10^{-5}	3.96×10^{-6}	4.75×10^{-7}
5.00%	1.41×10^{-4}	1.47×10^{-5}	4.49×10^{-6}	7.26×10^{-7}
6.67%	1.46×10^{-4}	1.71×10^{-5}	5.19×10^{-6}	8.18×10^{-7}
10.00%	1.45×10^{-4}	2.06×10^{-5}	7.13×10^{-6}	1.10×10^{-7}
13.33%	1.51×10^{-4}	3.06×10^{-5}	8.20×10^{-6}	1.27×10^{-6}

The rate of acrolein formation at 350°C (Table 3.10) indicated that the formation of acrolein within propylene concentration of 5% – 13.33% were only improved by 7%, which was approximately within the 10% GC error range, therefore the difference can be said insignificant. In addition to the aforementioned result, the 5% was selected as the optimum propylene concentration in addition due to economical reason (i.e. price of propylene feedstock).

The experimental study on the differential reactor was therefore included that the 5% propylene cund 10% oxygen was the optimum concentration composition for the acrolein formation. The trends of the formation of by-products at this optimum

composition of reactants at total flow rate of 120 ml.min^{-1} are plotted in Figures 3.35–3.37.
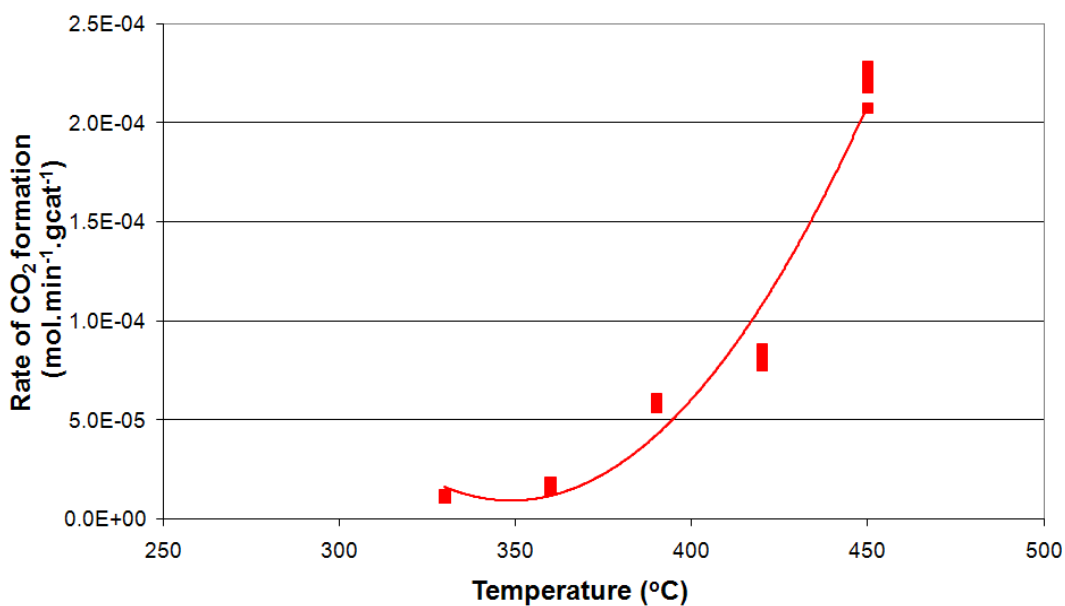
Figure 3.34: Rate of carbon dioxide formation at 5% propylene and 10% oxygen of 120ml.min^{-1} total flow rate over the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst
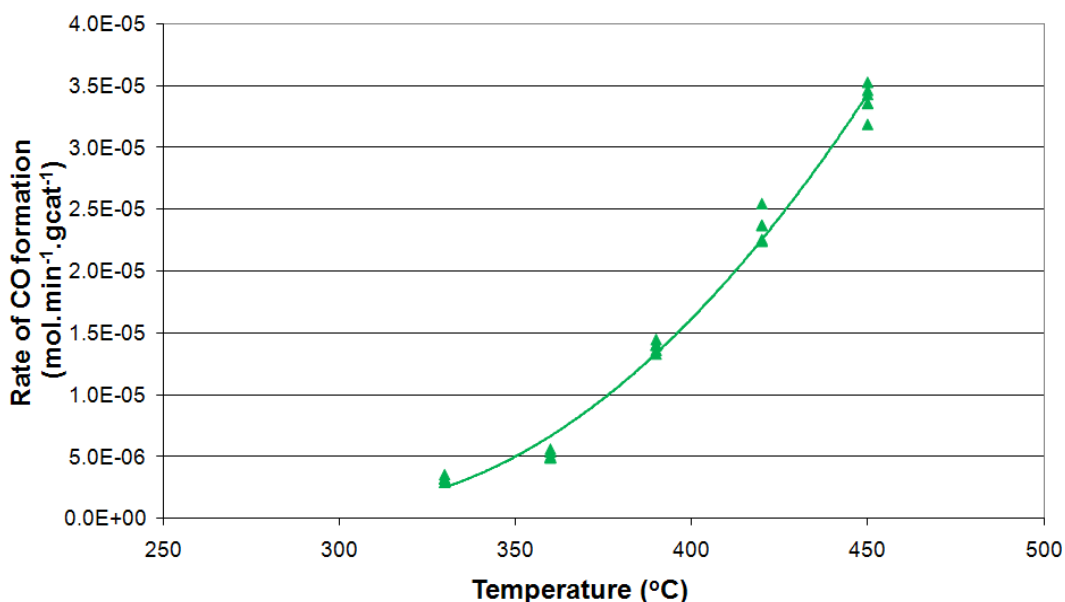
Figure 3.35: Rate of carbon monoxide formation at 5% propylene and 10% oxygen of 120ml.min^{-1} total flow rate over the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst
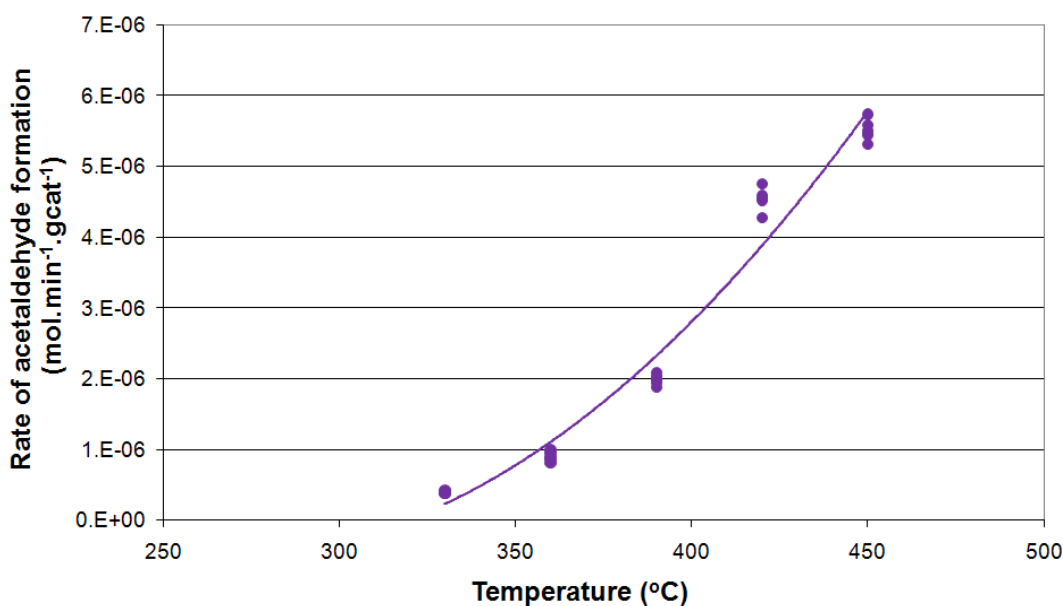
Figure 3.36: Rate of acetaldehyde formation at 5% propylene and 10% oxygen of
120ml.min^{-1} total flow rate over the
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst

3.6 CONCLUSIONS ON CATALYST DEVELOPMENT

The $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst achieved the targeted performance, i.e. 95% selectivity to acrolein at temperature of 350^oC. The techniques in catalyst preparation have proven to be practical. This catalyst also demonstrated the reliability to maintain high activity and selectivity when using a typical propylene feedstock from by-product in refineries without prior purification as the feed gas. Therefore this catalyst certainly owned attractive industrial values.

The study of reaction rate using a differential reactor at total flow rate of 120ml.min^{-1} concluded that 5% propylene and 10% oxygen was the optimum concentration of reactant at reaction temperature of 350^oC. Therefore further investigation on the application of the best performance catalyst in the fixed bed industrial reactor (Chapter 4) was based on the above mentioned optimum condition. The data on the reaction rate can be used as preliminary data for future work in the kinetics study.

CHAPTER 4

CATALYSTS FOR APPLICATION
IN FIXED BED REACTOR

A fixed bed reactor is the most common reactor type for the production of acrolein from oxidation of propylene (as discussed in literature review). The catalyst produced from precipitation method, as described in Chapter 3, was in the form of powder and therefore it had to be physically modified into a suitable catalyst particle size in order to minimise the pressure drop in the fixed bed reactor. This chapter describes the production of two types of the catalysts for fixed bed reactor: the coated catalyst spheres and the cylindrical catalyst pellets. The final form of catalysts should have acceptable physical strength to withstand pressure when loading or unloading the catalyst into or out of the reactor, as well as still produce an adequate level of propylene conversion to acrolein. Therefore all catalysts had to go through a series of screening test for characterisation of the activity properties. The catalysts that had a reasonable activity and selectivity were then tested into a series of in-house physical strength tests for relatively justifying the ability of catalysts to withstand pressures.

4.1 COATED CATALYSTS

4.1.1 PREPARATION PROCEDURE OF COATED CATALYSTS

The quality of coated catalyst is influenced by not only the coating procedure, but also the selection of coating components such as the catalyst carrier, binder and pore former. Catalyst carriers are usually inert and available in various forms, particle

sizes, surface areas and pore size distributions. This project was carried out using two types of commercial carriers: 3 mm in diameter Al_2O_3 from Sigma Aldrich and 1 mm in diameter Al_2O_3 from Alcoa.

A binder was used to help the catalyst powder anchor onto the surface of the carrier. In this work, the most common binder, glucose and the possible binder type, high temperature cement (Extra-strength High Alumina Castable CAST 15 ES from Matthew) were tested separately. No literature has been found about using high temperature cement as the catalyst binder. In addition, the pentaerythriol ($C_5H_{12}O_4$) was added as a pore former to improve the porosity of the coated catalysts (You et al. 2001; Allen et al. 2002 & 2003). The amount of pentaerythriol added into the catalyst solution was approximately 5 weight % of the parent catalyst powder.

Three techniques of coating were used in this project. Their procedures were similar and can be summarised as follows. It began with weighing a specified volume of Al_2O_3 spheres. On a separate container, a mixture of catalyst powder, catalyst binder and pore former were mixed thoroughly and made into a homogeneous suspension with addition of distilled water. This suspension was then used to coat the Al_2O_3 spheres on the specified coating instrument. The coating process was done with the help of a manual stirrer, i.e. the operator holds a small stainless steel stick to stir the mixture of catalyst suspension and Al_2O_3 spheres. After the Al_2O_3 spheres were uniformly coated with the catalysts, they were calcined at the catalyst calcination temperature of 450°C for two hours. It was also proven later in the results on catalytic performance and physical strength tests on the coated catalysts (Section 4.1.4.1) that the higher calcined temperatures up to 600°C was not significantly different from those calcined at 450°C. Therefore 450°C was regarded to be the optimised calcination temperature for the coated catalysts.

For the purpose of distinguishing the different batches of coated catalysts; each batch was named using "CC-coating technique-batch number". For example CC-1-1 means coated catalysts prepared based on coating technique 1 and batch 1. Three coating techniques were employed in this project.

4.1.1.1 COATING TECHNIQUE 1

The first coating technique was carried out in the very simple instrument set up consisting of a Pyrex dish on top of a sand bath that was heated on top of an electric hot plate as illustrated in Figure 4.1. The temperature at the surface of the sand bath was approximately 70°C. Two batches of coated catalysts, namely CC-1-1 and CC-1-2, were prepared based on this technique. The specifications of these coated catalysts are tabulated in Table 4.1.
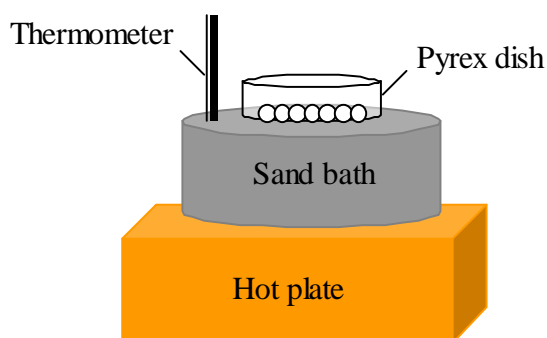
Figure 4.1:   Equipment set up for coating technique 1

Using similar initial compositions of ingredients (i.e. the similar amount of initial weight of catalyst carrier, same parent catalyst, binder and pore former), the final coated catalysts in both batches were different in terms of the catalyst loading on the carrier, i.e. 23.4 % for batch 1 and 13.9 % for batch 2. The inconsistency in the final catalyst loading might be due to the following reasons. Firstly, the direct contact of the Pyrex dish to the hot sand bath caused the temperature at the bottom of the dish was higher than that of the surface of Al_2O_3 beads, which caused the water in the catalyst mixture at the dish evaporated quicker than that around the beads. Consequently much catalyst was lost without had chanced to stick onto the beads. Secondly, the manual skill used in the shaking or rotating the Pyrex dish that contained the catalyst carrier and the coating solution could be the reason in inconsistency in the results. The first coating technique could only accommodate limited size of production (less than 10 g) and the procedure was found to be time consuming and labour intensive.

Table 4.1:   Specifications of coated catalyst prepared based on technique 1

ID of the coated catalysts	CC-1-1	CC-1-2
Specification of the catalyst carrier:		
Name of the catalyst carrier	3 mm in diameter of Al_2O_3 spheres	
Approximate volume of the cat carrier (ml)	10	10
Initial weight of the catalyst carrier (g)	6.2130	6.3806
Specification of the initial solution for coating:		
Formula of the parent catalyst powder	$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$	
Initial weight of the catalyst powder (g)	3.1240	3.2051
Name of the catalyst binder	Glucose	
Initial composition of binder (as wt % of cat)	5	5
Initial weight of the binder (g)	0.1601	0.1600
Name of the pore former	Pentaerythritol	
Initial weight of the pore former (g)	0.1613	0.1620
Volume of distilled H_2O (ml)	4	4
Specification of the final coated catalysts after calcination at 450^oC for 2 hours:		
Total weight of the final coated catalysts (g)	8.1142	7.4186
Loading of catalyst on the carrier (weight %)	23.4	13.9
Loading of binder on the carrier (weight %)	0	0

4.1.1.2 COATING TECHNIQUE 2

Based on the limitations of the first coating technique, different instrument set up was designed for the second coating technique (Figure 4.2). It was carried out using a 250 ml glass beaker rotated at 20 rpm on a sand bath of 70°C. Having a 250 ml glass beaker instead of a Pyrex dish for the coating container made it possible for a larger production (up to 50 g of coated catalysts per batch). A motor was installed in order to replace the manual involvement in rotating the beaker that contained the beads and the catalyst mixture. Having a motor to do the rotation of the beaker certainly reduced the dependency on the manual skill. In addition it also made the coating process quicker and the catalyst coated onto the beads uniformly.
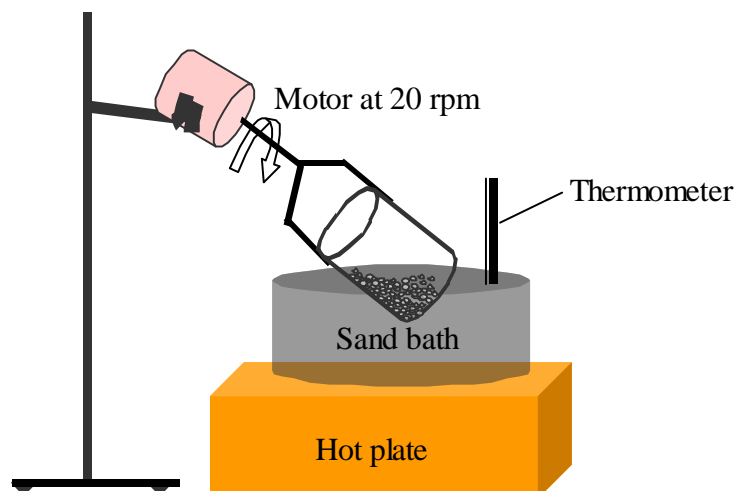
Figure 4.2:　Equipment set up for coating technique 2

Table 4.2 presents the specifications of eight batches of coated catalysts prepared with the parent catalyst of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ based on the second technique. Four batches (CC-2-1 to CC-2-4) were coated around 3 mm Al_2O_3 beads, in which all of them were coated with high temperature cement as the binder. The other four batches were coated around 1 mm Al_2O_3 beads, in which two of them were coated with high temperature cement (CC-2-5 and CC-2-7) and the rest were coated with glucose (CC-2-6 and CC-2-8) as the binder.

It should be noted that unlike glucose that was burnt during the calcination process, the high temperature cement was stayed in the final coated catalyst even after calcination at high temperature. The final composition of the binder was therefore the same as the initial one. For example CC-2-1, which had the initial catalyst solution consisted of binder whose amount was equal to 5 weight % of catalyst powder, had final composition of component loading on the carrier: 25.8% of catalyst and 1.3% of binder. It should be noted that 1.3% binder loading was equivalent to 5% of 25.8% catalsyt loading.

Using the coated catalysts prepared based on the first and second techniques as listed in Tables 4.1 and 4.2, the effects of the following preparation parameters were studied: the temperature of final calcination (Section 4.1.2.1), the size of catalyst carrier (Section 4.1.2.2) and the types of binder (Section 4.1.2.3.1).

Table 4.2: Specifications of coated catalysts prepared based on the coating technique 2

ID of the coated catalyst	CC-2-1	CC-2-2	CC-2-3	CC-2-4	CC-2-5	CC-2-6	CC-2-7	CC-2-8
Specification of the catalyst carrier:								
Diameter of Al_2O_3 spheres (mm)	3 mm in diameter of Al_2O_3 spheres				1 mm in diameter of Al_2O_3 spheres			
Approximate volume of the catalyst carrier (ml)	5	5	5	5	5	5	10	10
Initial weight of the catalyst carrier (g)	3.9470	3.1279	3.1241	3.1261	4.5855	4.8712	8.8274	8.8518
Specification of the initial solution for coating:								
Formula of the parent catalyst powder	$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$							
Initial weight of the catalyst powder (g)	3.4556	1.020	1.1007	1.0986	3.5572	3.7572	1.5492	1.5955
Name of the catalyst binder (HTC=High Temperature Cement; G=Glucose)	HTC	HTC	HTC	HTC	HTC	G	HTC	G
Initial composition of binder (as wt % of catalyst)	5	5	5	5	10	10	5	5
Initial weight of the binder (g)	0.1710	0.0502	0.0552	0.0598	0.3000	0.3741	0.0821	0.0779
Name of the pore former	Pentaerythritol							
Initial weight of the pore former (g)	0.1553	0.0500	0.0543	0.0530	0.1700	0.1824	0.0723	0.0743
Volume of distilled H_2O (ml)	5	3	3	3	4	4	6	6
Specification of the final coated catalysts after calcination at specified temperature for 2 hours:								
Calcination temperature (^{o}C)	450	450	500	600	450	450	450	450
Total weight of final coated catalysts (g)	5.4098	3.7108	3.7850	3.7479	6.2893	6.5719	10.1764	10.1777
Loading of catalyst on carrier (weight %)	**25.8**	**15.0**	**16.6**	**15.8**	**25.8**	**25.8**	**12.6**	**13.0**
Loading of binder on carrier (weight %)	1.3	0.8	0.8	0.8	2.6	0	0.7	0

4.1.1.3 COATING TECHNIQUE 3

The third instrument set up was similar to the second one. Likewise the second technique, the third coating technique also used a 250 ml glass beaker rotated at 20 rpm as the coating container. The difference was that the third coating method uses the hot air (from 1500 W hair drier) to dry the coated catalysts rather than the hot sand bath. The equipment set up of coating technique 3 illustrates in Figure 4.3.
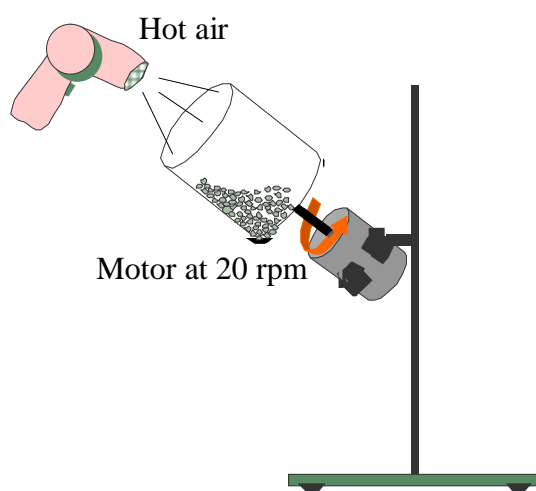
Figure 4.3:   Equipment set up for coating technique 3

Table 4.3 displays the specifications of coated catalysts prepared with the parent catalyst of $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ based on the third technique. Using hot air was found to be more effective to evaporate the water in the catalyst solution as the hot air created a uniform temperature around and inside the glass beaker therefore it also reduced the amount of catalyst loss during the coating process significantly. Less amount of catalyst loss during the third coating technique was indicated by comparing the catalyst loading of CC-3-1 to that of CC-2-1. Both of these coated catalysts were prepared based on the similar initial compositions (CC-2-1: 3.9470 g of 3 mm Al_2O_3 beads, 3.4556 g of catalyst powder, and 0.171 g of high temperature cement; and CC-3-1: 3.3172 g of 3 mm Al_2O_3 beads, 3.3809 g of catalyst powder and 0.17 g of high temperature cement). The catalyst loading in the final coated catalysts were 25.7% for CC-2-1 and 37.0% for CC-3-1. The results showed that the coated catalysts prepared by the third technique (CC-3-1) had more catalyst loading and therefore less catalyst loss during the coating process if it

compare to that prepared by the second technique (CC-2-1). The third technique was also proven to be repeatable (CC-3-1 to CC-3-6) in using both types of binder, as the final specifications of these coated catalysts were very similar, i.e. (36.3 ± 0.8) % of catalyst loading.

The coated catalysts prepared based on the third techniques in Table 4.3 were used to study the effects of the types of binder (Section 4.1.4.3.2), the effects of binder compositions (Section 4.1.4.4) and the effects of catalyst loading compositions (Section 4.1.4.5).

Table 4.3: Specifications of coated catalysts prepared based on the coating technique 3

ID of the coated catalysts	CC-3-1	CC-3-2	CC-3-3	CC-3-4	CC-3-5	CC-3-6
Specification of the catalyst carrier:						
Name of the catalyst carrier	3 mm in diameter of Al_2O_3 spheres					
Approximate volume of the catalyst carrier (ml)	5	5	5	5	5	5
Initial weight of the catalyst carrier (g)	3.3172	3.4762	3.3528	3.2629	3.4208	3.3789
Specification of the initial solution for coating:						
Formula of the parent catalyst powder	$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$					
Initial weight of the catalyst powder (g)	3.3809	3.4762	3.3486	3.2573	3.3980	3.3060
Name of the catalyst binder	HTC	G	HTC	G	HTC	G
Initial composition of binder (as wt % of catalyst)	5	5	5	5	5	5
Initial weight of the binder (g)	0.1700	0.1709	0.1698	0.1631	0.1702	0.1641
Name of the pore former	Pentaerythriol					
Initial weight of the pore former (g)	0.1733	0.1804	0.1705	0.1697	0.1699	0.1602
Volume of distilled H_2O (ml)	5	5	5	5	5	5
Specification of the final coated catalysts after calcination at 450^oC for 2 hours:						
Total weight of final coated catalysts (g)	5.4367	5.4743	3.3903	5.0848	5.4628	5.2549
Loading of catalyst on carrier (weight %)	**37.1**	**36.5**	**36.0**	**35.8**	**35.6**	**35.7**
Loading of binder on carrier (weight %)	1.9	0	1.8	0	1.8	0

4.1.2 PROCEDURE OF CATALYTIC SCREENING TESTS

The catalytic activity screening tests for coated catalysts were carried out in the laboratory scale stainless steel reactor (Figure 3.4), in which the overall equipment set up is illustrated in Figure 3.3. The instrument set up, the procedure, the experimental conditions and the analyses for the screening of coated catalysts were similar to that of the catalyst powders and are described in Section 3.1.2.

All screenings were carried out at total feed flow rate of 120 ml.min^{-1} gas mixture consisting of 5% propylene, 10% oxygen and 85% helium over reaction temperature of 300-450°C in atmospheric pressure. Prior any data measurement, each coated catalyst bed was pre-aged by passing the 120 ml.min^{-1} total flow rate of reactant gas comprising of 5% propylene, 10% oxygen and 85% helium at 400°C for at least eight hours or until the catalyst activity became steady. To make sure a steady state condition has been achieved; all measurements were taken at least five minutes after the thermocouple at the outlet of the catalyst bed indicated a constant temperature. Three catalytic measurements were taken at each reaction temperature.

The screening tests were carried out using 5 ml of coated catalyst bed. Prior to the placement of the sample in the reactor, the sample was selected manually in terms of uniformity of physical appearances, such as the thickness and the smoothness of catalyst loading onto the spheres. The 5 ml sample for catalytic screening tests contained active catalyst powder of various weights. Therefore for the purpose of data comparison, the screening data was calculated based on the percentage propylene converted per gram of catalyst at the experimental conditions (total flow rate of propylene concentration).

The activity and selectivity of coated catalysts to acrolein and other by-products were calculated based on Equations 3.4 and 3.5 respectively. The catalytic activity and selectivity were calculated based on the number of carbon atom as oxidation of propylene can also produce less carbon molecules such as carbon dioxide and carbon monoxide. The carbon balances were performed for each measurement and the error was found to be less than $\pm$ 5%.

4.1.3 PROCEDURE OF PHYSICAL STRENGTH TESTS

The coated catalysts that had optimum acrolein selectivity higher than 60% were then further investigated in terms of their relative physical strength. Four in-house equipments were set to perform the physical strength tests of the coated catalysts: the dropping, compression, rotating, and steam resistance tests.

4.1.3.1 DROPPING TEST

The dropping or impact test examined the ability of catalyst particles to withstand the impact by dropping a sample from known height (Figure 4.4). A glass container was placed onto the floor and a cylinder of some specific height was placed on top of it. The pre-weighed sample of (either 1 mm or 3 mm in diameter) coated catalyst beads were then carefully dropped through the middle of the cylinder. The sample was reweighed and the weight was recorded before it was sieved through a 1 mm x 1 mm mesh sieve. The collapsed material was defined at the matter that was smaller than 1 mm x 1 mm and passed through the sieve. The amount of collapsed material was weighed again and the percentage of collapsed material was calculated.
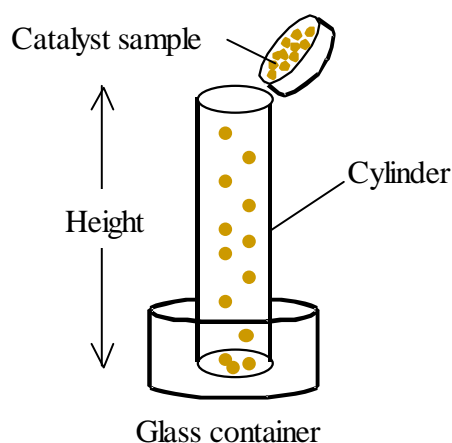
Figure 4.4:   Equipment set up for the dropping test

4.1.3.2 COMPRESSION TEST

The second test was a compression (or crushed) test as it was developed to examine the ability of catalysts to withstand the pressure by exerting presure on the catalysts placed between two horizontal plates (Figure 4.5). The pre-weighed coated catalysts

were arranged layer by layer in the container before a specific load was applied onto them. The catalyst sample was then sieved through a 1 mm x 1 mm mesh sieve in order to separate the collapsed material from the catalyst beads. The collapsed material was defined at the matter that was smaller than 1 mm x 1 mm and passed through the sieve. The amount of collapsed material was weighed again and the percentage of collapsed material was calculated.
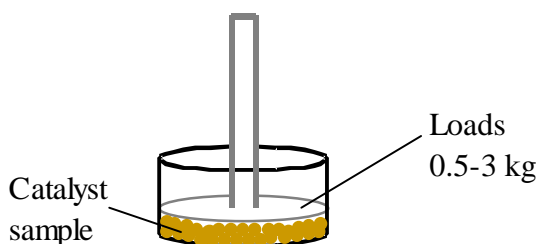
Figure 4.5:   Equipment set up for the compression test

4.1.3.3 ROTATING TEST

The third physical test was named the rotating test as it was designed to examine the catalyst strength by rotating a specific amount of catalyst sample inside a cylinder (Figure 4.6). Catalyst sample was put into a sealed plastic container, which was placed into another cylinder and rotated at a specific speed. At every 10 to 30 minutes, the collapsed material was recorded and a percentage of the collapsed material to the initial weight was calculated. The collapsed material was defined at the matter that was smaller than 1 mm x 1 mm and passed through the 1 mm x 1 mm mesh sieve. Prior the experiment, the dimension range of tumbling container was calculated based on the formula for centrifugal acceleration (Perry et al. 1998). The calculation showed that a container of 3.3 cm diameter was suitable to perform physical strength test on 6 cm diameter roller rotating at 100 rpm.

Catalyst sample in a
plastic container
(d_i = 3.3 cm & l = 8.5 cm)

Roller (d_o = 6 cm)
at 100 rpm
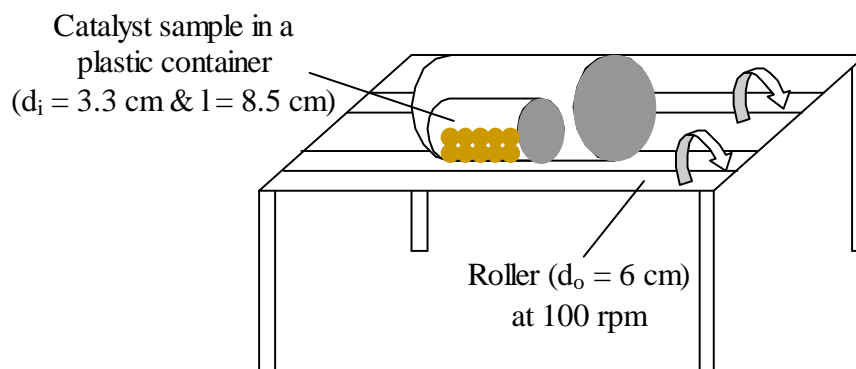
Figure 4.6:   Equipment set up for the rotating test

4.1.3.4 STEAM RESISTANCE TEST

As steam (up to 80%) is often used to dilute the reactants in the process of selective oxidation of propylene, it was important to examine the catalyst capability when it was exposed to steam. The presence of water vapour in the reaction mixture during the oxidation reaction of propylene is known to depress the formation of carbon oxides and would improve the selectivity. The fourth test was then designed to observe physical and activity degradation of catalyst during the exposure to steam over a period of time. The equipment set up is illustrated in Figure 4.7 at which steam was produced from boiling the water.

Catalyst
sample

Thermometer

Boiling water to
create steam

Electric Hot
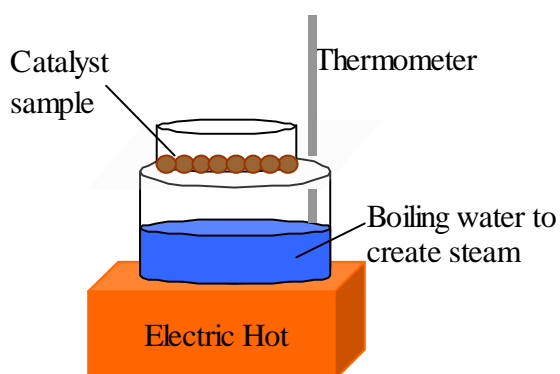
Figure 4.7:   Equipment set up for the steam resistance test

4.1.4 RESULTS AND DISCUSSION ON THE COATED CATALYST STUDY

The screening tests for measurement of catalytic activity and selectivity were performed at total flow rates of 120 ml.min^{-1} (5% propylene, 10% oxygen and 85% helium) over temperatures of 300-450°C. Approximately 5 ml of coated catalysts was used for the screening test sample. Before it was put in the reactor, the sample was manually selected in terms of physical uniformity. Details of the screening tests are described in Section 4.1.2.

Five main parameters in the preparation of coated catalysts that were studied in this project included the calcination temperatures, the carrier sizes, the binder types, the composition of binder and the composition of catalyst loading. Among the coated catalysts prepared, therefore the effects of those parameters were studied by comparing coated catalysts of various specifications firstly in terms of their catalytic properties by screening tests. The physical strength tests were also carried out in addition to the screening tests for some of the studies in order to have more convincing judgments. The outcomes of this study would recommend the specification of the coated catalyst that would be most suitable for the use in fixed bed reactor for acrolein production from propylene oxidation.

4.1.4.1 THE EFFECTS OF CALCINATION TEMPERATURES

The effects of calcination temperatures in the final step of coating technique were investigated in the 3 mm $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts having catalyst loading of (16 ± 1) weight % and high temperature cement as the binder. The specifications of catalysts used to investigate the effects of calcination temperature are listed in Table 4.4. Three temperatures of calcination were tested in this work, i.e. 450°C (CC-2-2), 500°C (CC-2-3), and 600°C (CC-2-4). A minimum temperature of 450°C was selected because the parent catalyst powder used in the coating was activated at that temperature.

Table 4.4: Specifications of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts used to study the effects of calcination temperatures

Specifications	ID of the coated catalyst		
	CC-2-2	CC-2-3	CC-2-4
Diameter of Al_2O_3 spheres (mm)	3	3	3
Catalyst loading (weight %)	15.0	16.6	15.8
Binder type (HTC=High Temperature Cement)	HTC	HTC	HTC
Initial composition of binder (weight % of catalyst)	5	5	5
Calcination temperature (^{o}C)	450	500	600
Sample for screening tests: Volume (ml)	5	5	5
Total weight (g)	3.711	3.785	3.748
Weight of catalyst powder loading (g)	0.557	0.628	0.592

The screening tests for these catalysts were carried out over temperature 300-450°C. Due to low catalyst loading (<20%), the propylene conversion was low (approximately 20% at 450°C) and the acrolein was at first detected at 350°C, in which the yield was about 2.7 % per gram of catalyst for all three catalysts. The overall results did not indicate any obvious difference on the catalytic properties of these catalysts (CC-2-2, CC-2-3 and CC-2-4).

Dropping tests (from 20, 40, 60, 80 and 100 cm height) were carried out to relatively compare the physical strength tests over the coated catalysts prepared at various calcination temperatures. The results in terms of cumulative weight % of catalyst collapsed are plotted in Figure 4.8
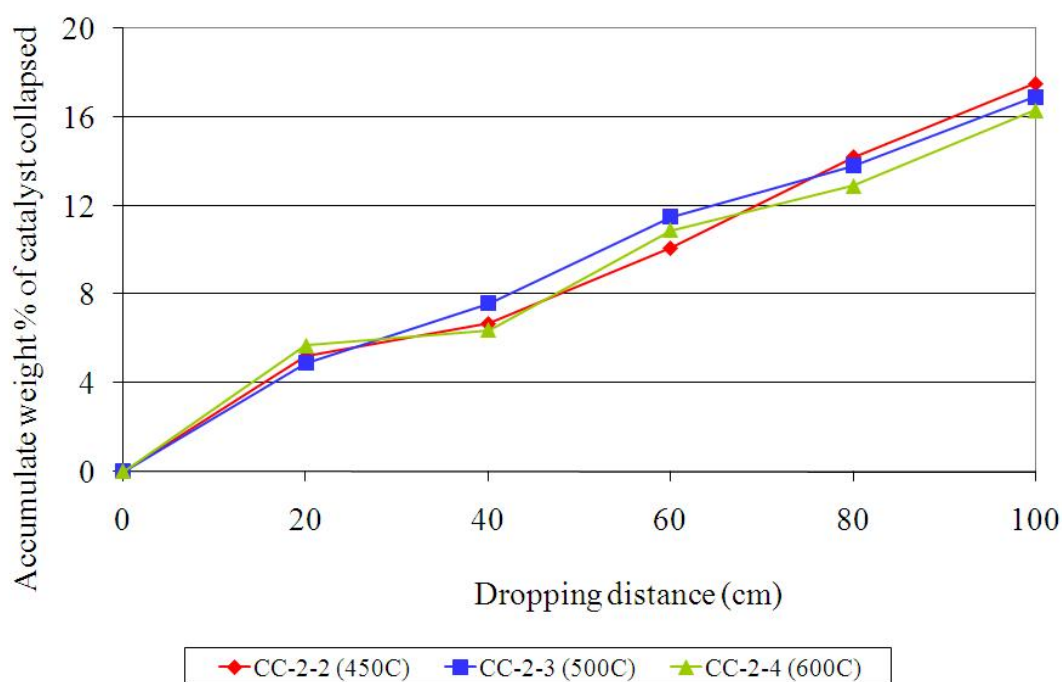
Figure 4.8:   Dropping test results for the 3 mm $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts prepared at various calcinations temperature

The results on the dropping tests of coated catalysts that were calcined at temperatures range of 450-600°C did not show specific trends for the variation of calcinations temperature. No significant difference on both the physical strength and the catalytic activity with the variation of calcination temperatures might be due to the short range of study temperature (450-600°C). Therefore 450°C was regarded to be sufficient for the calcination step of the final catalysts in this project.

4.1.4.2 THE EFFECTS OF CATALYST CARRIER SIZES

The effect of the carrier size on the coated catalyst activity was investigated by comparing the screening results of two sets of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts, i.e. the coated catalysts that was prepared using high temperature cement as the binder (CC-2-1 and CC-2-5) and the coated catalysts that was prepared using glucose as the binder (CC-1-1 and CC-2-6). The specifications of these catalysts are listed in Table 4.5. The coated catalysts were chosen manually in terms of their physical uniformity to ensure that the samples for screening tests from each batch were in the same quality and therefore the comparison results were reliable.

Table 4.5: Specifications of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts used to study the effects of binder types and carrier sizes

Specifications	ID of the coated catalyst			
	CC-1-1	CC-2-1	CC-2-5	CC-2-6
Diameter of Al_2O_3 spheres (mm)	3	3	1	1
Catalyst loading (weight %)	23.4	25.8	25.8	25.8
Binder type (G = Glucose & HTC = High Temperature Cement)	G	HTC	G	HTC
Initial composition of binder (weight % of catalyst)	5	5	5	5
Sample for screening tests: Volume (ml)	5	5	5	5
Total weight (g)	4.465	3.880	4.691	4.717
Weight of catalyst powder loading (g)	1.045	1.001	1.210	1.217

The screening results are presented in terms of propylene conversion (Figures 4.9), acrolein selectivity (Figure 4.10), acetaldehyde selectivity (Figure 4.11), carbon dioxide selectivity (Figure 4.12) and carbon monoxide selectivity (Figure 4.13).

(a)

(b)
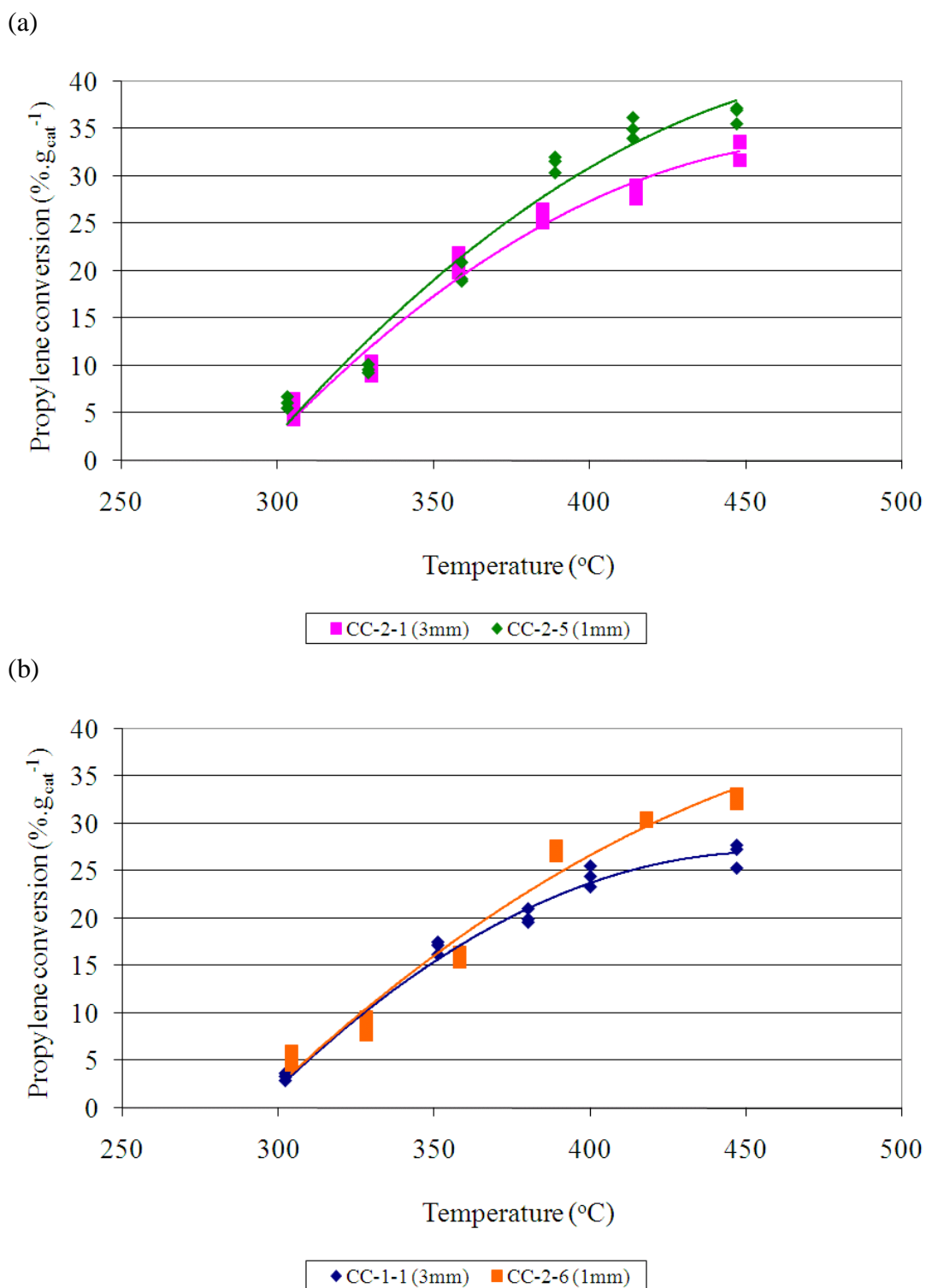
Figure 4.9:   The effect of carrier size for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the propylene conversion
(a) high temperature cement catalysts (b) glucose catalysts

(a)
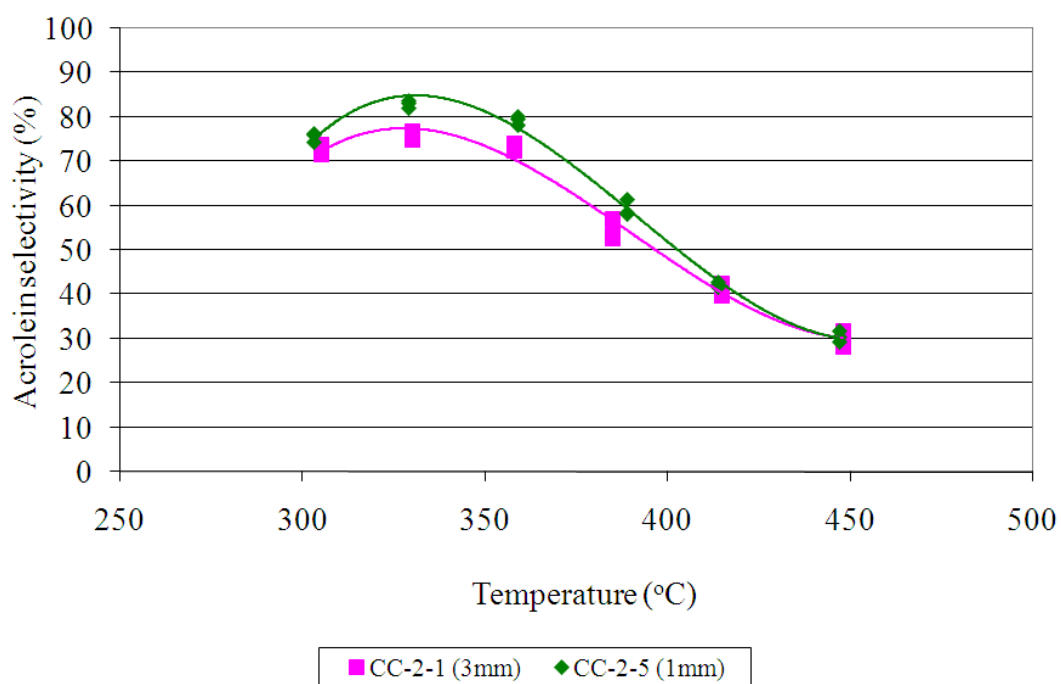
(b)
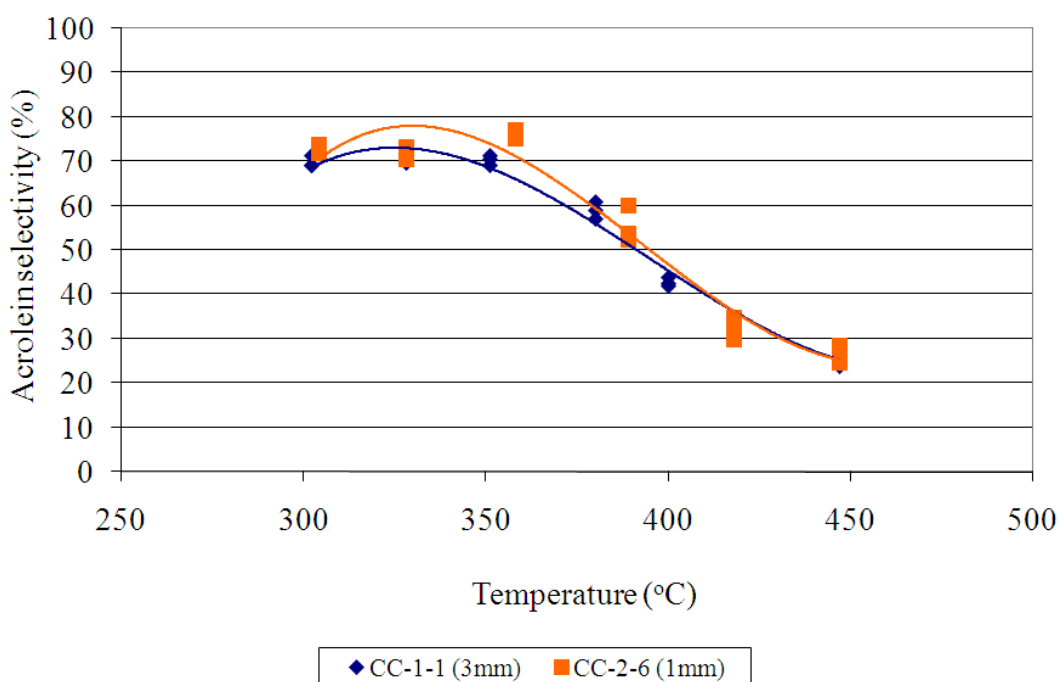
Figure 4.10: The effect of carrier size for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the acrolein selectivity (a) high temperature cement catalysts (b) glucose catalysts

(a)

(b)
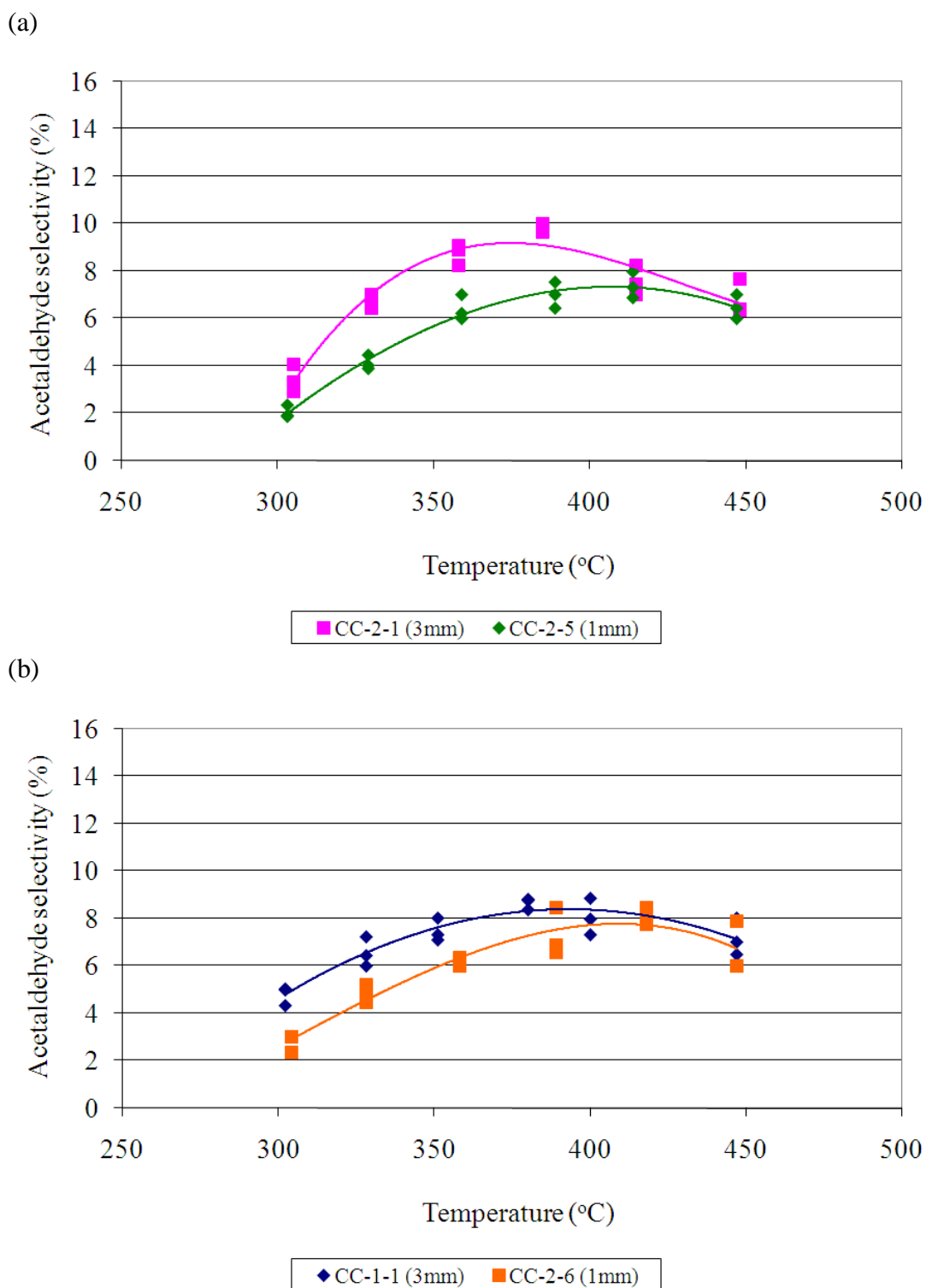
Figure 4.11: The effect of carrier size for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the acetaldehyde selectivity (a) high temperature cement catalysts (b) glucose catalysts

(a)

(b)
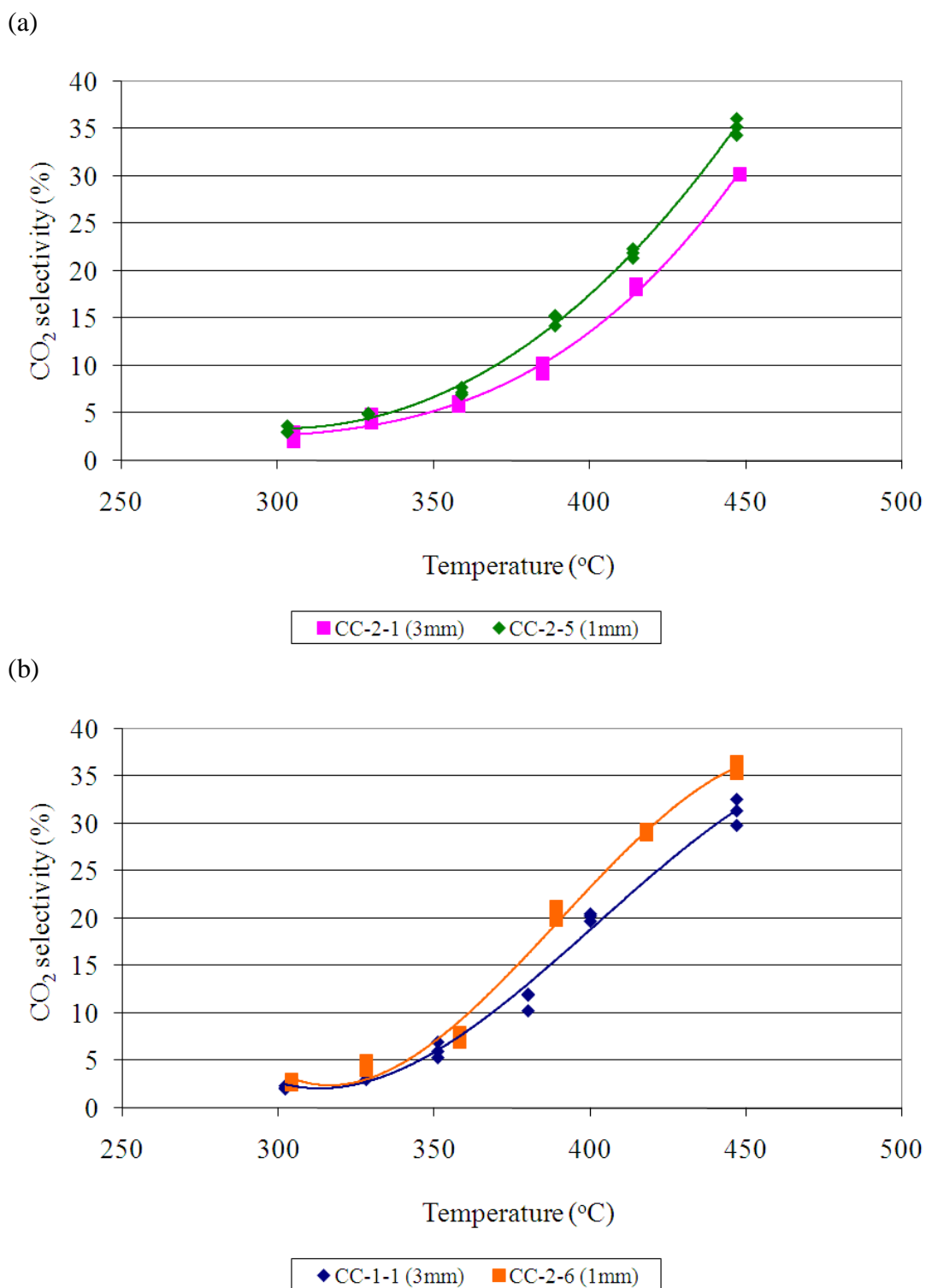
Figure 4.12: The effect of carrier size for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the carbon dioxide selectivity (a) high temperature cement catalysts (b) glucose catalysts

(a)

(b)
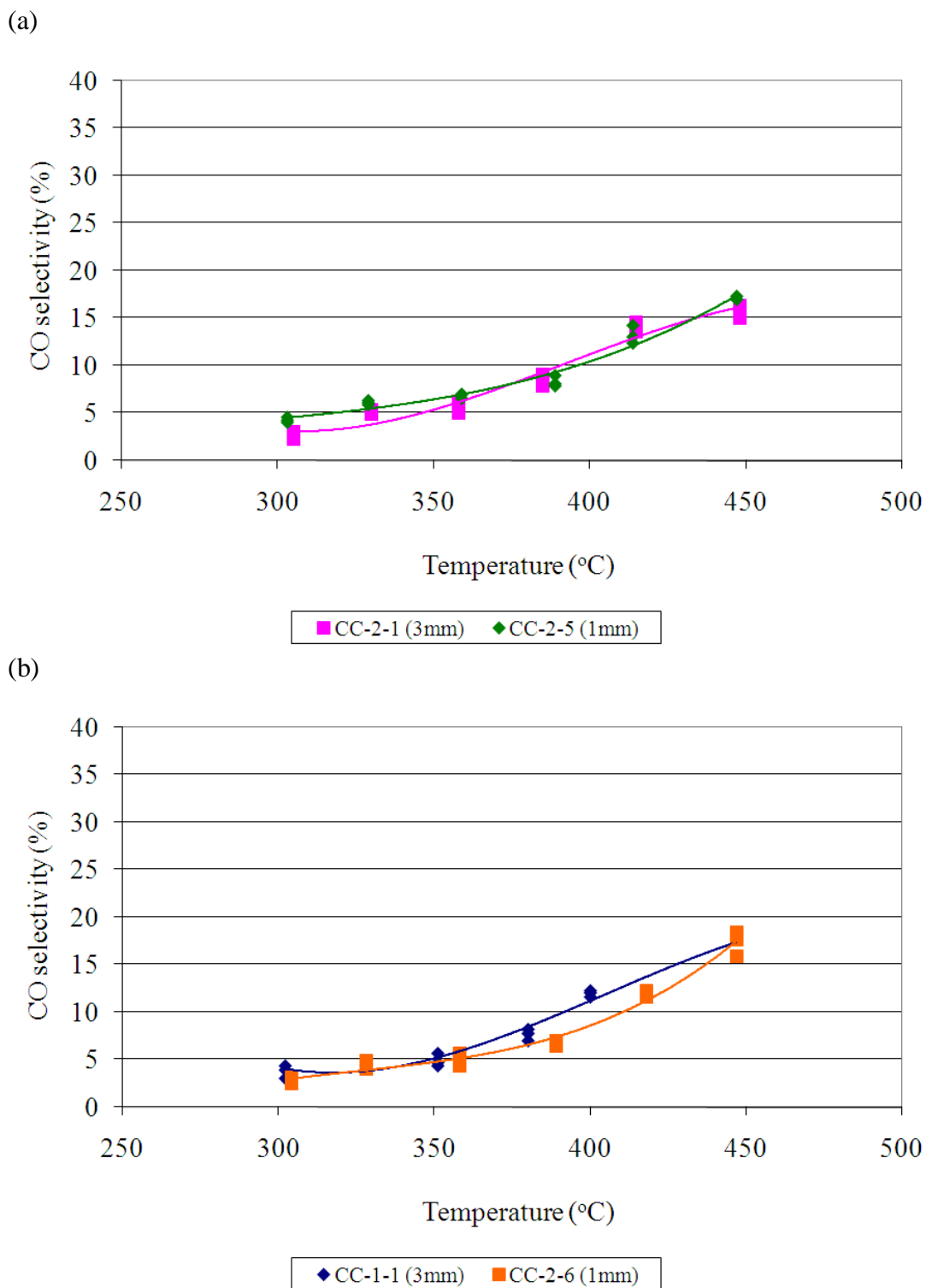
Figure 4.13: The effect of carrier size for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the carbon monoxide selectivity (a) high temperature cement catalysts (b) glucose catalysts

Two obvious effects could be detected as the size of catalyst carrier was varied, i.e. the 1 mm coated catalysts had better conversion of propylene and selectivity to acrolein than the 3 mm ones. Figure 4.9 shows that the propylene conversion of these two catalysts was similar at lower temperature less than $350^{o}C$ however the 1 mm catalysts converted increasingly more of the initial propylene as the reaction temperature increased.

These catalysts (CC-1-1, CC-2-1, CC-2-5, and CC-2-6) gave similar trend of acrolein selectivity (Figure 4.10). As the reaction temperature increased, the selectivity to acrolein first slightly increased until it reached the maximum temperature at $330^{o}C$ for the high temperature cement catalysts (CC-2-1 and CC-2-5) and $350^{o}C$ for the glucose catalysts (CC-1-1 and CC-2-6). After that the acrolein selectivity decreased significantly with increasing reaction temperature. It was shown that the variation in catalyst sizes did not affect the maximum reaction temperature, however the smaller catalysts had better selectivity to acrolein.

The decrease in acrolein selectivity at higher range of reaction temperatures could be explained by the increase products from the complete oxidation of propylene to form carbon dioxide (Figure 4.12). The other side products of propylene oxidation were acetaldehyde and carbon monoxide. The screening results on the selectivity to side products indicated that the 1 mm catalysts produced less acetaldehyde (Figure 4.11) but more carbon dioxide (Figure 4.12) and similar amount of carbon monoxide (Figure 4.13) if it compared to that of the 3 mm catalysts at the same reaction temperature.

The study of the effect of carrier size on the catalytic activity and selectivity of the coated catalyst concluded that the smaller size of coated catalysts (1 mm) converted more initial propylene to acrolein than the larger ones (3 mm). This conclusion was consistent with the general trend of the effect of particle size on the catalyst activity, i.e. the smaller particles are generally more active than the larger ones.

However coating catalyst powder around the 1 mm was much more difficult in practice, which might be due to the high surface tension around small particles and therefore made it difficult for the particle surface to anchor the catalyst powder. Consequently the 1 mm coated catalysts were more fragile than the 3mm ones. This

statement was proven by the results of dropping tests in Figure 4.14. The 1 mm coated catalysts had more amount of collapsed material compared to that of 3 mm.
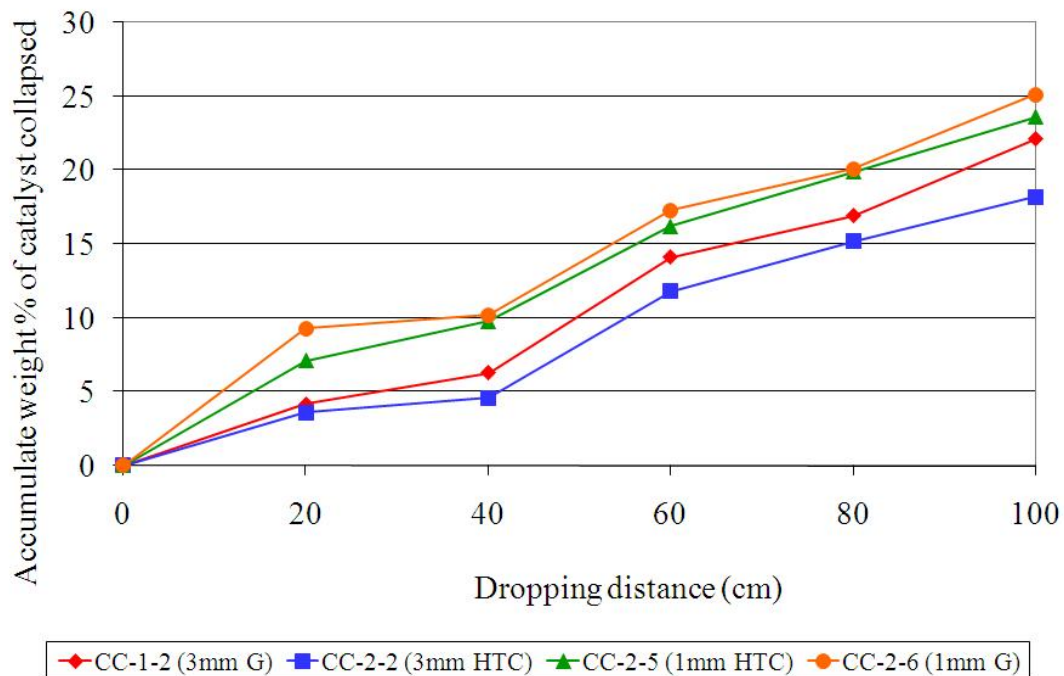
Figure 4.14:   Dropping test results for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts prepared at with various size of catalyst carrier

Based on the physical strength of the coated catalyst in addition to the practically and easiness in the catalyst preparation, the 3 mm Al_2O_3 spheres was recommended over the 1 mm ones to be used as the catalyst carrier in this project.

4.1.4.3 THE EFFECTS OF BINDER TYPES

The effects of binder types (high temperature cement versus glucose) on the catalyst activity and selectivity were carried out on two sets of coated catalysts that used $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ or $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ as the parent catalyst.

4.1.4.3.1 THE EFFECTS OF BINDER TYPES ON $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_X$ COATED CATALYSTS

Using the screening data on the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ catalysts coated around both 1 mm and 3 mm Al_2O_3 spheres listed in Table 4.5, the effects of binder types were investigated by plotting the data accordingly.

The catalytic performance of coated catalysts using different type of binder on 3 mm diameter of Al_2O_3 were investigated by comparing the screening results of catalyst CC-1-1 (in which glucose was used as the binder) to that of CC-2-1 (in which high temperature cement was used as the binder). The screening results in terms of the propylene conversion and the selectivity to acrolein and other side products are illustrated in Figures 4.15 to 4.19. To ensure that the data from various coated catalyst could be comparable, the data was calculated based on the mole (volume) percentage of propylene converted per gram of catalyst powder at the experimental conditions.

(a)

(b)
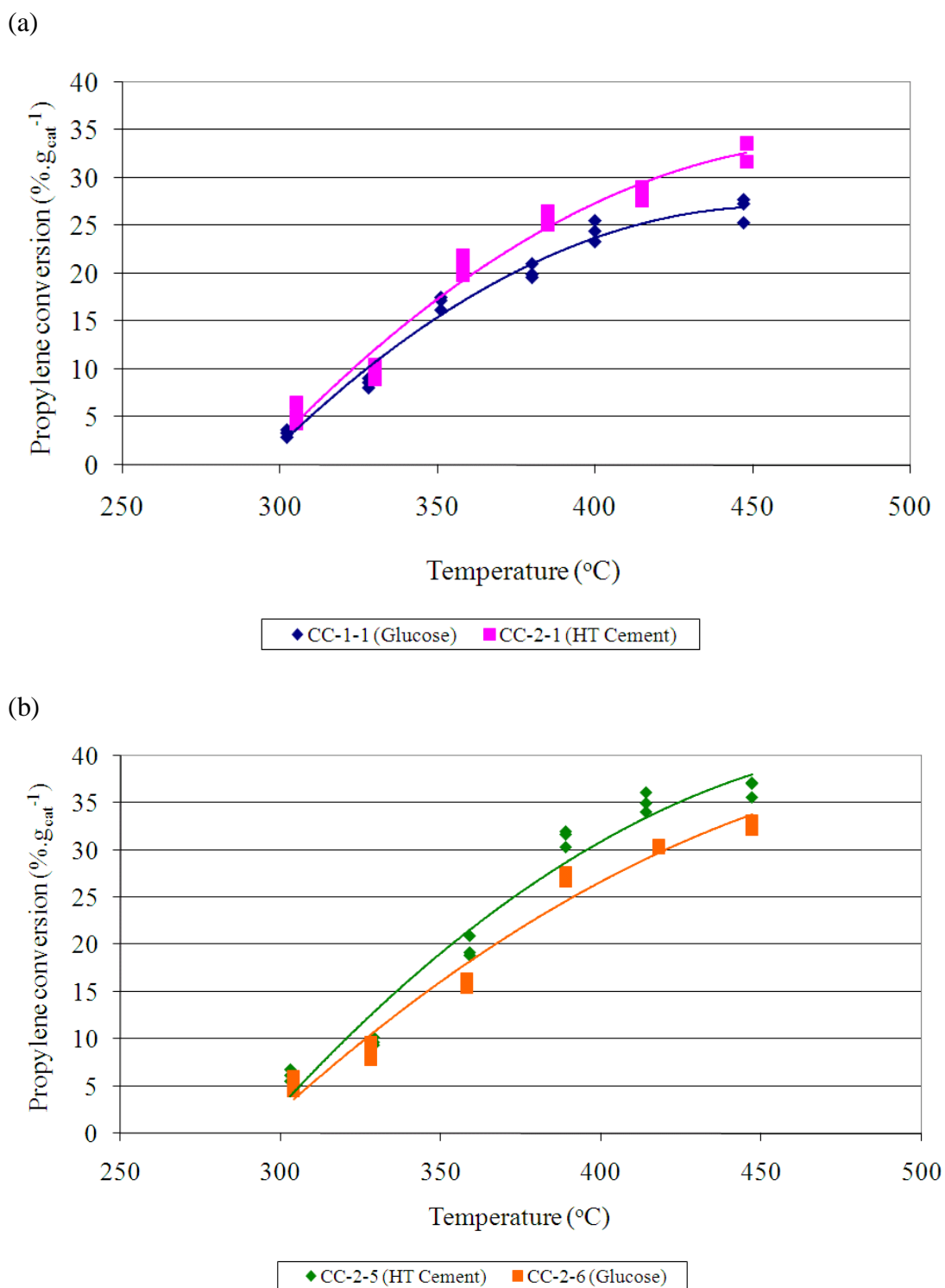
Figure 4.15   The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$
coated catalysts on the propylene conversion
(a) 3 mm coated catalysts (b) 1 mm coated catalysts

(a)
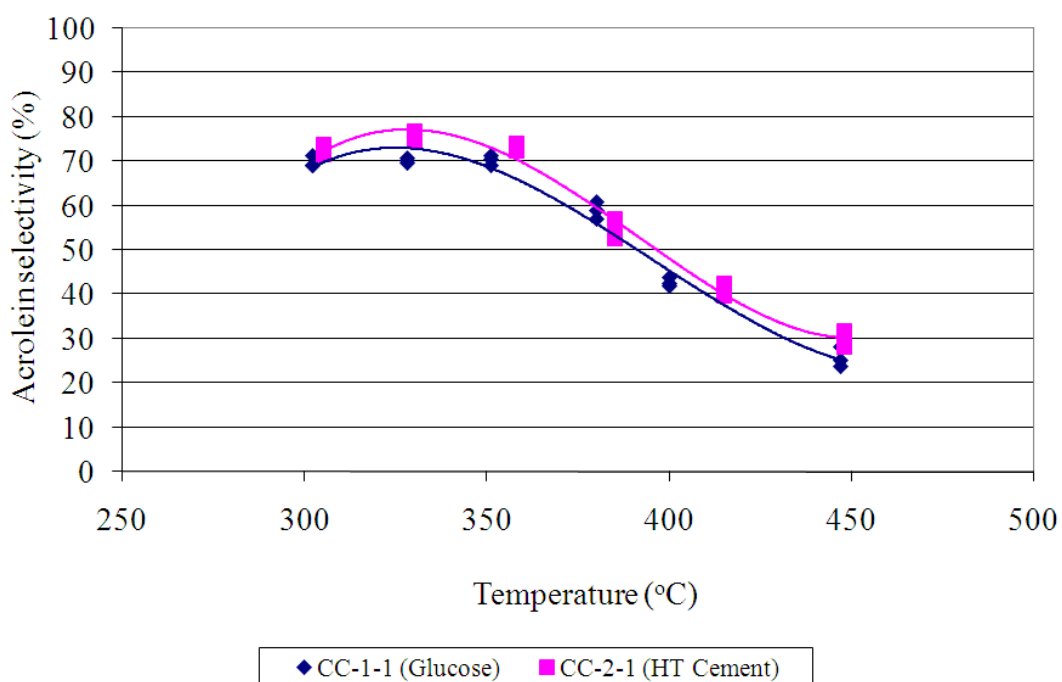
(b)
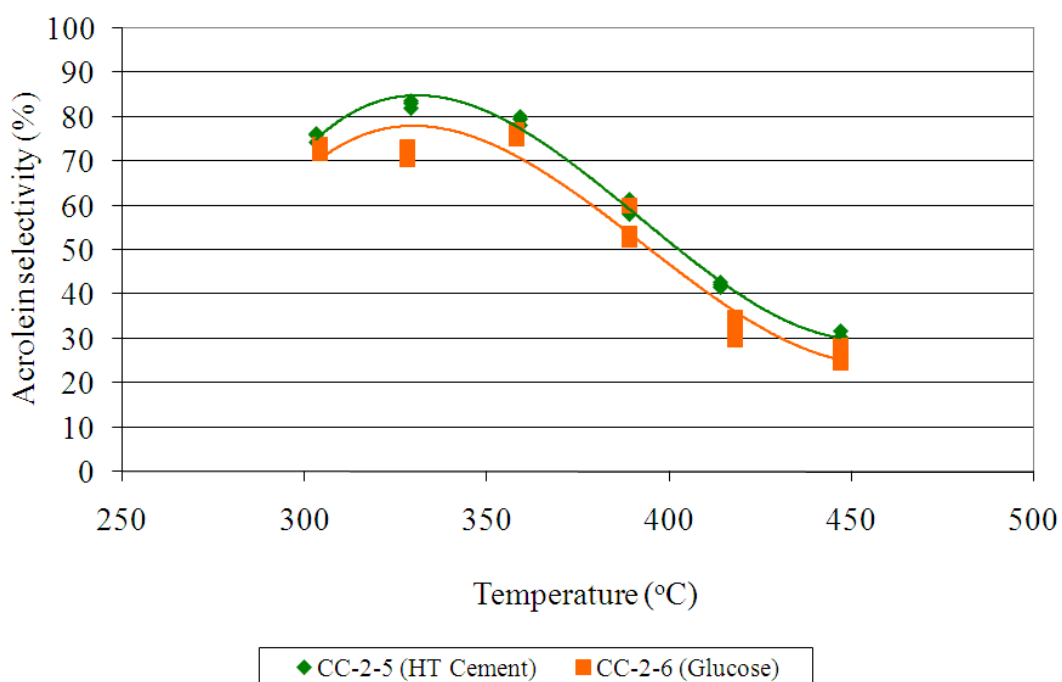
Figure 4.16: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the acrolein selectivity
(a) 3mm coated catalysts (b) 1 mm coated catalysts

(a)
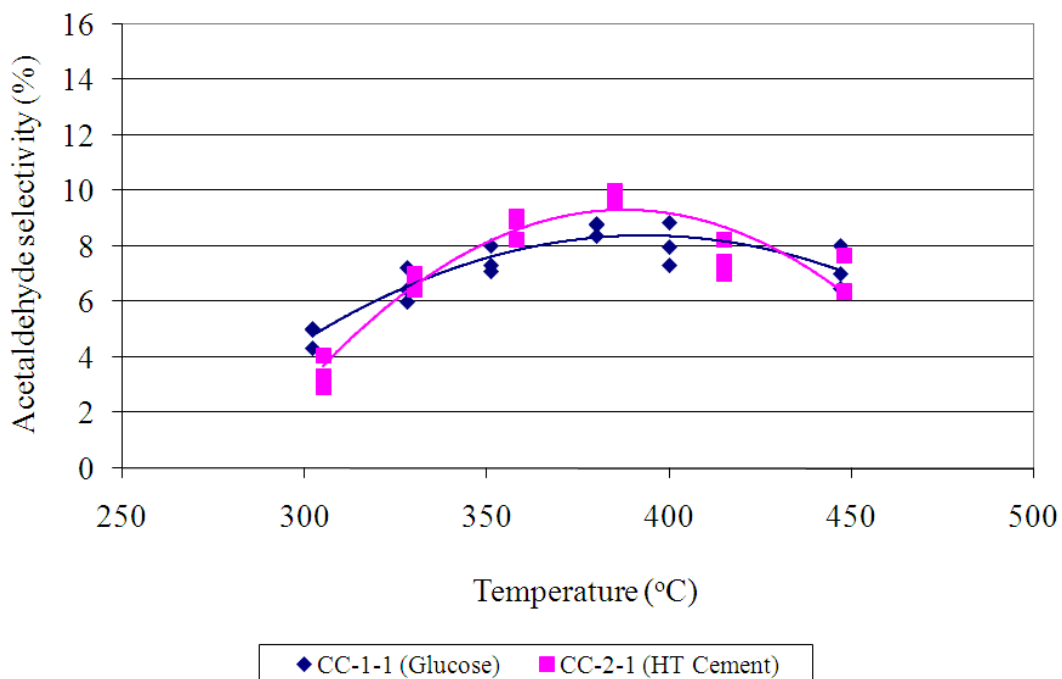
(b)
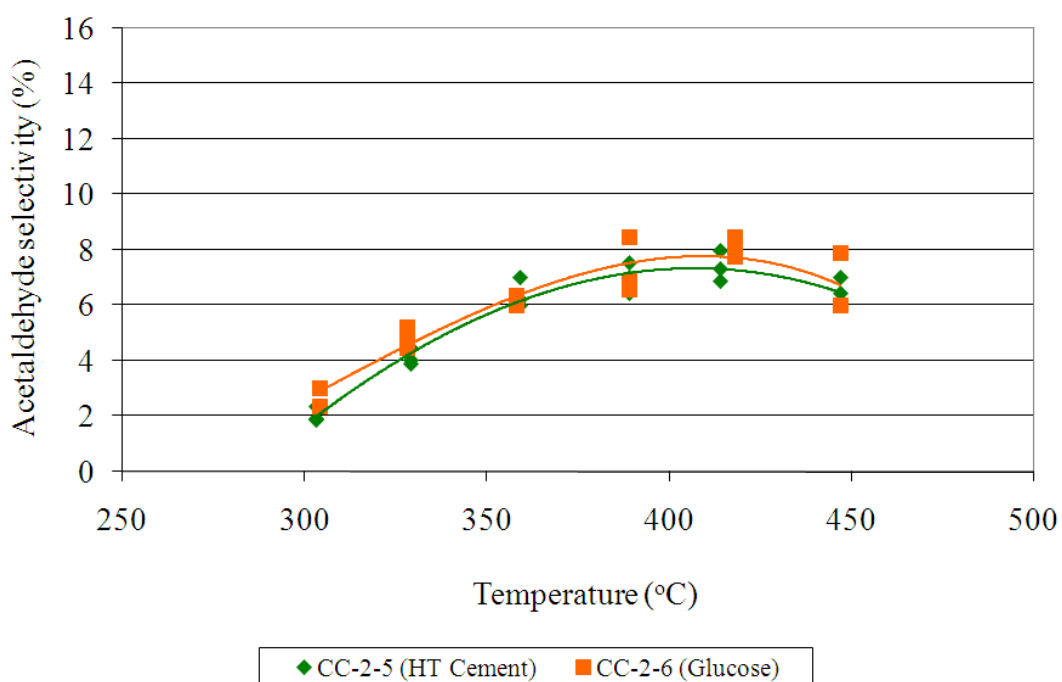
Figure 4.17: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the acetaldehyde selectivity
(a) 3 mm coated catalysts (b) 1 mm coated catalysts

(a)

(b)
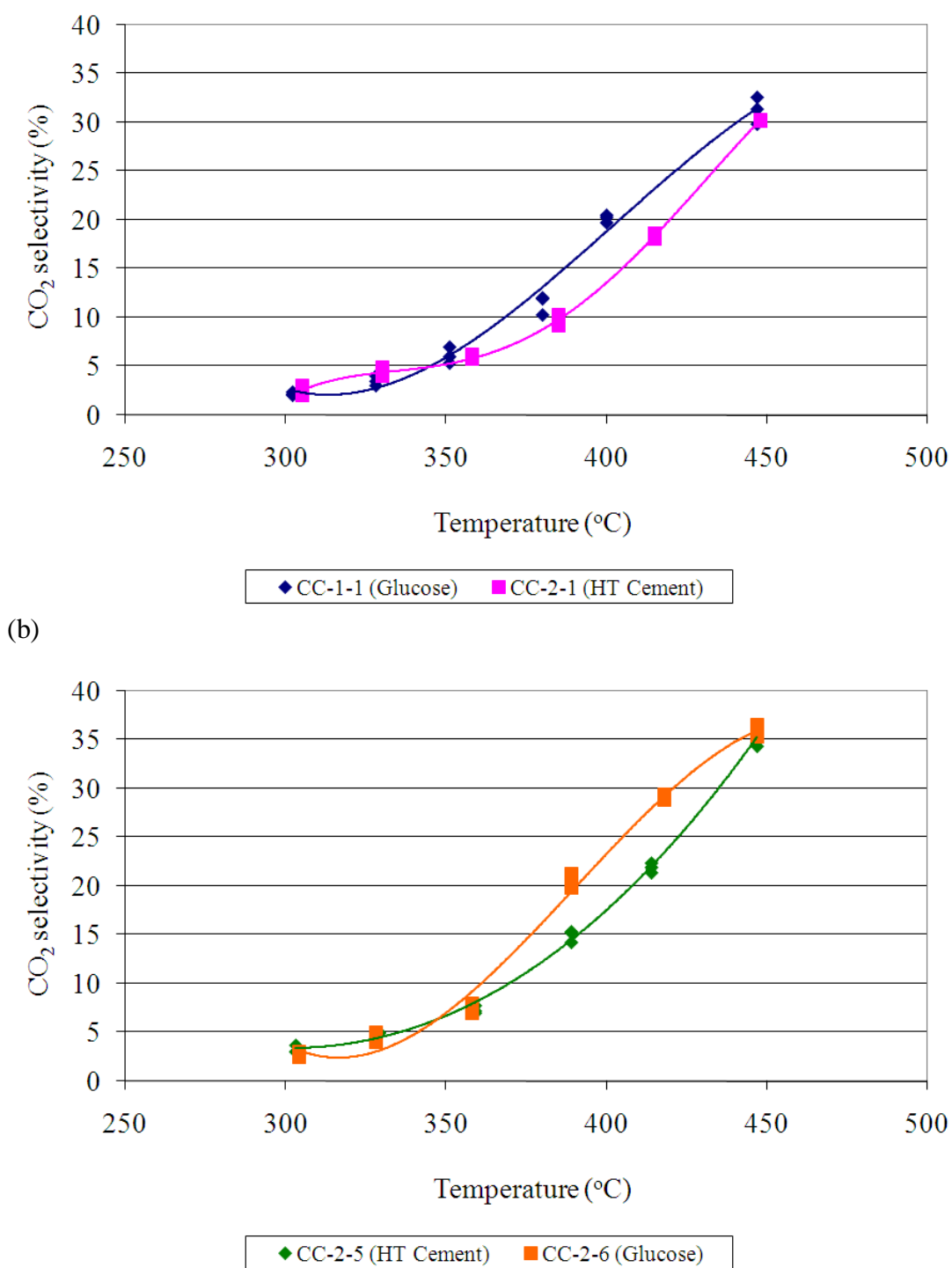
Figure 4.18: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the carbon dioxide selectivity
(a) 3 mm coated catalysts (b) 1 mm coated catalysts

(a)

(b)
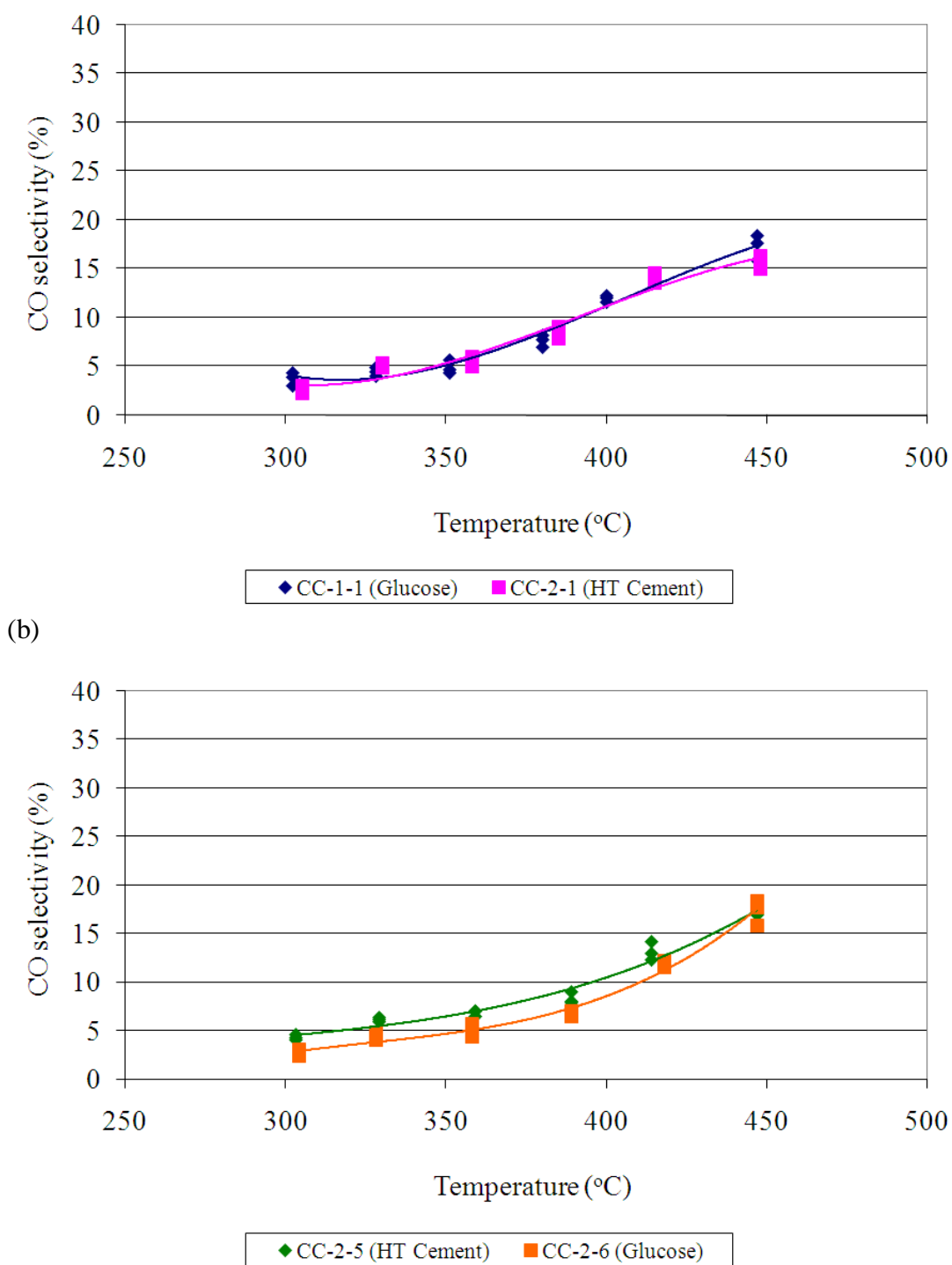
Figure 4.19: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts on the carbon monoxide selectivity
(a) 3 mm coated catalysts (b) 1 mm coated catalysts

The trends of catalytic performances (i.e. propylene conversion and selectivities to acrolein and other side products) over the range of study temperature (300-450°C) of

3 mm coated catalysts were similar to those of 1 mm ones. The results on the study of binder type on the coated catalyst $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ could be summarised as follows: (1) The high temperature cement catalysts converted (up to 10%) more propylene than the glucose ones; (2) The high temperature cement had lower the optimum reaction temperature (330°C for high temperature cement catalysts and 350°C for glucose catalysts); (3) The high temperature cement catalysts had better selectivity to acrolein (approximately 5% more) than the glucose ones; (4) No significant difference could be said in the selectivity to acetaldehyde; (5) The glucose catalysts had higher selectivity to carbon dioxide at temperature more than 350°C; and (6) No significant distinction was observed in the formation of carbon monoxide.

The physical strengths of these catalysts were also compared, which the result is presented in the previous section and illustrated in Figure 4.14. Over the experimental condition, the coated catalysts with high temperature cement as binder had relatively better physical strength than the coated catalysts with glucose.

The investigation of binder type effects on the coated catalyst $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ concluded that the high temperature cement catalysts performed catalytically better than the glucose catalysts due to better propylene conversion, better acrolein selectivity, lower maximum reaction temperature and less carbon dioxide formation at temperature higher than 350°C. The high temperature cement as binder in the coated catalysts also produced relatively stronger coated catalysts than the glucose. Due to these remarkable effects in both catalytic and physical properties of the final coated catalysts, the high temperature cement was a better choice for the catalyst binder compared to glucose.

4.1.4.3.2 THE EFFECTS OF BINDER TYPES ON
$MO_{12}BI_{1.5}FE_{0.8}CO_{3.5}W_{0.6}K_{0.06}SI_{1.4}P_{0.7}O_X$ COATED CATALYSTS

The effects of binder types were also carried out in the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts, which the specifications are listed in Table 5.6. The $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst was the selected catalyst that was used in the pilot plant as it yielded the highest selectivity to acrolein (95%) at relatively low reaction temperature (350°C) among all catalysts studied (Chapter 3). All coated catalysts in Table 4.6 were in 3 mm size and were prepared based on the third coating technique using calcination temperature of 450°C. Prior the screening in the laboratory size reactor, the samples from each batch were chosen manually in terms of their physical uniformity.

Table 4.6: Specifications of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts used to study the effects of binder types

Specifications	ID of the coated catalyst (CC-)					
	3-1	3-2	3-3	3-4	3-5	3-6
Diameter of Al_2O_3 spheres (mm)	3	3	3	3	3	3
Catalyst loading (weight %)	37.1	36.5	36.0	35.8	35.6	35.7
Binder type (G=Glucose & HTC=High Temperature Cement)	HTC	G	HTC	G	HTC	G
Initial composition of binder (weight % of catalyst)	5	5	5	5	5	5
Calcination temperature (^{o}C)	450	450	450	450	450	450
Sample for screening tests: Volume (ml) Total weight (g) Weight of catalyst powder loading (g)	5 3.367 1.249	5 3.703 1.352	5 3.499 1.260	5 3.784 1.355	5 3.543 1.261	5 3.866 1.380

The effects of binder types were investigated by comparing three sets of screening data (CC-3-1 versus CC-3-2; CC-3-3 versus CC-3-4; and CC-3-5 versus CC-3-6). The trends shown in these three sets of coated catalysts were similar; therefore only

two sets of screening data (CC-3-2 versus CC-3-3 and CC-35 versus CC-3-6) are presented here in Figures 4.20 to 4.24.

(a)
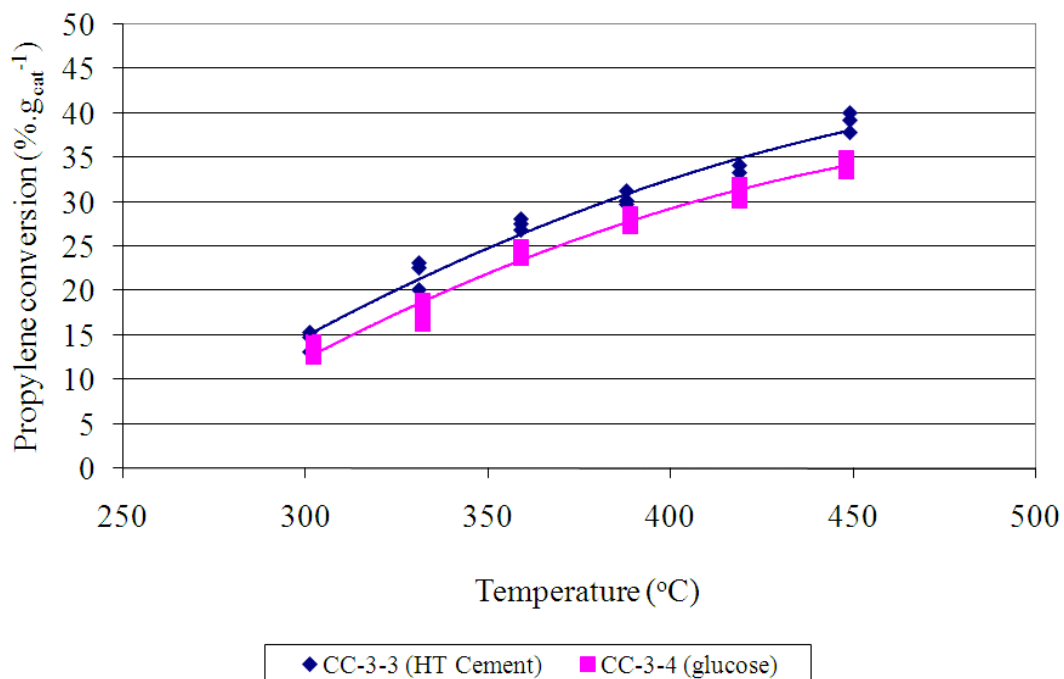
(b)
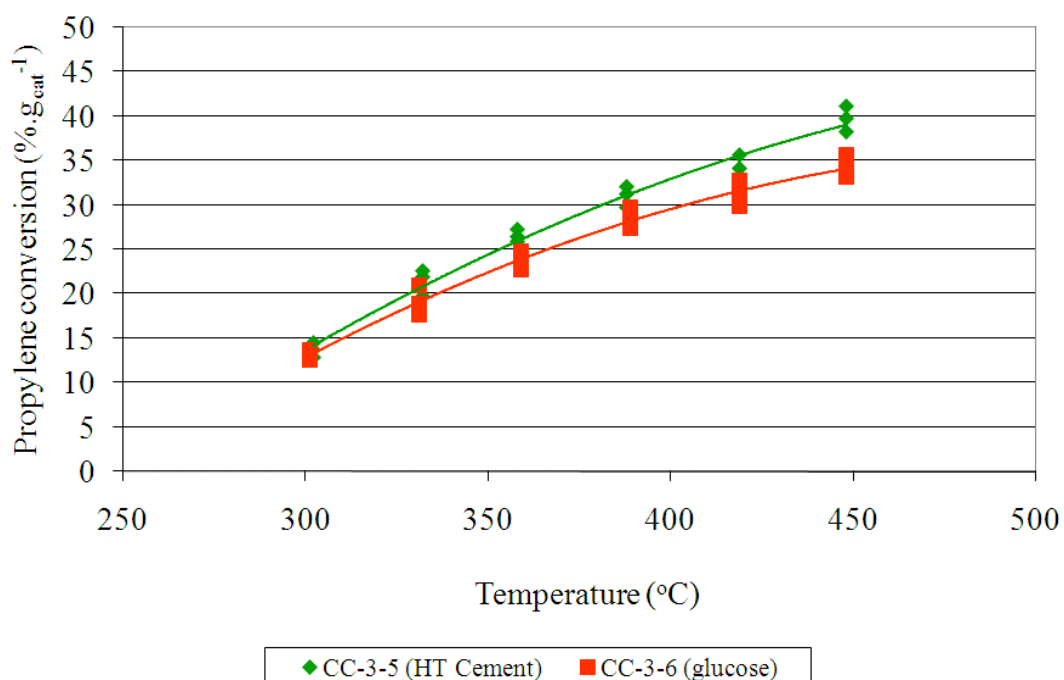
Figure 4.20: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts on the propylene conversion
(a) CC-3-3 versus CC-3-4 (b) CC-3-5 versus CC-3-6

(a)
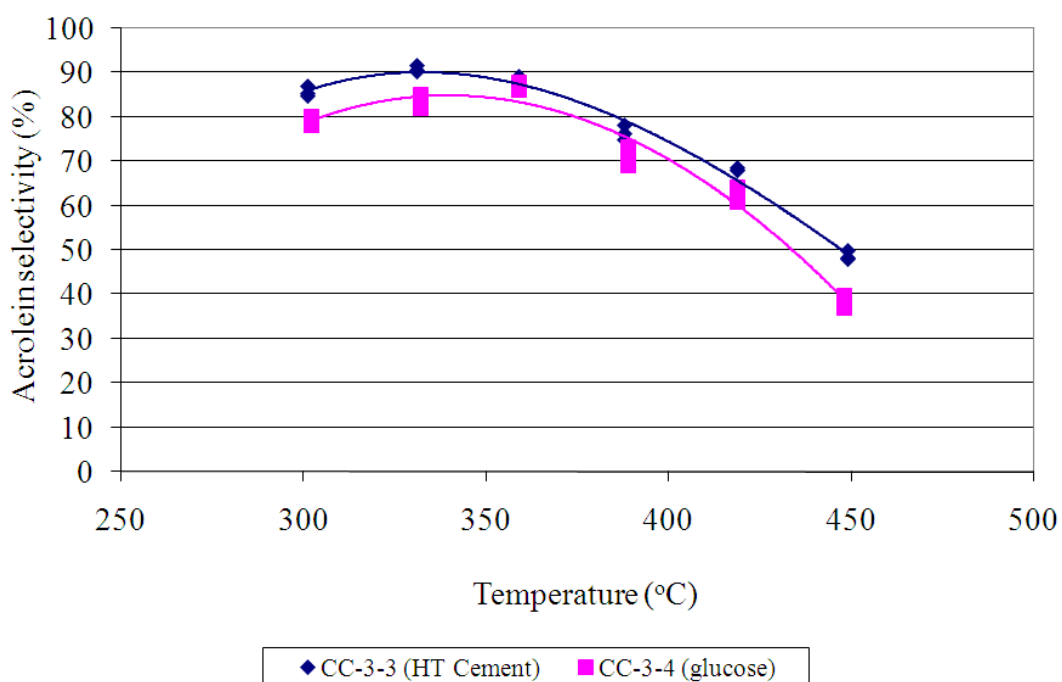
(b)
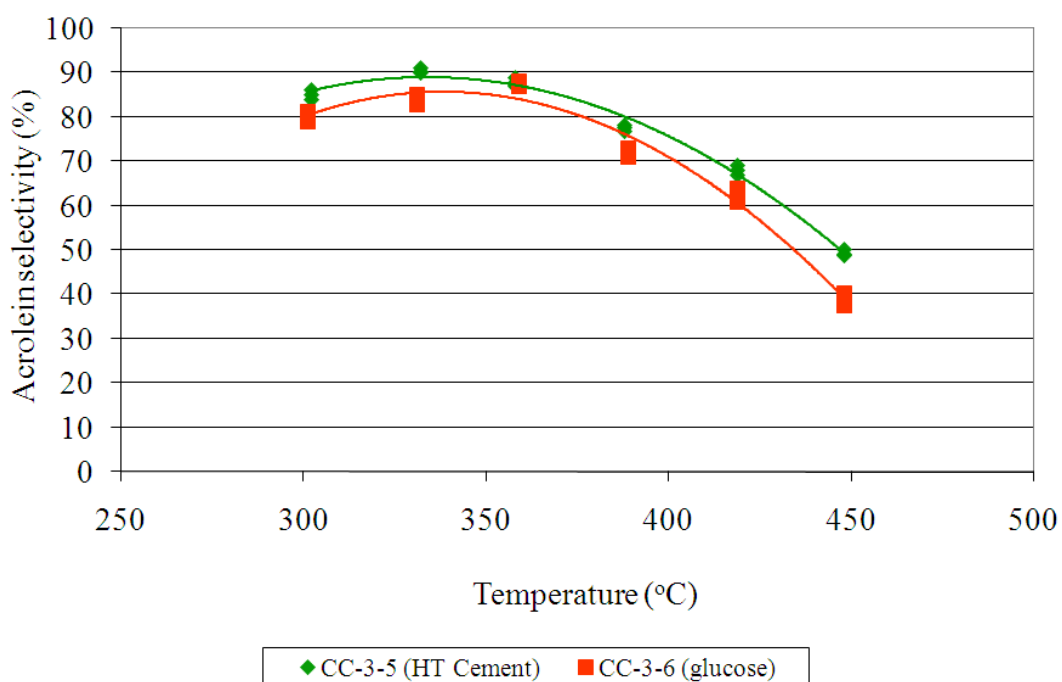
Figure 4.21: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts on the acrolein selectivity
(a) CC-3-3 versus CC-3-4 (b) CC-3-5 versus CC-3-6

(a)

(b)
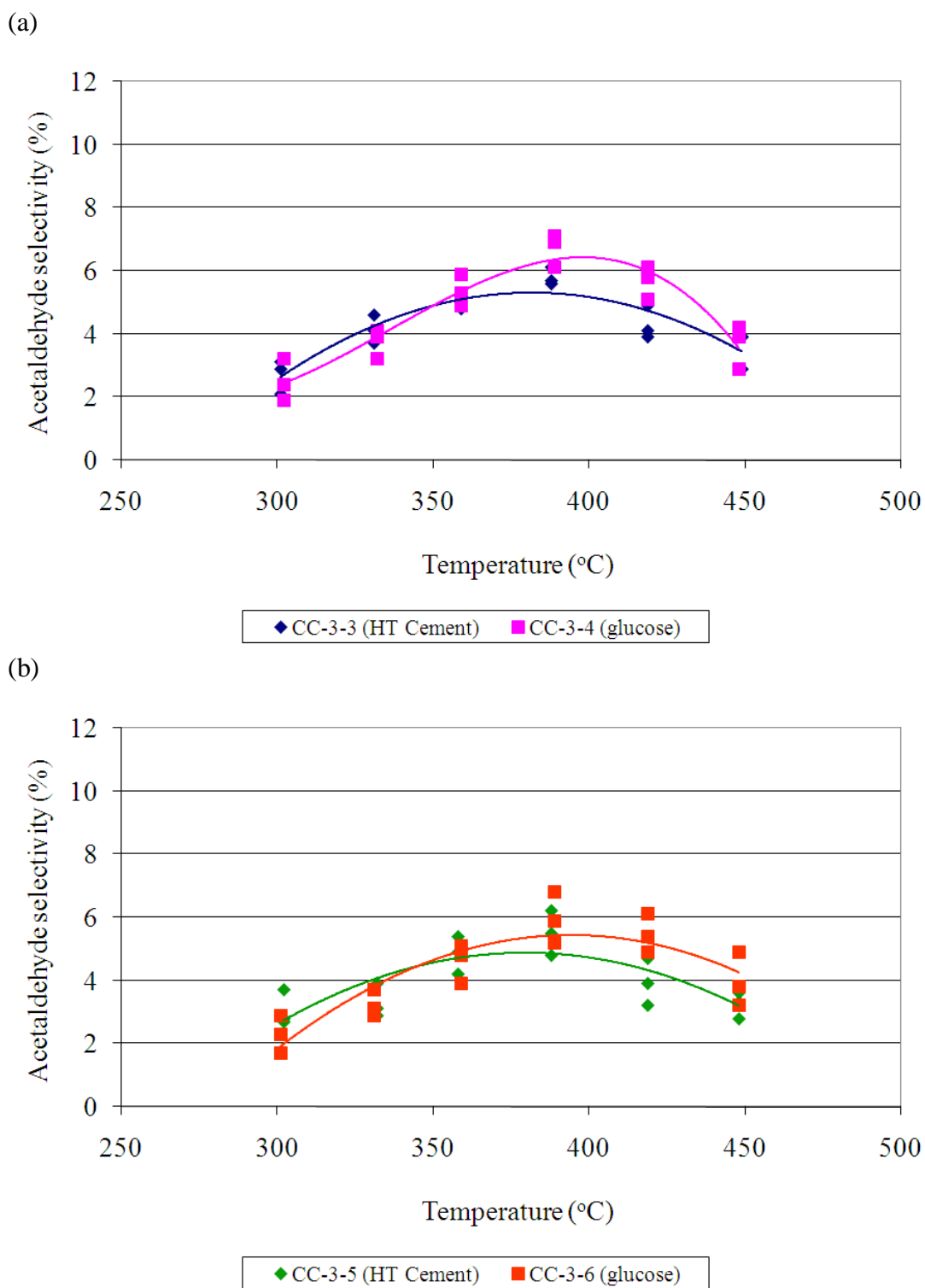
Figure 4.22: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts on the acetaldehyde selectivity
(a) CC-3-3 versus CC-3-4 (b) CC-3-5 versus CC-3-6

(a)
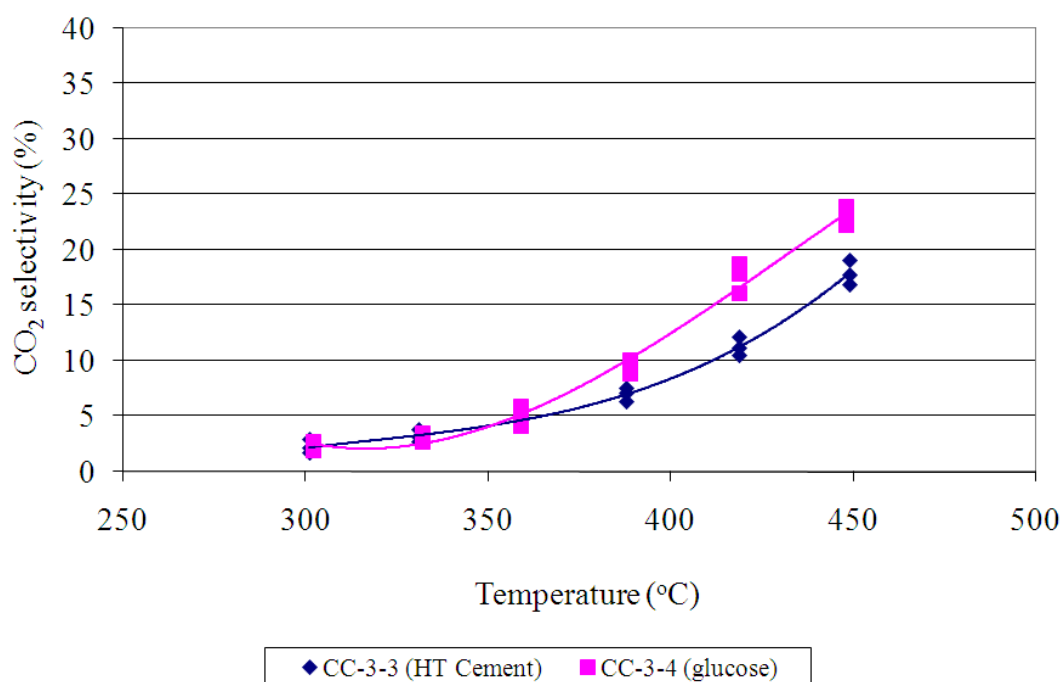
(b)
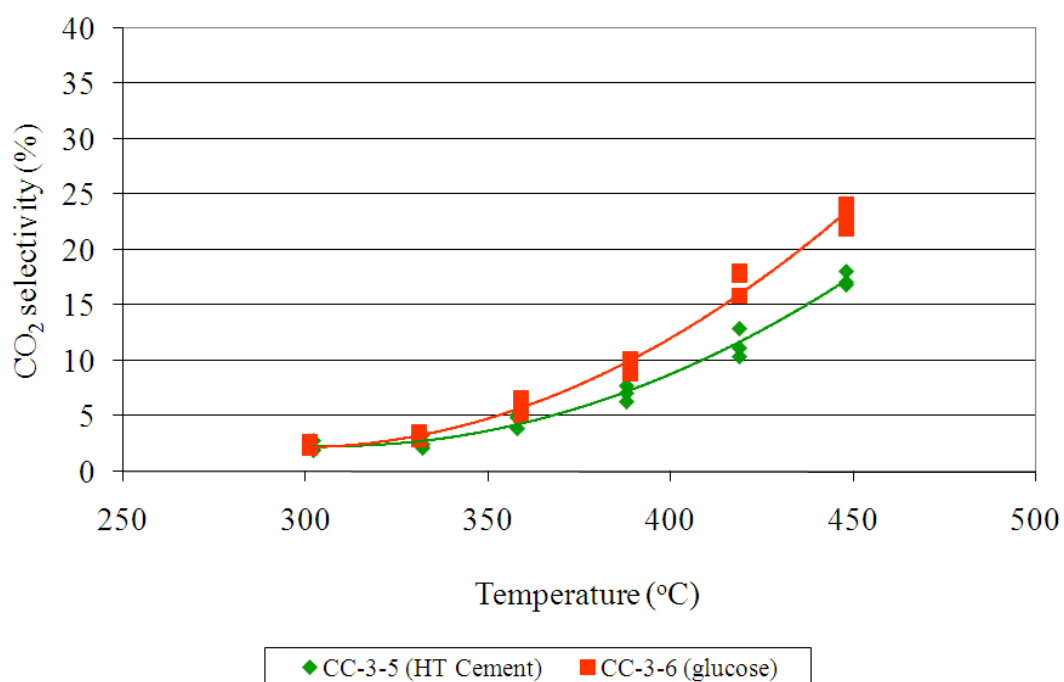
Figure 4.23: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts on the carbon dioxide selectivity
(a) CC-3-3 versus CC-3-4 (b) CC-3-5 versus CC-3-6

(a)

(b)
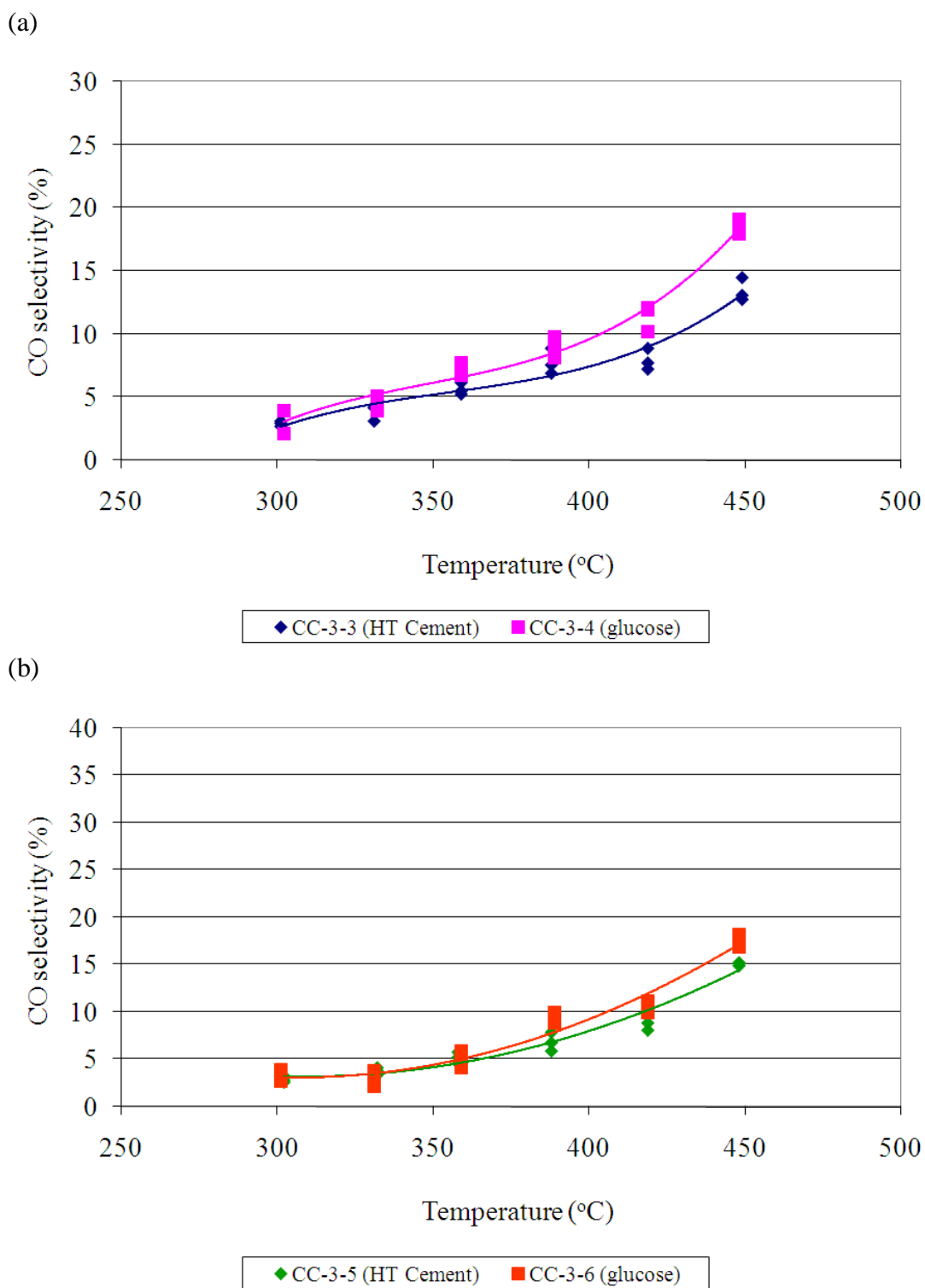
Figure 4.24: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts on the carbon monoxide selectivity (a) CC-3-3 versus CC-3-4 (b) CC-3-5 versus CC-3-6

The study of the binder types on the catalytic performance of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts had similar conclusions to that of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}O_x$ coated catalysts. Figure 4.20 indicates that the high temperature cement catalysts (CC-3-3 and CC-3-5) had higher conversion of propylene than the glucose catalysts (CC-3-4 and CC-3-6).

Two improvements indicated on the trends of acrolein selectivity (Figure 4.21) by replacing the glucose with high temperature cement as the binder. Firstly over the range of reaction temperature, the high temperature cement catalyst (CC-3-3 and CC-3-5) had better selectivity of acrolein (approximately 10% more) than the glucose catalyst (CC-3-4 and CC-3-6). Secondly, the high temperature cement had lowered the optimum reaction temperature (i.e. the temperature at which the catalysts had maximum acrolein selectivity) at $330^{o}C$ from $350^{o}C$ (the glucose catalyst).

Acetaldehyde was one of the detected side products. No significant difference could be observed between the catalysts that used high temperature cement and the catalysts that used glucose on the acetaldehyde selectivity (Figure 4.22)

As expected, the formation of carbon dioxide increased as the increase in reaction temperature (Figure 4.23). This phenomenon might be due to the complete oxidation of propylene or/and of acrolein. Figures 4.23 and 4.24 demonstrate that the glucose catalysts (CC-3-3 and CC-3-5) and (CC-3-4 and CC-3-6) had more formation of both carbon dioxide and carbon monoxide at reaction temperatures higher than $350^{o}C$.

These catalysts were also exposed to the dropping test from height of 20, 40, 60, 80 and 100 cm in order to compare their physical strength (Figure 4.25). It was shown that the catalysts with high temperature cement were comparatively stronger than the catalysts with glucose. The innovative idea of using high temperature cement therefore had proven to work better than glucose as the catalyst binder due to the improved physical strength and catalytic properties of the final coated catalysts.
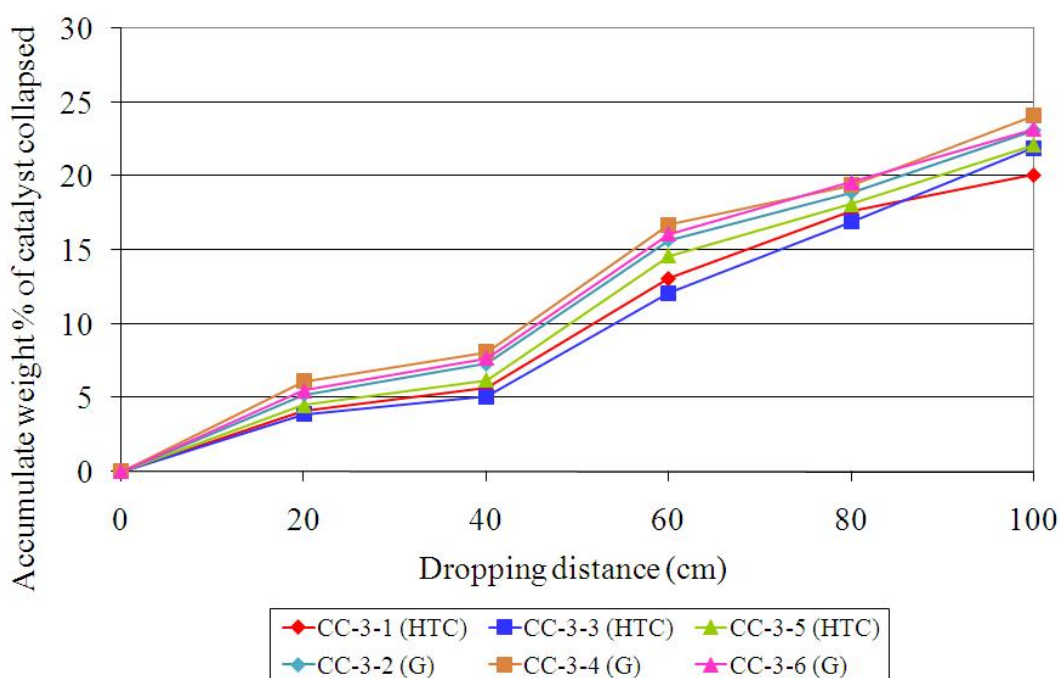
Figure 4.25: Dropping test results for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$
coated catalysts with different types of binder
(HTC = high temperature cement; G = glucose)

4.1.4.4 THE EFFECTS OF BINDER COMPOSITIONS

The effects of binder types for coated catalysts (high temperature cement versus glucose) and the binder compositions (5, 10, 15 and 20%) were investigated on the coated catalysts listed in Table 4.7. The coated catalysts of study were prepared using the parent catalyst powder, $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$, based on coating technique 3. Alumina spheres of 3 mm in diameter were used as the catalyst carriers. Either the glucose or the high temperature cement was used to bind the catalyst into the spheres. Once the alumina spheres were completely coated with the catalyst, they were calcined at $450^{o}C$ for two hours.

Table 4.7: Specifications of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts used to study the effects of binder compositions on the physical strength of the final coated catalysts

Specifications	ID of the coated catalyst			
	CC-3-7	CC-3-8	CC-3-9	CC-3-10
Diameter of Al_2O_3 spheres (mm)	3	3	3	3
Catalyst loading (weight %)	23.4	25.8	25.8	25.8
Binder type	High temperature cement			
Initial composition of binder (weight % of catalyst)	5	10	15	20
Specifications	ID of the coated catalyst			
	CC-3-11	CC-3-12	CC-3-13	CC-3-14
Diameter of Al_2O_3 spheres (mm)	3	3	3	3
Catalyst loading (weight %)	23.9	22.3	24.6	21.9
Binder type	Glucose			
Initial composition of binder (weight % of catalyst)	5	10	15	20

The reliability of using high temperature cement as an alternative for conventional binder such as glucose was investigated in terms of the physical strength of the final coated catalysts. For the purpose of achieving this objective, approximately 5 ml sample from each batch was exposed in four tests: dropping, compression, rotating, and steam resistance tests. The results of these tests were presented in terms of weight % of accumulated catalyst collapsed.

Dropping tests from 20, 40, 60, 80 and 100 cm height were performed on all coated catalysts, which the specifications are listed in Table 4.7. The results of coated catalysts with high temperature cement were compared to that of coated catalysts with glucose and are plotted in Figure 4.26. In addition to the dropping tests, the same batches of coated catalysts using high temperature cement were also exposed to the compression test (Figure 4.27), the rotating test (Figure 4.28) and the steam resistance test (Figure 4.29) in order to investigate the effect of various binder compositions on the physical strength of the final catalysts.
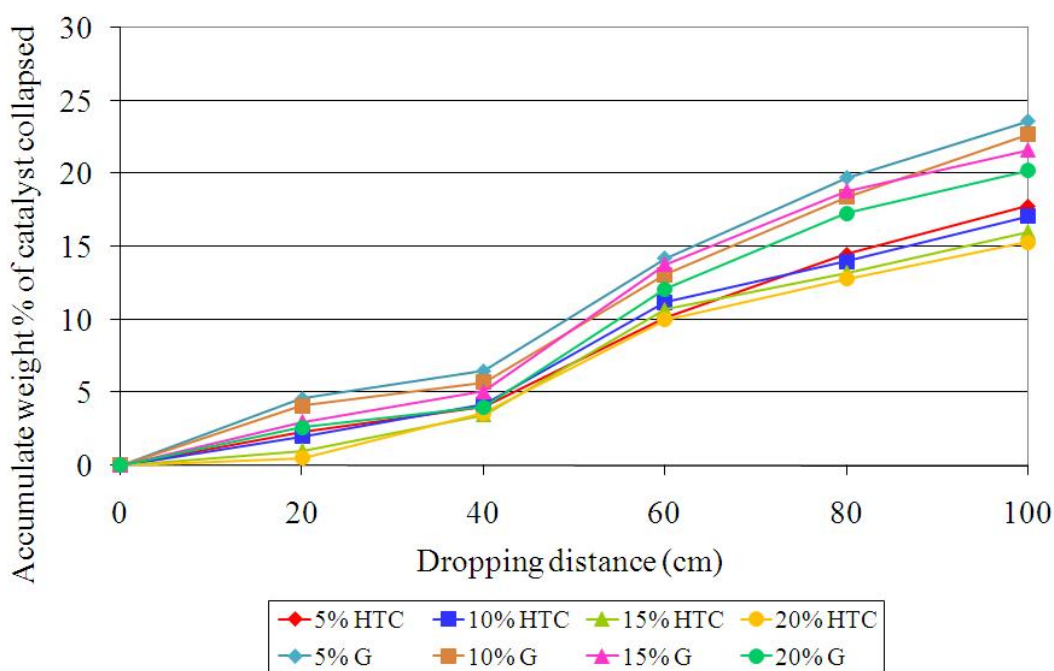
Figure 4.26: Dropping test results for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts with either high temperature cement or glucose of various binder compositions
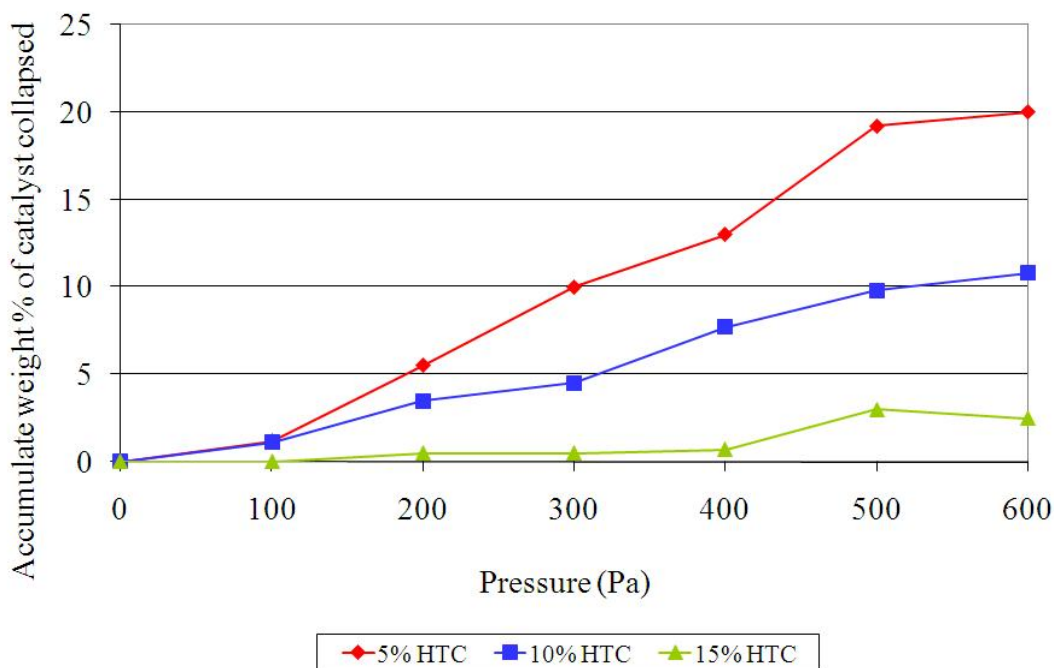
Figure 4.27: Compression test results for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts with high temperature cement of various compositions
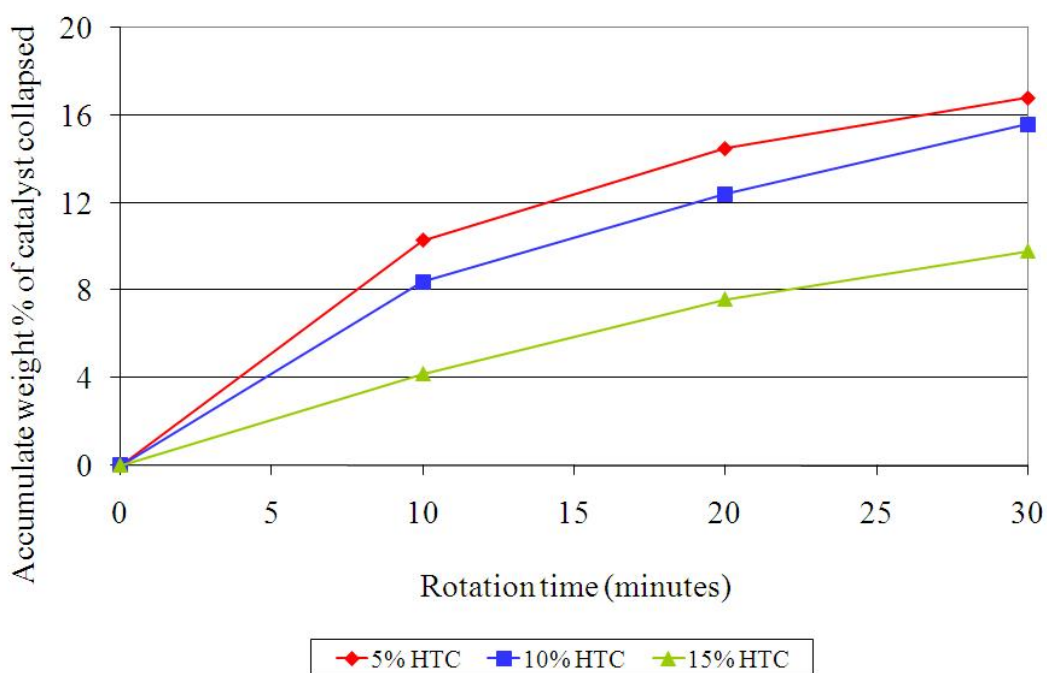
Figure 4.28: Rotating test results for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts with high temperature cement of various compositions
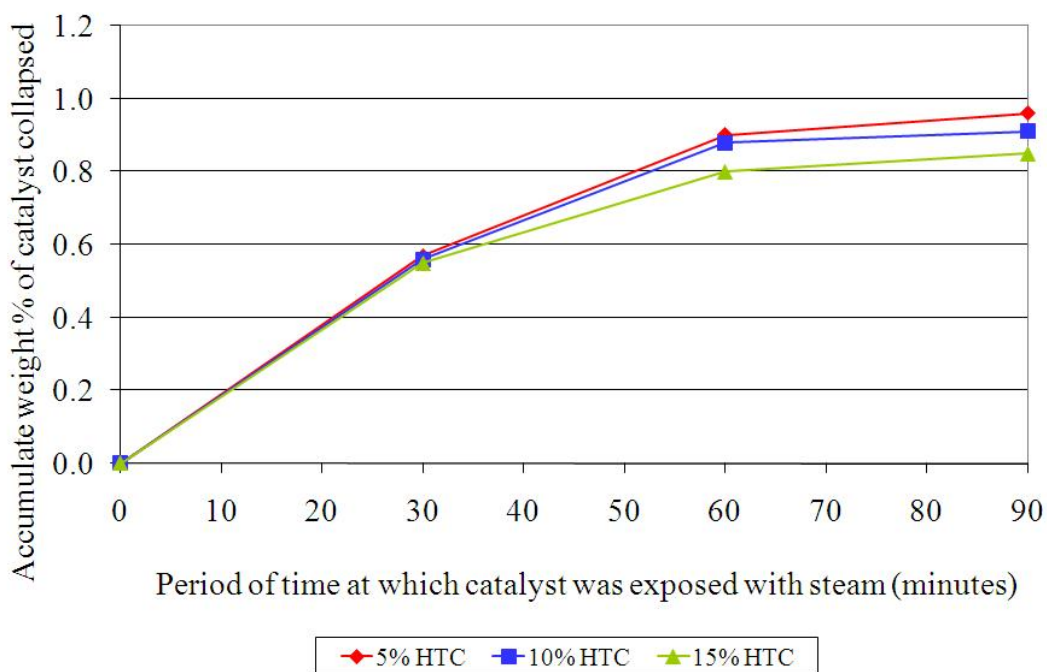
Figure 4.29: Steam resistance test results for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts with high temperature cement of various compositions

The dropping test results (Figure 4.26) showed that for an equivalent initial composition of binder, the catalysts coated with high temperature cement produced much better physical strength than those coated with glucose. The abovementioned results, therefore confirmed the improvement made by high temperature cement as an alternative binder to glucose.

The plots on Figures 4.27 to 4.29 indicate that increase in the binder compositions improves the physical strength of the final catalysts. The higher composition of binder, however, means less catalyst loading for the same total weight of coating solution, consequently less catalytic activity. This phenomenon was to be investigated by conducting series of catalytic screening tests on the high temperature cement catalysts with various binder compositions, which the specifications are listed in Table 4.8.

Table 4.8: Specifications of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ high temperature cement coated catalysts used to study the effects of binder compositions on the catalytic properties of the final coated catalysts

Specifications	ID of the coated catalyst			
	CC-3-7	CC-3-8	CC-3-9	CC-3-10
Diameter of Al_2O_3 spheres (mm)	3	3	3	3
Catalyst loading (weight %)	23.4	25.8	25.8	25.8
Binder type	High temperature cement			
Initial composition of binder (weight % of catalyst)	5	10	15	20
Sample for screening tests: Volume (ml)	5	5	5	5
Total weight (g)	3.561	3.567	3.510	3.489
Weight of catalyst loading (g)	0.833	0.920	0.906	0.900
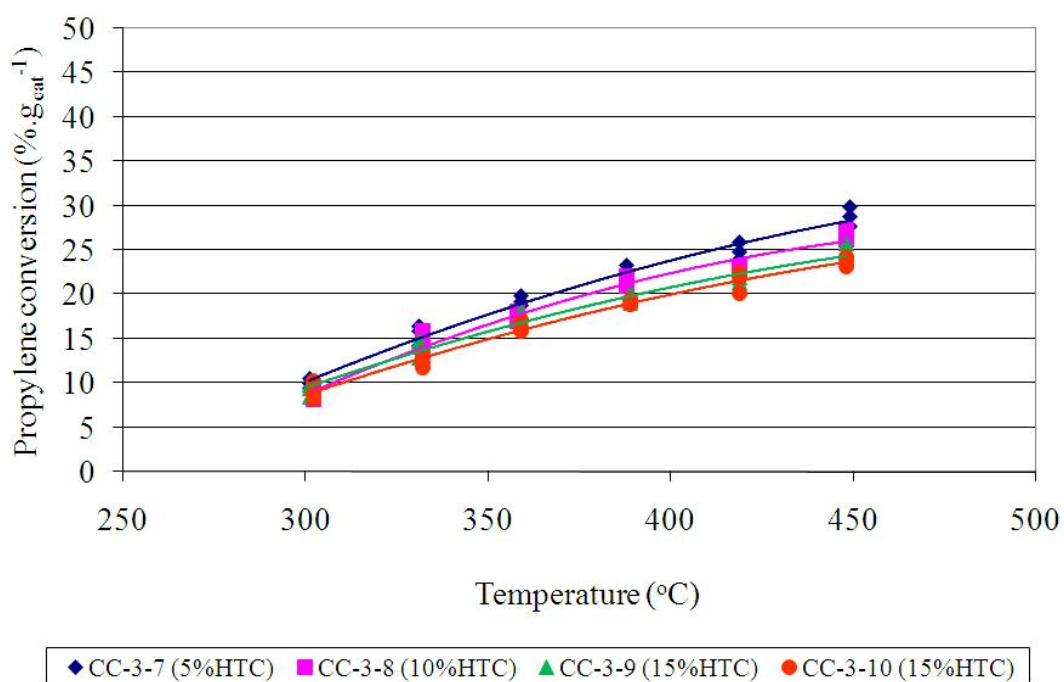
Figure 4.30: The effect of binder compositions for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ high temperature coated catalysts on the propylene conversion
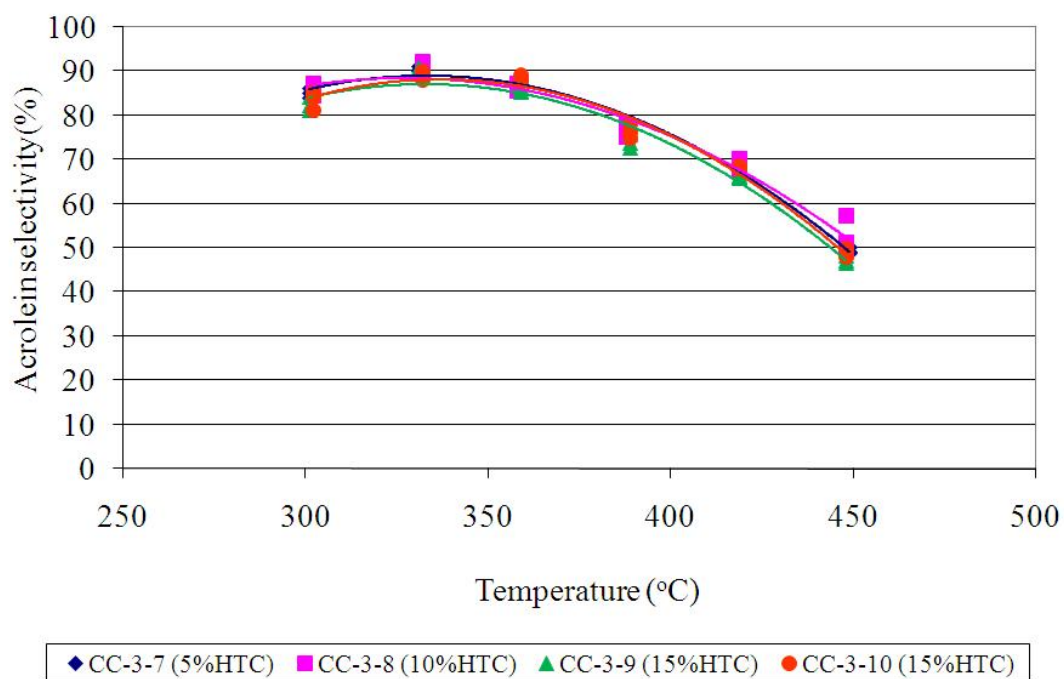
Figure 4.31: The effect of binder compositions for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ high temperature cement coated catalysts on the acrolein selectivity

The trends of propylene conversion (Figure 4.30) indicated that as the binder compositions increased, the final coated catalysts converted less of initial propylene. However the increase in compositions of high temperature cement did not show any specific trends in the selectivity to acrolein (Figure 4.31) and other side products (acetaldehyde, carbon dioxide, and carbon monoxide).

The study of the binder compositions on the catalytic and physical properties of the final coated catalysts concluded: (1) the coated catalysts with high temperature cement was stronger than that with glucose as the binder; (2) the increase in the binder compositions improved the physical strength of the final coated catalysts; and (3) the increase in binder compositions reduced the ability of the final coated catalysts to convert propylene.

Considering the aforementioned findings, the 5% of initial composition of high temperature cement was used to produce the final coated catalysts for the use in Chemeq pilot plant reactor to produce 100 g of acrolein in eight hours operation (Pham 2003). The binder composition higher than 5% was not crucial for the coated catalyst preparation since the exposure in the fixed bed reactor would not be as tough as the pressure in the in-house tests (dropping, compression, and rotating tests).

4.1.4.5 THE EFFECTS OF CATALYST LOADING COMPOSITIONS

Coated catalysts of various catalyst loading compositions (15%, 25%, 30% and 35% of parent catalyst $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$), which the specifications are outline in Table 4.8. Approximately 5 ml of sample from these catalsyts were exposed to the dropping tests from 100 cm and the comparative results are plotted in Figure 4.32.

Table 4.9: Specifications of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts used to study the effects of catalyst loading compositions

Specifications	ID of the coated catalyst			
	CC-3-15	CC-3-16	CC-3-17	CC-3-18
Diameter of Al_2O_3 spheres (mm)	3	3	3	3
Catalyst loading (weight %)	15.1	24.9	30.9	35.9
Binder type	High temperature cement			
Initial composition of binder (weight % of catalyst)	5	5	5	5
Sample for screening tests: Volume (ml) Total weight (g) Weight of catalyst loading (g)	5 3.779 0.570	5 3.689 0.919	5 3.512 1.085	5 3.432 1.232
Specifications	ID of the coated catalyst			
	CC-3-19	CC-3-20	CC-3-21	CC-3-22
Diameter of Al_2O_3 spheres (mm)	3	3	3	3
Catalyst loading (weight %)	14.7	24.9	30.8	35.8
Binder type	Glucose			
Initial composition of binder (weight % of catalyst)	5	5	5	5
Sample for screening tests: Volume (ml) Total weight (g) Weight of catalyst loading (g)	5 3.699 0.544	5 3.612 0.899	5 3.589 1.105	5 3.488 1.249

Figure 4.32: Dropping test results from 100 cm height for the
$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts of various
catalyst loading compositions

The trends of dropping test results in Figure 4.32 reconfirmed the previous results that the coated catalysts with high temperature cement were relatively stronger than that with glucose as binder. The trends show that the higher catalyst loading results in higher percentage of collapsed catalyst, thus more fragile of the final catalysts.

All catalysts listed in Table 4.8 were put into the laboratory size fixed bed reactor for the screening tests in order to comparatively identify the effect of catalyst loading compositions in catalytic performance of the final coated catalysts. The screening results for propylene conversion and acrolein selectivity are presented in Figures 4.33 and 4.34.

(a)

(b)
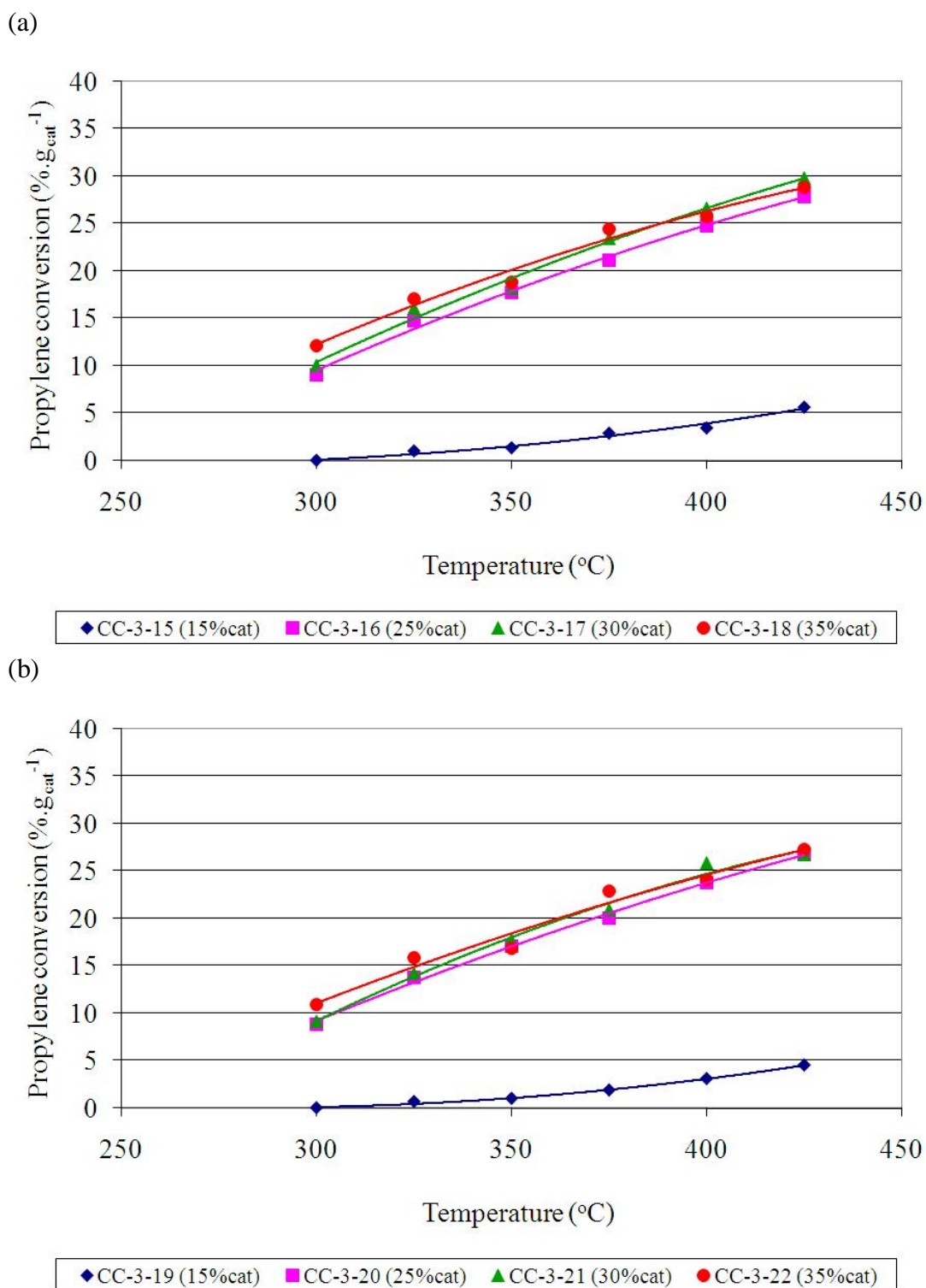
Figure 4.33: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts on the propylene conversion
(a) high temperature cement catalysts (b) glucose catalysts

(a)

(b)
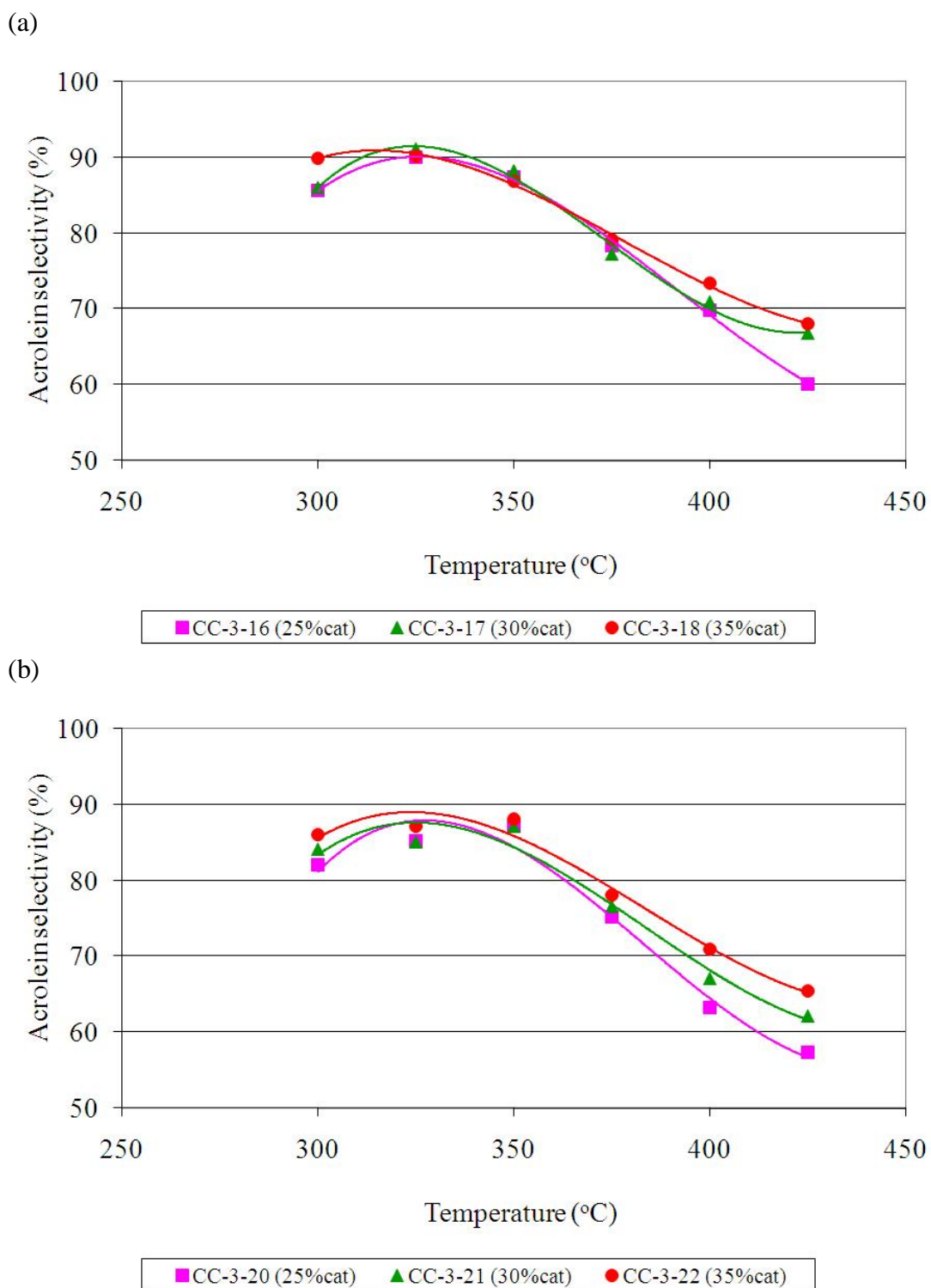

Figure 4.34: The effect of binder types for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ coated catalysts on the acrolein selectivity
(a) high temperature cement catalysts (b) glucose catalysts

As expected and shown in Figures 4.33 and 4.34 an increase in the catalyst loading of final coated catalysts improved the catalytic performance, however the increase in the catalyst loading compositions higher than 25% was insignificant. The coated catalysts with 15% catalyst loading (CC-3-15 and CC-3-19) had very low conversion of propylene.

The study of catalyst loading on the physical strength and catalytic properties of the final coated catalysts led to the recommendation for coated catalyst production to be used in the Chemeq pilot plant reactor (Pham 2003), i.e. 25-30% catalyst loading. The reasons were that the coated catalysts of 25% catalyst loading had relatively better physical strength as well as relatively similar catalytic properties (propylene conversion and acrolein selectivity) than that of higher catalyst loadings (30% and 35%). The other advantage of having 25% catalyst loading compared to the higher catalyst loading was the easiness to coat less amount catalyst powder onto the alumina carrier.

4.1.5 CONCLUSIONS ON THE COATED CATALYST STUDY

The results on the study of the coated catalysts concluded that the 3 mm Al_2O_3 spheres as the carrier, the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ as the parent catalyst, and high temperature cement as the binder were the best combination of coating materials. The temperature of 450^oC for two hours was sufficient condition of final calcination to prepared coated catalysts with 25-30% of catalyst loading for the use in Chemeq pilot plant reactor to produce 100 g per eight hours operation.

The coated catalysts in general however have some limitations. As the ability to convert the propylene depends on the mass of the active catalyst (catalyst loading), the coated catalysts contained higher catalyst loadings would perform catalytically better. However the higher catalyst loading means the more difficult for the catalyst powder to anchor into the carrier. Having two different materials (the catalyst and the alumina) in the coated catalysts means different thermal expansion of these two materials would lead to more fragile form of final catalysts than if it forms from one homogeneous material. Based on these reasons, it is therefore necessary to develop a procedure for catalyst pellet productions.

4.2 CATALYST PELLETS

4.2.1 PREPARATION PROCEDURE OF CATALYST PELLETS

Two methods, pelletising (or tableting) and extruding, were employed to produce cylindrical forms of catalyst pellets. Techniques of pelletising and extruding were mainly differed from two aspects, i.e. the initial form of material and the pressure used to produce the pellets.

Pelletising required the feed to be in a dry form and uniform particle size in order to ensure good flow characteristics, i.e. minimum friction between the particles and formed aggregates. Because of these reasons, the parent catalyst used in the pelletising was in the readily active form of catalyst that had been calcined at $450^{\circ}C$. The catalyst powder for pelletising was prepared based on the preparation procedure as described in Section 3.1.1 previously. On the other hand, pellet production by extruding method was obtained from pastes of catalyst that has not been activated nor calcined at $450^{\circ}C$.

The pelletising technique aimed to produce strong pellets of high physical strength, whilst the extruding technique intended to produce low density, high porosity pellets. The pelletising therefore required much higher pressure than the extruding for production of pellets with desired properties accordingly. For this purpose, a single die-puncher (technique 1) was used to produce strong pellets, whereas an "icing funnel and bag" (technique 2) was used to manually produce extruded pellets.

4.2.1.1 PELLETISING METHOD

In this project, pelletising technique for the first technique of catalyst pellet production was carried out manually using a single die-puncher set as shown in Figure 4.35. Two batches of catalyst pellets, namely CP-1-1 and CP-1-2, were produced by means of a single die-puncher set using the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$ catalyst powder, which the preparation procedure was described in Section 3.1.1. The catalyst powder was mixed with the high temperature cement and polysaccharide, which the initial composition of each

component was 5 weight% of the catalyst. The specifications of all components are listed in Table 4.10. After these components were mixed in dry form, a few drops of distilled water were added. This 'wet' mixture was then put into the single die and pressured manually with the puncher. The pressure applied on the piston for the pellet production of the first batch was relatively more than the second one. Finally the pellets were calcined at 450°C for two hours in air.

Piston
d = 6 mm

d_o = 15 mm
t = 1 mm
h = 12 mm

d_i =   6 mm
t   = 2 mm
h = 20 mm
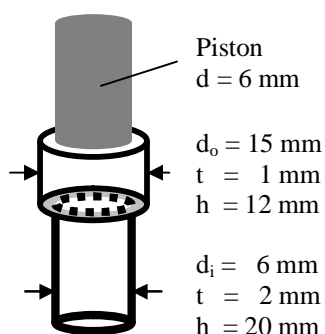
Figure 4.35: The die-puncher set for catalyst pellet preparation 1

Table 4.10: Specifications of catalyst pellets prepared based on the pelletising method

ID of the catalyst pellets	CP-1-1	CP-1-2
Specification of the initial components:		
Formula of the catalyst powder	$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$	
Initial weight of the catalyst powder (g)	10.708	10.909
Name of binder	High temperature cement	
Initial weight of binder (g)	0.547	0.533
Name of pore former	Polysaccharide	
Initial weight of pore former (g)	0.544	0.529
Specification of the final catalyst pellet:		
Weight of catalyst pellet after calcinations (g)	7.342	7.423
Final composition of binder (weight %)	5.6	5.6
Weight of binder in pellet (g)	0.408	0.412

The final pellets had dimensions of 6 mm in diameter and 2-9 mm in height. The pellet production using a single die-puncher set was very time consuming as it was

done manually one by one. It was also difficult to get the pellets out of the die subsequently the final catalyst pellets were inconsistent in the dimension. Due to these limitations, the extruding method for catalyst pellet preparation using an "icing funnel and bag" was carried out.

4.2.1.2 EXTRUDING METHOD

Productions of catalyst pellets by extruding method were obtainable from the catalyst pastes. In this project, the pastes were formed into cylindrical shapes by using an "icing funnel and bag" (that is usually used for cake decorator). The produced catalyst pellets had soft appearance, therefore had to be dried subsequently at 130°C for four hours, at 250°C for four hours, finally at 450°C for eight hours. In the extruding technique, both high temperature cement and glycol (ethanediol) were used separately as the catalyst binder.

Following the success of high temperature cement as binder for the coated catalyst, the high temperature cement was added in the process of pellet preparation (CP-2-1, CP-2-2, and CP-2-3) in the purpose for improving the strength of the final catalyst pellets. The high temperature cement (up to 25% in composition) could mix well with the catalyst and formed a solid pellet shaped substances. It was noticed that the more amount of high temperature cement added, the darker was the mixture.

Instead of high temperature cement, ethanediol (glycol) was used as binder in the preparation of CP-2-4, CP-2-5 and CP-2-6. It was found that the addition of glycol had physical effect on the catalyst as it made the catalyst mixture slightly more liquid-like in texture. It was still adequate for moulding through the "icing funnel and bag", however concentration of greater than 10 weight% of glycol in the catalyst was found to be too wet.

On overall, using an "icing funnel and bag" as the media of catalyst pellet production was much easier and time effective as well as produced a better, more uniform row of catalyst pellets than if using a die-puncher set (in the pelletising method).

The procedure of catalyst pellet preparation by extruding method using an "icing funnel and bag" was as follows:

1. Preparation and mixing of the initial solutions

    1.1 The following solutions were prepared in separate beakers:

        Solution 1: 18.2560 g of $Co(NO_3)_2.6H_2O$ was dissolved completely in 5 ml distilled water.

        Solution 2: 6.0745 g of $Fe(NO_3)_3.9H_2O$ was dissolved completely in 2 ml distilled water.

        Solution 3: 12.6815 g of $Bi(NO_3)_3.5H_2O$ was dissolved in 5 ml distilled water, and 0.8 ml of H_3PO_4 (85 weight %) was added to the solution.

        Solution 4: 3.6340 g of SiO_2 (40 weight %) was mixed with 2.7 ml KOH solution (0.24mol/l).

    1.2 On the porcelain bowl that was placed on a warm sand bath of $70^{o}C$, 38.1915 g of $(NH_3)_6Mo_7O_{21}.4H_2O$ was mixed with 20 ml distilled water and stirred until it was a homogeneous mixture.

    1.3 On the Ammonium Molybdate Tetrahydrate solution, 2.3850 g of WO_3 was added and mixed for 10 minutes.

    1.4 Solution 1, 2, 3 and 4 were dropped slowly one by one into the precipitation container and mixed for 45 minutes until a homogeneous mixture was formed.

2. The mixture was divided into 3 sections and placed into a separate pre-weighed porcelain bowl. The weight of catalyst in each bowl was measured and the corresponding amount of binder (either high temperature cement or glycol) required was calculated accordingly. The specifications of all catalyst pellets produced based on the extruding method are tabulated in Table 5.10.

3. The binder (either high temperature cement or glycol) was weighed according to the calculated amount. It was noted for high temperature cement to be sieved to ensure their uniformity before they were weighed.

4. The catalyst mixture was then mixed thoroughly with the binder. In the case of using high temperature cement for the binder, the distilled water could be added to help combine the two substances.

5. The catalyst mixture was then filled into an "icing funnel and bag" that have four mm in diameter hole. The catalyst paste was extruded on a ceramic tile.

6. The tile contained of rows of catalyst mixture was put into an air oven and pre-heated at 130°C for four hours to obtain solid pellet-like catalysts. The catalysts was then put into porcelain bowls and weighed.

7. The catalyst pellets were put into the furnace and calcined at 250°C for four hours then reweighed.

8. The catalyst pellets were put back into the furnace and calcined at 450°C for eight hours for activation. The final catalyst pellets were weighed again.

Table 4.11:   Specifications of catalyst pellets prepared based on the extruding method

ID of the catalyst pellets	CP-2-1	CP-2-2	CP-2-3	CP-2-4	CP-2-5	CP-2-6	CP-2-7
Specification of the extruded catalyst:							
Formula of the catalyst	$Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$						
Initial weight of the catalyst (g)	26.105	26.217	26.705	27.143	25.779	26.072	26.625
Specification of the catalyst binder:							
Name of binder	-	High temperature cement			Ethanediol (glycol)		
Initial composition of binder (as wt % of cat)	-	3	11	25	2	5	10
Initial weight of binder (g)	-	0.785	2.927	6.784	0.508	1.315	2.720
Specification of the final catalyst pellet:							
Weight of catalyst pellet after calcinations (g)	11.099	10.507	10.249	14.507	6.600	7.765	6.107
Final composition of binder (weight %)	-	3	10	20	-	-	-
Weight of binder in pellet (g)	11.099	0.305	1.012	2.901	6.600	7.765	6.107

4.2.2 PROCEDURE OF CATALYTIC SCREENING

The procedure and instrument set up of catalytic screening tests for catalyst pellets were similar to those for catalyst powder (Section 3.1.2) and coated catalysts (Section 4.1.2). The screening tests were carried out in the 1 cm in diameter of stainless steel tubular reactor at total feed flow rate of 120 ml.min^{-1} gas mixture consisting of 5% propylene, 10% oxygen and 85% helium over reaction temperature of 300-450°C in atmospheric pressure.

All screening tests were carried out using 5 ml sample, which previously were chosen manually in terms of the physical quality and uniformity. Prior to any screening measurement, the catalyst bed was pre-aged at the standard condition (120 ml.min^{-1} feed flow rates consisted of 5% propylene, 10% oxygen and 85% helium) at 400°C for at least eight hours or until the catalyst activity became steady. Once the steady condition was achieved, at least three measurements were taken at each reaction temperature.

The catalytic performance of each batch of catalyst pellets were determined in term of the activity to convert the initial propylene (Equation 3.4) and the selectivities (Equation 3.5) to acrolein and other detected side products (acetaldehyde, carbon dioxide and carbon monoxide). All calculations were done based on the number of carbon atom and the carbon balances throughout the experiments were $\pm$ 5%. In order for the data to be comparable, the calculations were carried out based on the percentage propylene converted per gram extruded catalyst and the selectivities of the products were used for the comparison purpose.

4.2.3 PROCEDURE OF DROPPING TEST FOR PHYSICAL STRENGTH

The physical strength of catalyst pellets of various specifications were compared by performing the dropping test, as detailed in Section 4.1.3.1. An approximately 5 g sample of uniform size catalyst pellets was dropped through a cylinder of 1 m height. The amount of collapsed material was weighed and a percentage of collapsed

material was calculated. Here collapsed material was defined as the matter that was smaller than 1 mm x 1 mm and would therefore be sieved through the meshing.

4.2.4 RESULTS AND DISCUSSION ON THE CATALYST PELLET STUDY

4.2.4.1 CATALYST PELLETS BY PELLETISING METHOD

As mentioned previously (in Section 4.2.1.1) a single die-puncher set of 6 mm in diameter produced catalyst pellets with various length dimension (2-9 mm). In order to produce comparable results, the sample for the use in the screening and the dropping tests was chosen manually. The catalyst pellets of 4 mm height were to be used for the tests. Table 4.12 lists the specifications of catalyst pellets for the screening tests.

Table 4.12: Sample specifications of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets prepared by pelletising method used for screening tests

Specifications	ID of the catalyst pellet	
	CP-1-1	CP-1-2
Final composition of pellets: Catalyst (weight %) Binder* (weight %) *High temperature cement	5.6 94.4	5.6 94.4
Dimension of catalyst pellet: Diameter (mm) Height (mm)	6 4	6 4
Sample for screening tests: Volume (ml) Total weight (g) Weight of catalyst loading (g)	5 3.876 3.661	5 3.743 3.535

It should be noted that CP-1-2 was prepared with relatively less pressure than CP-1-1. Therefore the comparative screening results for these two catalyst pellets could be used to study the effect of applied pressure in the pellet production on the catalytic performance of the final catalyst pellets. The catalytic screening results are plotted in Figures 4.36 to 4.40.
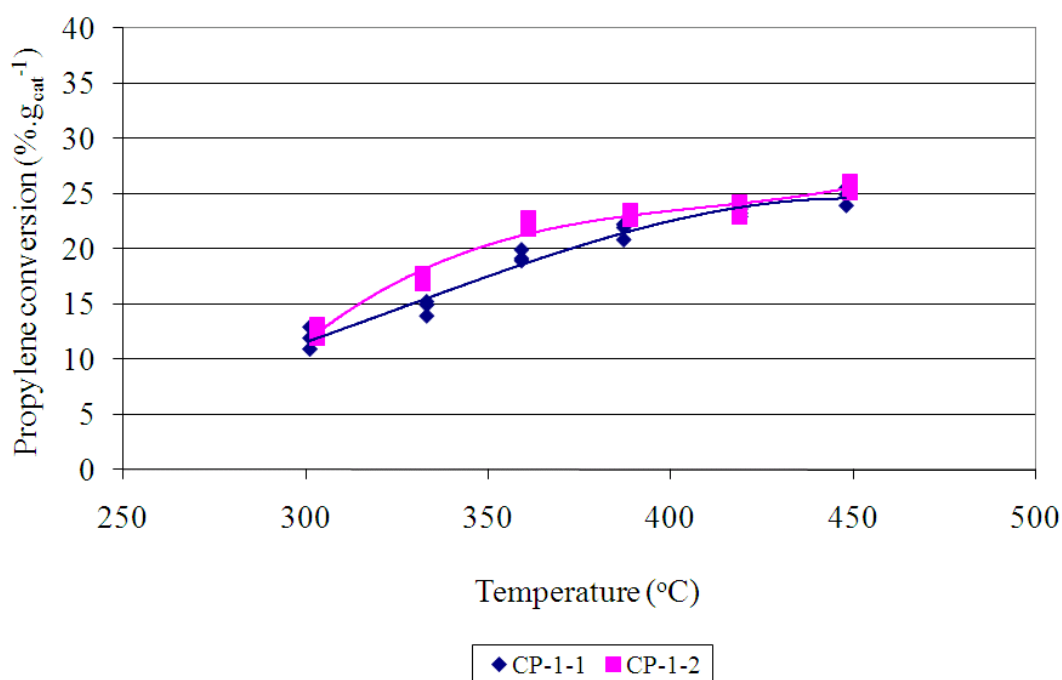
Figure 4.36: The effect of applied pressures in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the propylene conversion
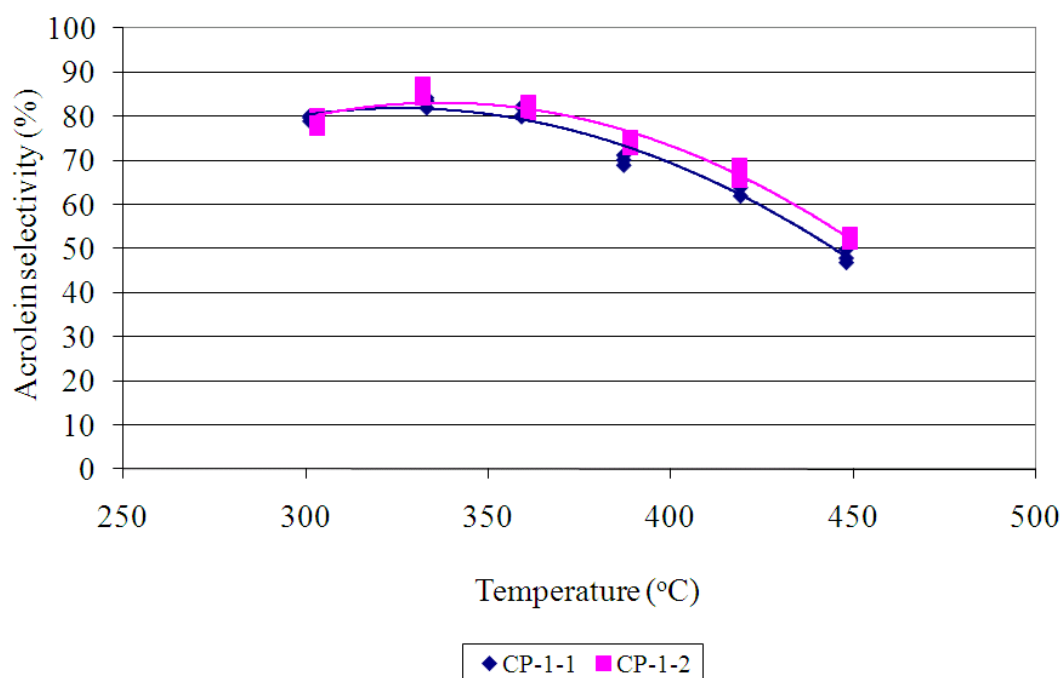
Figure 4.37: The effect of applied pressures in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the acrolein selectivity
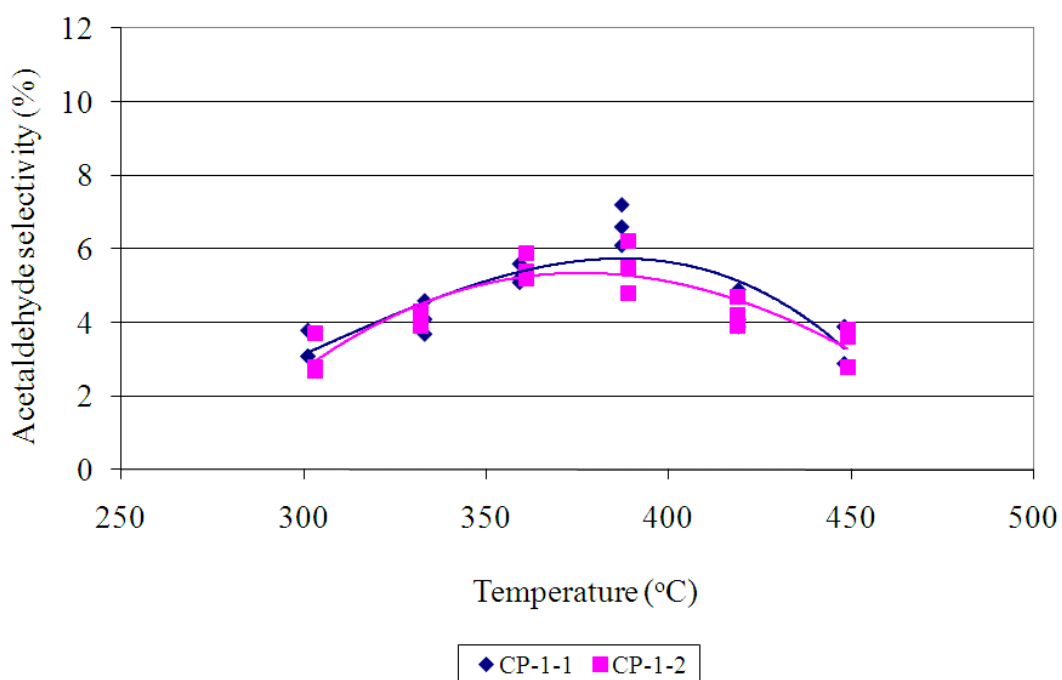
Figure 4.38: The effect of applied pressures in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the acetaldehyde selectivity
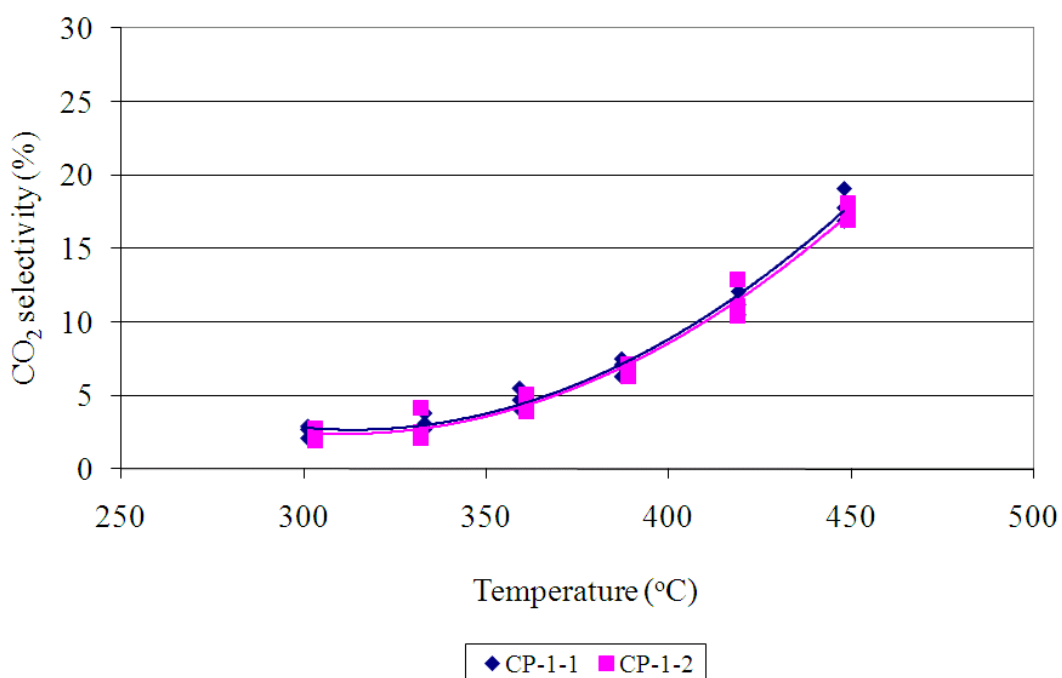
Figure 4.39: The effect of applied pressures in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the carbon dioxide selectivity
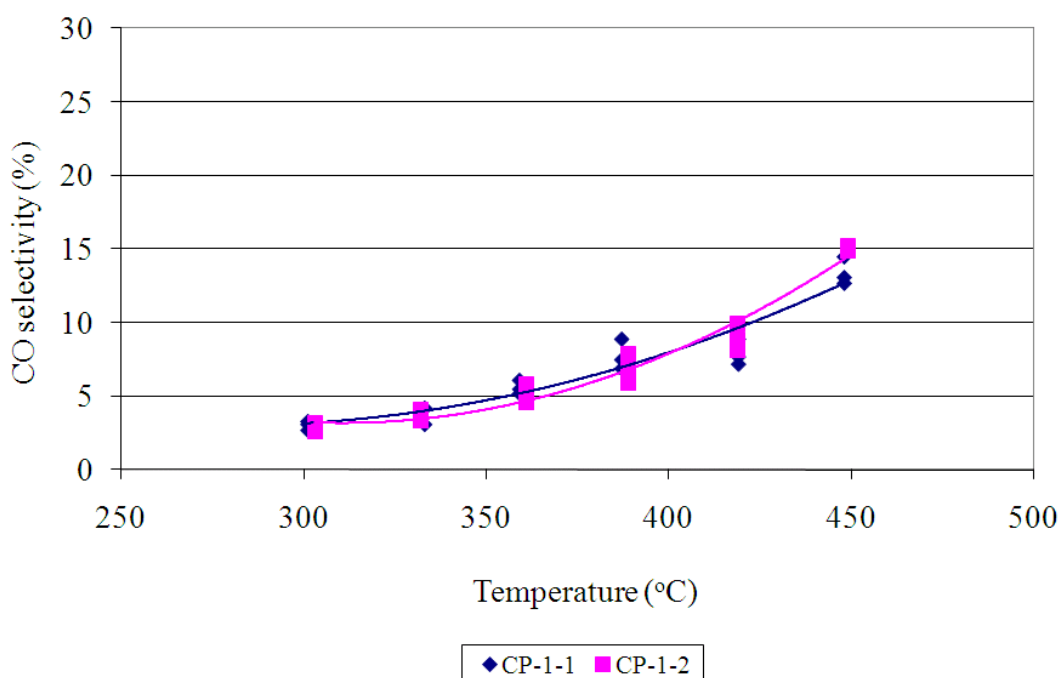
Figure 4.40: The effect of applied pressures in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the carbon monoxide selectivity

The pelletised $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.06}Si_{1.4}P_{0.7}O_x$ catalysts could retain its catalytic activity, consistent with its parent catalyst powder and the coated catalysts. The catalyst pellets CP-1-2 has slightly better catalytic performance than the catalyst pellets CP-1-1 in terms of more conversion of propylene (Figure 4.36) and higher selectivity to acrolein (Figure 4.37). The reason of CP-1-2 had slightly better activity and selectivity than CP-1-1 was the second batch of catalyst pellets were produced on the less pressure than the first one. Obviously less pressure can make the final catalyst pellets more porous and therefore more catalytically active.

From Figure 4.37 of acrolein selectivity, it was indicated that both CP-1-1 and CP-1-2 had the optimum reaction temperature of $330^{o}C$ at which the catalyst had the highest selectivity to targeted product, acrolein. The CP-1-1 converted 83% of reacted propylene into acrolein, whilst CP-1-2 had higher acrolein selectivity of 86% at the same reaction temperature. The selectivities to other side products of the reaction including acetaldehyde, carbon dioxide, and carbon monoxide are presented in Figures 4.38 to 4.40. No significant difference in the selectivity to side products was observed between CP-1-1 and CP-1-2.

The pellets were also put into the dropping tests from height of 20, 40, 60, 80 and 100 cm and the results are plotted in Figure 4.41. The dropping test results showed a maximum of 1% as accumulate weight percentage of collapsed material. This value (1%) was very low compared to that of coated catalysts (up to 28% in Figure 4.32). The pellets had proven to have better physical properties than the coated catalysts.
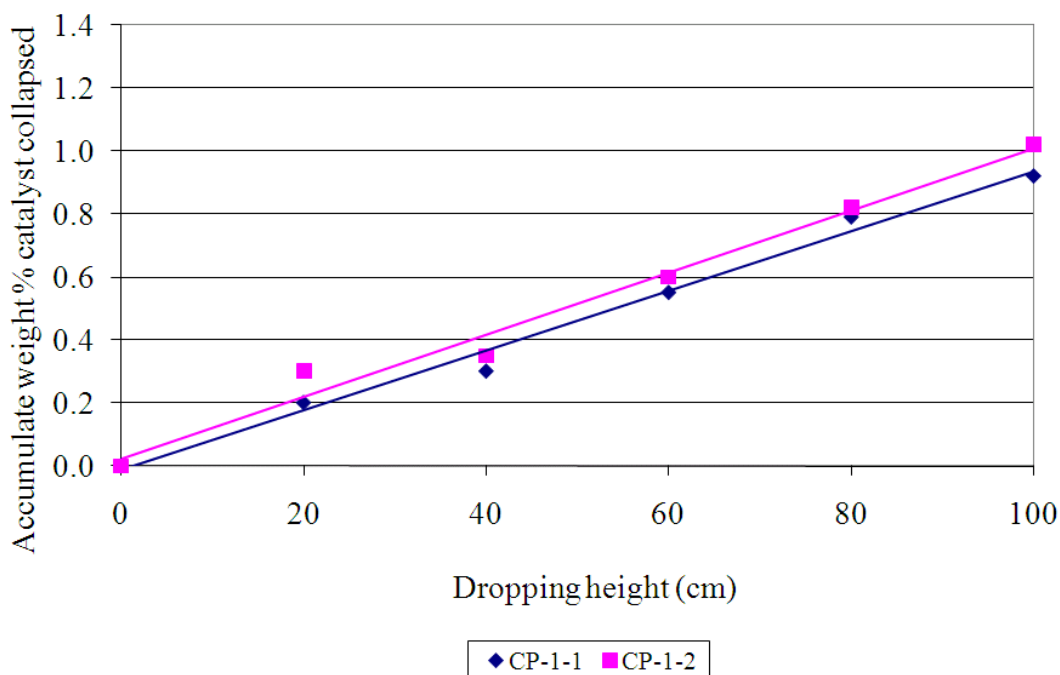

Figure 4.41:   The effect of applied pressures in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the catalyst physical strength, which relatively observed through dropping tests

The preliminary production of the catalyst pellets concluded that the pellets were relatively much stronger than the coated catalysts. The catalyst pellets were proven to be catalytically active. It was indicated that the catalyst pellets prepared by less pressure applied were performed catalytically more active and more selective than that prepared by more pressure applied. Due to the prior reason in addition to the difficulty in taking the pellets out of the die, the extruding method was proposed to produce more porous uniform size catalyst pellets than the pelletising method.

4.2.4.2 CATALYST PELLETS BY EXTRUDING METHOD

Using the samples listed in Table 4.13, the effects of binder types (high temperature cement and glycol) and their compositions were studied by performing both catalytic screening (Figures 4.42 to 4.46) and dropping (Figure 4.47) tests.

Table 4.13: Sample specifications of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets prepared by extruding method used for screening tests

Specifications	ID of the catalyst pellet						
	CP-2-1	CP-2-2	CP-2-3	CP-2-4	CP-2-5	CP-2-6	CP-2-7
Binder name (G = glycol, HTC = high temperature cement)	-	HTC	HTC	HTC	G	G	G
Initial composition of binder (as weight % of catalyst)		3	11	25	2	5	10
Final composition of pellets: Catalyst (weight %)	100	97	90	80	100	100	100
Binder* (weight %)	-	3	10	20	-	-	-
*High temperature cement							
Dimension of catalyst pellet: Diameter (mm)	4	4	4	4	4	4	4
Height (mm)	4	4	4	4	4	4	4
Sample for screening tests: Volume (ml)	5	5	5	5	5	5	5
Total weight (g)	3.67	3.57	3.66	3.64	3.59	3.64	3.65
Weight of catalyst loading (g)	3.67	3.47	3.30	2.91	3.59	3.64	3.65
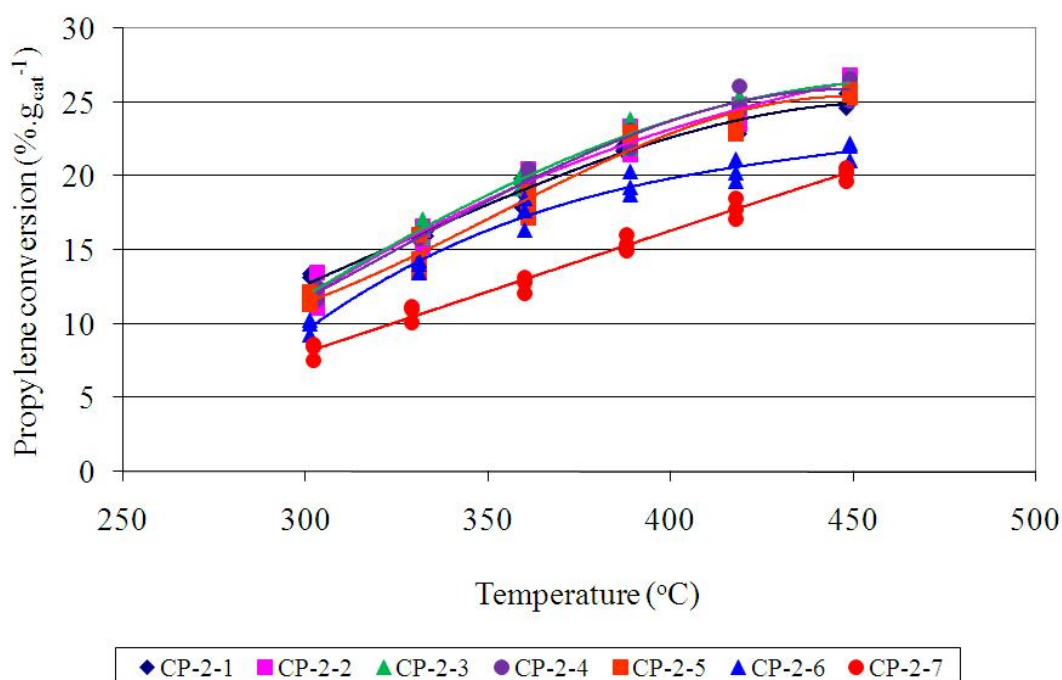
Figure 4.42:   The effect of binder types and their compositions in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the propylene conversion

The effects of binder types and their compositions on the conversion of propylene could be observed from Figure 4.42. The catalyst pellet using high temperature cement of initial compositions of 3% (CP-2-2) and that of 10% (CP-2-3) as well as the catalyst pellet using glycol of initial composition of 2% (CP-2-5) had similar levels of conversion to the pure catalyst pellet (CP-2-1). It was also indicated that higher initial compositions of glycol (CP-2-6 for 5% and CP-2-7 for 10%) and of high temperature cement (CP-2-4 for 25%) caused significant decrease in the propylene conversion. Due to the aforementioned reason (i.e. relatively lower propylene conversion of CP-2-4, CP-2-6 and CP-2-7) in addition to simplify the presentation of screening results, therefore only the results of CC-2-1, CP-2-2, CP-2-3, and CP-2-5 was presented in Figures 4.43 to 4.46. The carbon balances were performed and were found to be within the $\pm$ 5% error.
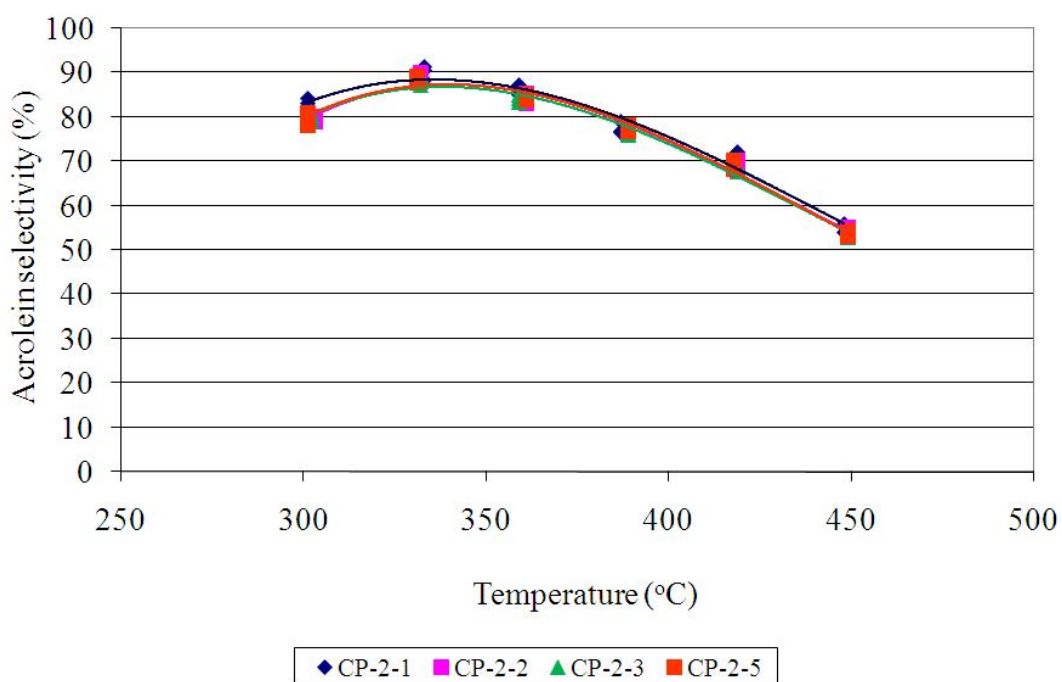
Figure 4.43: The effect of binder types and the compositions in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the acrolein selectivity
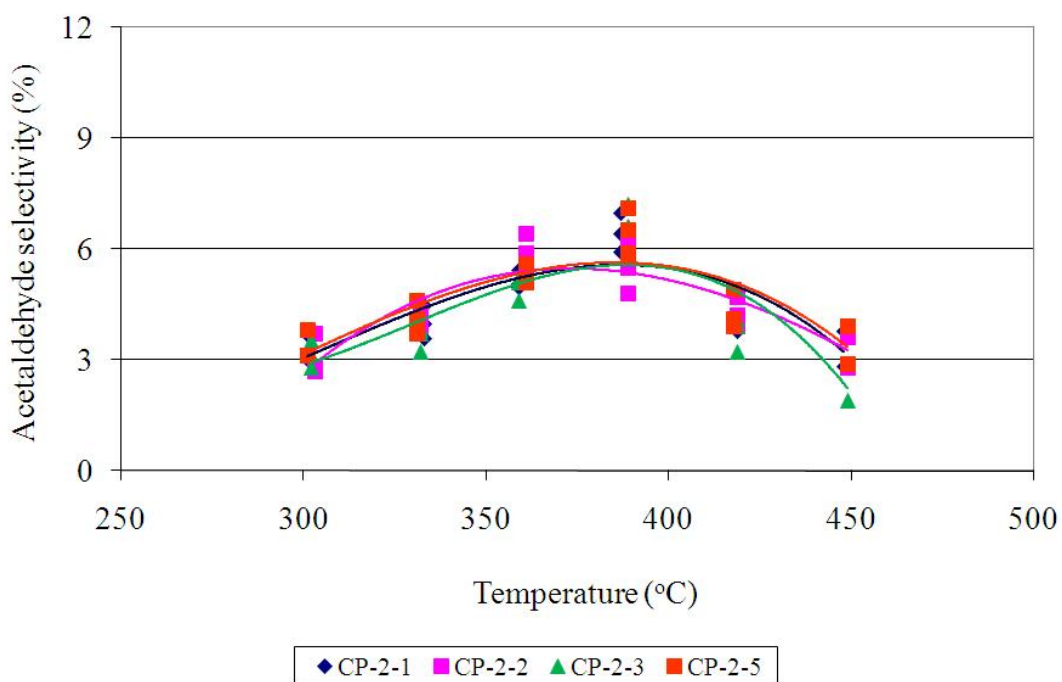
Figure 4.44: The effect of binder types and the compositions in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the acetaldehyde selectivity
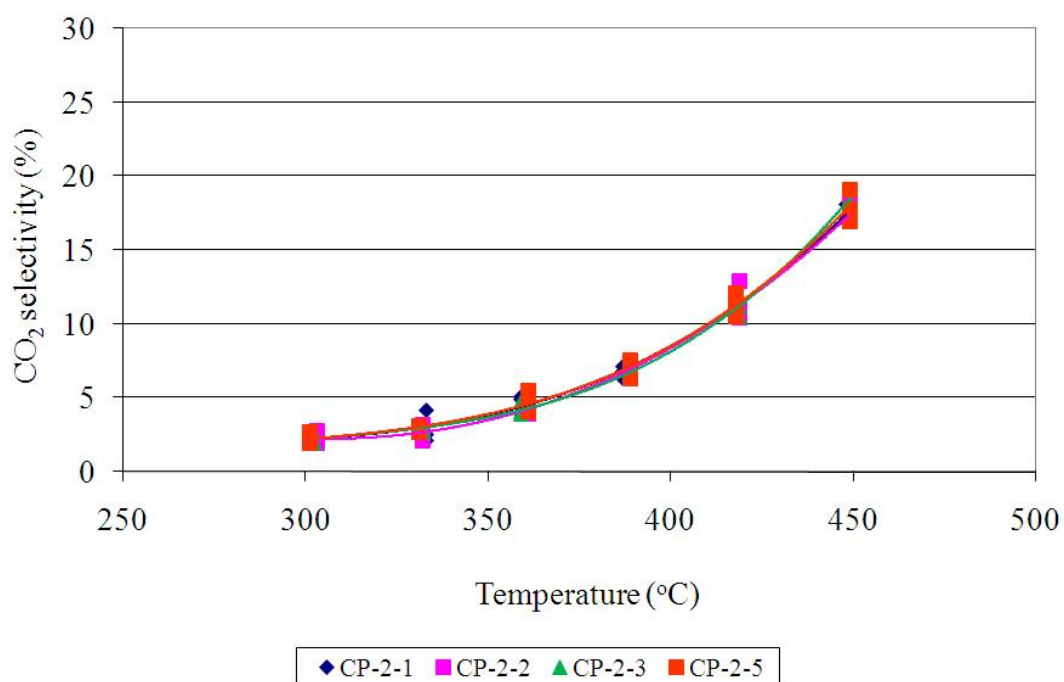
Figure 4.45: The effect of binder types and the compositions in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the carbon dioxide selectivity
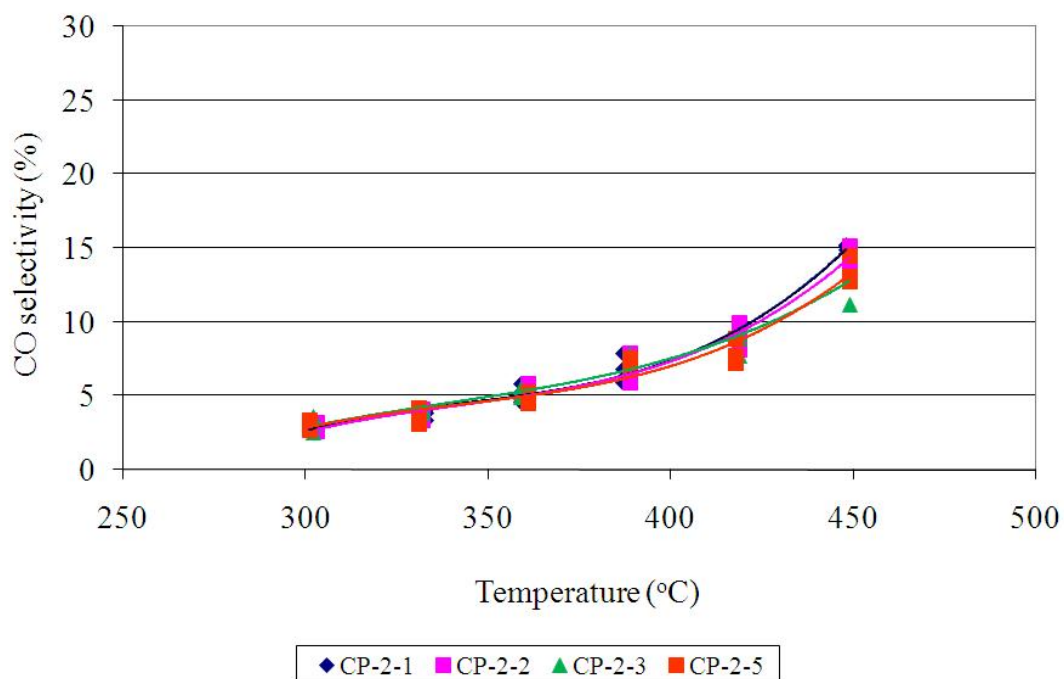

Figure 4.46: The effect of binder types and the compositions in the pellet production of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets on the carbon monoxide selectivity

No significant difference was detected in the selectivity to acrolein (Figure 4.43) among the catalytic performances of catalyst pellets prepared using either initial composition of 3% high temperature cement (CP-2-2) or 11% high temperature cement (CP-2-3) or 2% glycol (CP-2-5). These three catalyst pellets had maintained a high selectivity to acrolein up to 90% at low reaction temperature of $330^{o}C$, similar to the catalyst pellets that prepared using no addition of binder (CP-2-1).

Figures 4.44 to 4.46 present the plots of selectivities to side products of propylene oxidation, which were acetaldehyde, carbon dioxide and carbon monoxide. The plots show that there was no considerable difference detected on the side-products formed by these four catalyst pellets (CP-2-1, CP-2-2, CP-2-3 and CP-2-5). In overall, the screening results concluded that the binder additions of either high temperature cement up to 11% of the catalyst weight or glycol up to 3% of the catalyst weight did not have negative effects on the catalytic performance of the final extruded catalyst pellets.

Approximately 5 g of sample from all extruded catalyst pellets (listed in Table 4.12) were exposed to the dropping tests from 100 cm height. Prior to the tests, the pellets used for test material were manually selected in terms of the uniformity and quality. The dropping test results were plotted in terms of average percentage collapsed material versus the numbers of drops performed on each sample (Figure 4.47).
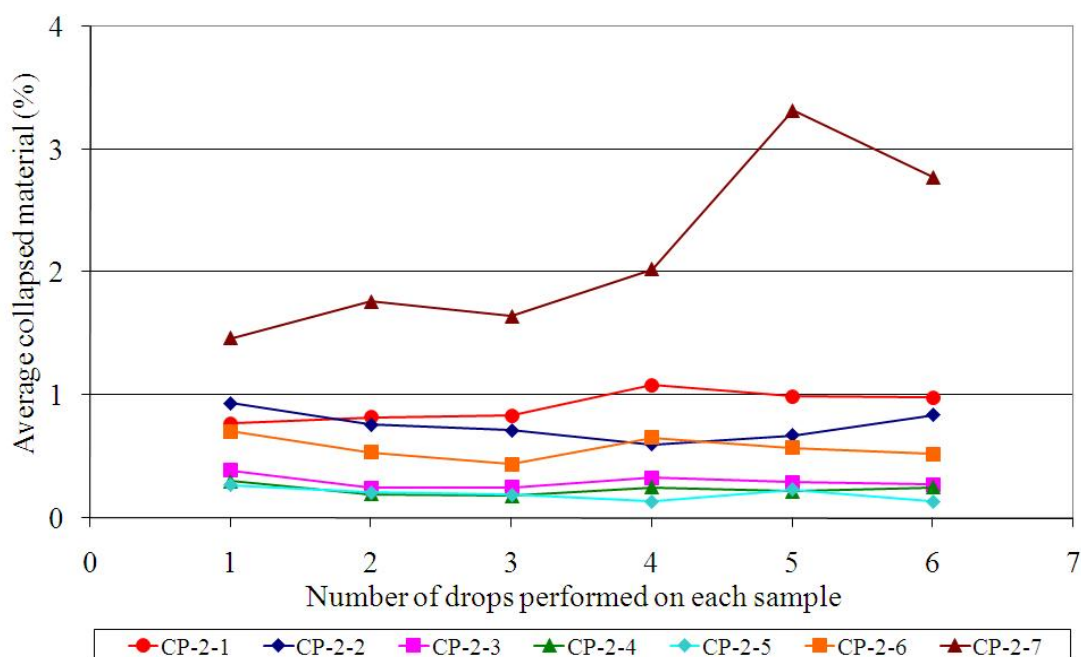
Figure 4.47: Dropping test results of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets produced by extruding method

It was shown from Figure 4.47 that addition of high temperature cement to the catalyst mixture proved to be effective to improve the physical strength of the pellets. Higher amount of high temperature cement produced stronger catalyst pellets. The addition of 11-25 weight% high temperature cement (CP-2-3 and CP-2-4) improved the strength of the catalyst pellets by a factor of two, whilst the addition of 3 weight% high temperature cement (CP-2-2) only improved the strength slightly.

The addition of glycol to the catalyst mixture was found to be less effective than that of the high temperature cement. The trends of dropping test results indicated that the more glycol added to the catalyst mixture, the weaker it became. The outstanding result was shown by the catalyst pellets with addition of 2 weight% of glycol (CP-2-5) as it produced the lowest percentage of collapsed material than any other sample. On overall, the most successful catalysts with the lowest breakability were the catalyst pellets with addition of either 11 weight% high temperature cement or 25 weight% high temperature cement or 2 weight% glycol.

Taking the consideration both conclusions on the catalytic screening and the dropping tests had resulted in the two best catalyst pellets, i.e. using either 11% of high temperature cement or 2% of glycol.

4.2.5 CONCLUSIONS ON THE CATALYST PELLET STUDY

The study on catalyst pellets had met the initial objectives, i.e. to produce another form of catalysts that were stronger than the coated catalyst and still maintained high catalytic properties of the parent catalyst ($Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$).

The dropping test results had proven that catalyst pellets both prepared based on the pelletising and extruding techniques were stronger than the coated catalysts. The improvement on the physical strength was mainly due to the homogeneity of the catalyst pellets.

The screening test results have proven that the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst pellets, which prepared using either high temperature cement or glycol as binder, were catalytically active. Low initial compositions of binder (i.e. less than 11% for high temperature cement and 2% for glycol) particularly had retained the high catalytic properties consistent with the catalyst pellets prepared without addition of binder, i.e. maximum acrolein selectivity of 90% at low reaction temperature of 330^oC. The catalyst pellets with 11 weight% of high temperature cement had been used in the Chemeq reactor and achieved the production target of 100 g acrolein per 8 hours operation (Pham 2003).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The objectives of this project have been achieved. At temperature of 350°C, the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst could convert 95% of the propylene into the targeted product, acrolein. The detected by-products of the reaction were carbon dioxide, carbon monoxide and acetaldehyde. The carbon balance in all screening test for catalytic performance was within $\pm$ 6% error. The X-ray analysis detected the main components of catalyst: MoO_3, α-$Bi_2Mo_3O_{12}$, $CoMoO_4$, BiO_3 and WO_3. Other minor components included $FeMoO_4$, $Fe(MoO_4)_3$, $Bi_3FeMo_2O_{12}$, $BiPO_4$, $MoOPO_4$ and $Bi_9PMo_{12}O_{52}$.

The catalyst was prepared based on the precipitation technique, in which the practicality and reliability had been verified by relatively consistent catalytic performance of several reproduction batches. The catalyst reproduction included various size of production from 50 g to 1.5 kg per batch and two methods of catalyst drying that were manually achieved by the hot petroleum drying technique and using spray drier.

The value of the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst was even more attractive, as it had proven its feasibility and consistency in maintaining its high activity and selectivity when using propylene feedstock straight from the by-product of refinery without prior purification. No other by-products than previously detected using high purity propylene was detected in the screening within the experimental conditions.

The rate of reaction for formation of acrolein was investigated using the differential reactor for the purpose of parameter optimisation. It was observed that within the experimental conditions of 120ml.min^{-1} with variation of reactant concentrations

within 3.33% - 13.33% for propylene and 3.75% - 15% for oxygen over reaction temperatures of 300 – 450°C, the 5% propylene and 10% oxygen was the optimum composition for acrolein yield at 350°C.

As the catalyst prepared by precipitation technique was in the form of powder, therefore it had to be physically modified for application in the most common reactor type for the acrolein production, i.e. fixed bed reactor. Two final catalyst types were prepared and investigated in this project: the coated catalyst spheres and the catalyst pellets. Both of the catalyst types had shown the feasibility to be used in the laboratory scale fixed bed in terms of the activity properties and the physical strength.

Optimisation in preparation parameters of the coated catalysts was indicated that the 3 mm Al_2O_3 spheres as the carrier, the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst powder as the parent catalyst and high temperature cement as the binder are the best combination of coating materials. The final catalyst with 25-30% of catalyst loading calcined at 450°C for two hours had successfully been utilised to produce 100 g of acrolein per 8 hours operation in Chemeq reactor.

The catalytic conversion in general depends on the mass of the catalyst, in which for the coated catalyst means the mass of catalyst loading on the carriers. Therefore, the higher catalyst loadings would catalytically perform better. However, the higher catalyst loading means the more difficult for the catalyst to anchor into the carrier. Having two materials (the catalyst and the alumina) in the coated catalysts also means having different thermal expansion that would lead to a more fragile form of the final catalyst compared to the catalyst that forms from one homogeneous material. Based on the limitations in the preparation procedure and the physical strength of the coated catalyst, therefore the catalyst pellet was manufactured as the alternative form of catalyst for the use in the fixed bed reactor.

There were two techniques in the preparation of catalyst pellets in this project: the pelletising and the extruding techniques, in which both had proven to be catalytically active and physically stronger than the coated catalyst spheres. In particular, the catalyst pellets with low composition of binder (i.e. 11% for high temperature cement and 2% for glycol) had maintained high catalytic properties (optimum acrolein selectivity of 90% at 330°C) consistent with the catalyst pellets prepared without the addition of binder. The catalyst pellets with 10% high temperature

cement was used in the Chemeq reactor pilot plant and could achieve the target production of 100 g acrolein per 8 hours operation.

The results on both coated catalysts and catalyst pellets indicated that the innovative idea of using high temperature cement as an alternative to conventional binders (glucose and glycol) was justified.

5.2 RECOMMENDATIONS

The following points are recommended for future studies:

- To scale up the production plant for the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst so that the development of catalyst preparation procedure for large scale can be verified.

- To carry out the stability study of catalyst, including the catalyst decay and the catalyst life time.

- To develop the regeneration procedure for the catalyst.

- To gather more data on the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst including the catalyst characteristics, the catalyst morphology and the catalyst reproducibility. Once enough convincing data is obtained, it is recommended to patent the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst.

- To study the kinetics of partial oxidation of propylene to acrolein over the $Mo_{12}Bi_{1.5}Fe_{0.8}Co_{3.5}W_{0.6}K_{0.04}Si_{1.4}P_{0.7}O_x$ catalyst using the differential fixed bed reactor.

- To achieve a better understanding on how high temperature cement works better than the alternative binders.

REFERENCES

ACTED Consultant 1997, *Acrylic acid manufacture in Western Australia*, viewed 18 February 2002, http://www.chemlink.com.au/acryful.htm

Adams, CR & Jennings, TJ 1963, 'Investigation of the mechanism of catalytic oxidation of propylene to acrolein and acrylonitrile', *Journal of Catalysis*, vol. 2, no. 1, pp. 63-68.

Adams, CR & Jennings, TJ 1964a, 'Mechanism studies of the catalytic oxidation of propylene', *Journal of Catalysis,* vol. 3, no. 6, pp. 549-558.

Adams, CR, Voge, HH, Morgan, CZ & Armstrong, WE 1964b, 'Oxidation of butylenes and propylene over bismuth molybdate', *Journal of Catalysis,* vol. 3, no. 4, pp. 379-386.

Allen, CS, Annan, N, Blankenship, RM, Gallagher, MK, Gore, RH, Lamola, AA & You, Y 2002, *Porous materials*, United States Patent 6420441.

Allen, CS, Annan, N, Blankenship, RM, Gallagher, MK, Gore, RH, Lamola, AA & You, Y 2003, *Porous materials*, United States Patent 6602804.

Aliev, VS, Rustamov, MI & Zeinalov, RI 2004, 'Static characteristics of the direct heterogeneous oxidation of propylene to acrolein in a reactor with a fluidized catalyst bed, *Chemistry and Technology of Fuels and Oils*, vol. 7, no. 10, pp. 739-742.

Arntz, D, Knapp, K & Prescher, G 1982, 'Catalytic air oxidation of propylene to acrolein: Modelling based on data from an industrial fixed-bed reactor' in *Chemical Reactor Engineering – Boston*, eds. Wei, J & Georgakis, C, Boston, vol. 196, pp. 3-14.

Arntz, D, Prescher, G & Heilos, J 1984, *Process for preparing by catalytic oxidation in oxygen-containing gas mixtures, acrolein from propylene and methacrolein from isobutylene or tertiary butanol*, United States Patent 4442308.

Baerns, M, Buyevskaya, OV, Kubik, M, Maiti, G, Ovsitser, O & Seel, O 1997, 'Catalytic partial oxidation of propane to acrolein', *Catalytic Today*, vol. 33, no. 1-3, pp. 85-96.

Batist, PA, Van de Moesdijk, CGM, Matsuura, I & Schuit, GCA 1971, 'The catalytic oxidation of 1-butene over bismuth molybdates: promoters for the $Bi_2O_3.3MoO_3$ catalyst', *Journal of Catalysis,* vol. 20, no. 1, pp. 40-57.

Benaichouba, B, Bussiere, P & Vedrine, JC 1995, 'In-situ Mössbauer spectroscopic study of iron site evolution in iron and cobalt molybdates catalysts in propene oxidation reaction conditions', *Applied Catalysis A: General*, vol. 130, no. 1, pp. 31-45.

Bergna, HE 1987, *Attrition resistant catalysts, catalyst precursors and catalyst supports and process for preparing same*, United States Patent US4677084.

Bettahar, MM, Constentin, G, Savary, L & Lavalley, JC 1996, 'On the partial oxidation of propane and propylene on mixed metal oxide catalysts', *Applied Catalysis A: General,* vol. 145, pp. 1-48.

Bielanski, A & Haber, J 1991, *Oxygen in Catalysis*, Marcel Dekker, Inc., New York.

Bub, G, Mosler, J, Maschmeyer, D, Sabbagh, A, Fornika, R & Peuckert, M 2005, *Process for the production of acrylic acid*, United States Patent 20050171380A1.

Buyevskaya, OV & Baerns, M 2002, 'Oxidative functionalization of ethane and propane', *Catalysis*, vol. 16, pp.155-197.

Brazdil, JF, Suresh, DD & Grasselli, RK 1980, *Process for forming multi-component oxide complex catalysts*, United States Patent 4212766.

Bromly, JH & Roga, P 1980, 'Nonlinearities in flame ionization detector response', *Journal of Chromatographic Science*, vol. 18, pp. 606-613.

Brückman, K, Haber, J & Turek, W 1988, 'Kinetics of the oxidation of propene on MoO3 based model catalysts', *Journal of Catalysis*, vol. 114, pp. 196-199.

Callahan, JL, Grasselli, RK, Milberger, EC & Strecker, HA 1970, 'Oxidation and ammoxidation of propylene over bismuth molybdate catalyst', *Industrial Engineering Chemical Product: Research and Development,* vol. 9, no. 2, pp. 134-142.

Carrazan, SRG, Martin, C, Rives, V & Vidal, R 1996a, 'An FT-IR spectroscopy study of the adsorption and oxidation of propene on multiphase Bi, Mo, and Co catalysts', *Spectrochimica Acta Part A,* vol. 52, pp. 1107-1118.

Carrazan, SRG, Martin, C, Rives, V & Vidal, R 1996b, 'Selective oxidation of isobutene to methacrolein on multiphasic molybdate-based catalysts', *Applied Catalysis A: General,* vol. 135, pp. 95-123.

Chang, TS, Cho, DH, Lee, DK & Yun, SS 2001 ' Effect of transition metal cation on multicomponent bismuth phosphate catalyst in propylene ammoxidation', *Bulletin of the Korean Chemical Society*, vol. 22, no. 1, pp. 117-119.

Contractor, RM, Andersen, MW, Campos, D, Hecquet, G, Kotwica, R, Pham, C, Simon, M & Stojanovic, M 2002, *Vapor phase oxidation of propylene to acrolein*, United States Patent 6437193.

Cullis, CF & Hucknall, DJ 1982, 'Selective Oxidation of Hydrocarbons', in GC Bond & G Webb (eds.), *Catalysis*, vol. 5, The Royal Society of Chemistry, London, pp. 273-307.

Daniel, C & Keulks, GW 1973, 'The catalytic oxidation of propylene: II. Iron-based bismuth molybdate catalysts for the partial oxidation of propylene', *Journal of Catalysis*, vol. 29, no. 3, pp. 475-478.

Desikan, AN, Zhang, WM & Oyama, ST 1995, 'The effect of acid-base properties of supported molybdenum oxide in propylene oxidation', *Journal of Catalysis*, vol. 157, no. 2, pp. 740-748.

Dieterle, M, Diefenbacher, A, Schindler, GP, Klanner, C, Mueller-Engel, KJ & Adami, C 2009, *Preparation of acrolein or acrylic acid or a mixture thereof by heterogeneously catalysed partial gas phase oxidation of propylene*, United States Patent 7592483.

Dieterle, M, Diefenbacher, A, Schindler, GP, Klanner, C, Muller-Engel, KJ & Adami, C 2006a, *Method for the production of acrolein, acrylic acid, or mixture thereof by means of heterogeneously catalysed partial gas phase oxidation of propylene*, World Intellectual Property Organisation Patent WO/2006/002708.

Dieterle, M, Mestl, G, Jager, J, Uchida, Y, Hibst, H & Schlogl, R 2001, 'Mixed molybdenum oxide based partial oxidation catalyst: 2. Combined X-ray diffraction, electron microscopy and Raman investigation of the phase stability of $(MoVW)_5O_{14}$-type oxides', *Journal of Molecular Catalysis A: Chemical*, vol. 174, no. 1-2, pp. 169-185.

Dieterle, M, Petzoldt, J, Müller-Engel, KJ & Arnold, H 2005, *Heterogeneously catalysed partial gas phase oxidation of propene to acrylic acid*, United States Patent 6888024.

Dieterle, M, Petzoldt, J & Müller-Engel, KJ 2006b, *Heterogeneously catalysed partial gas phase oxidation of propene to acrolein*, United States Patent 7019176.

Dieterle, M, Petzoldt, J, Arnold, H, Ruppel, W & Müller-Engel, KJ 2007a, *Heterogeneously catalysed partial gas oxidation of acrolein to acrylic acid*, United States Patent 7157597.

Dieterle, M, Petzoldt, J & Müller-Engel, KJ 2007b, *Long-term operation of a heterogeneously catalysed gas phase partial oxidation of propene to acrylic acid*, United States Patent 7211692.

Dieterle, M, Schindler, GP & Klanner, C 2006c, *Process for stably operating a continuous preparation process for obtaining acrolein or acrylic acid or a mixture thereof from propane*, United States Patent 7396956.

Dubois, JL 2008, *Improved method for producing acrolein and/or acrylic acid from propylene*, World Intellectual Property Organization Patent WO/2008/135676.

Dubois, JL 2009, *Acrolein preparation method*, United States Patent 7531699.

Etzkorn, WG, Kurland, JJ & Neilsen, WD 1991, 'Acrolein and derivatives', in Kirk, RE, Othmer, DF, Kroschwitz, JI & Howe-Grant, M (eds), *Encyclopaedia of Chemical Technology*, 4th ed., vol. 1, John Wiley & Sons, New York, pp. 232-251.

Etzkorn, WG & Harkreader, G 1993a, *Anhydrous diluent process for the propylene oxidation reaction to acrolein and acrolein oxidation to acrylic acid*, United States Patent 5183936.

Etzkorn, WG & Harkreader, G 1993b, *Anhydrous diluents for the propylene oxidation reaction to acrolein and acrolein oxidation to acrylic acid*, United States Patent 5198578.

Fansuri, H, Pham, GH, Wibawanta, S, Radford, R & Zhang, DK 2003, 'The effect of phosphorous addition on the activity of bismuth molybdite catalyst for partial oxidation of propylene to acrolein', in *Australian Symposium on Combustion & The 8th Australian Flames Days*, Melbourne.

Fansuri, H 2005, 'Catalytic partial oxidation of propylene to acrolein: the catalyst structure, reaction mechanisms and kinetics', PhD thesis, Curtin University of Technology.

Farkas, A 1985, Catalysis and catalysts in W Gerhartz (eds), *Ullmann's encyclopedia of industrial chemistry*, VCH Verlagsgesellschaft mbH, Weinheim, vol. A5, pp. 313-367

Fauconet, M, Laurent, D & Stojanovic, M 2006, *Method for purifying acrylic acid obtained by oxidation of propylene and/or acrolein*, United States Patent 6995282.

Feng, QY, Luo, GH & Wei, F 2008, 'Production of acrylic acid via catalytic partial oxidation of propylene in a two-stage fluidized bed', *The Chinese Journal of Process Engineering* (Guocheng Gongcheng Xuebao), vol. 8, no. 1, pp. 83-87.

Fogler, HS 1999, *Elements of chemical reaction engineering*, Prentice Hall, Upper Saddle River.

Gel'bstein, AI, Stroeva, SS, Kul'kova, NV, Bakshi, YM & Lapidus, VL 1965, 'Mechanism of partial oxidation and oxidative ammonolysis of propylene in the presence of MoO3-Bi2O3', *Neftekhimiya*, vol. 5, no. 1, pp. 118-125.

Golunski, S & Walker, A 2000, 'Lowering the operating temperature of selective oxidation catalysts', *Chemical Communications*, pp. 1593-1594.

Grasselli, RK 1982, 'Selective oxidation and ammoxidation catalysis: history of catalyst design', in *Surface properties and catalysis by non-metals*, eds JP Bonnelle, B Delmon & E Derouane, Reidel Publishing Company, Dordrecht.

Grasselli, RK 1985, 'Selectivity and activity factors in bismuth-molybdate oxidation catalysts', *Applied Catalysis*, vol. 15, pp. 127-139.

Grasselli, RK, Suresh, DD & Knox, K 1970, 'Crystalline structures of USb$_3$O$_{12}$ and USbO$_5$ in acrylonitrile catalysts', *Journal of Catalysis*, vol. 18, no. 3, pp. 356-358.

Haber, J 1985, 'Catalysis by transition metal oxides', in Grasselli, RR & Brazdil, TF (eds), *Solid State Chemistry in Catalysis*, American Chemical Society, Washington, pp. 1-19.

Hagen, J 1999, *Industrial catalysis: a practical approach*, Wiley-VCH, Weinheim.

Hearne, GW & Adams, ML 1948, *Production of unsaturated carbonylic compounds*, United States Patent 2451485.

Hecquet, G, Schirmann, JP, Simon, M, Descat, G & Etienne, E 2000, *Process for the manufacture of acrolein from propylene by a redox reaction and use of a solid mixed oxide composition as redox system in the said reaction*, United States Patent 6080893.

Hefner, W, Machhammer, O, Neumann, HP, Tenten, A, Ruppel, W & Vogel, H 1997, *Continuous heterogeneously catalysed gas-phase oxidation of propylene to acrolein, acrylic acid or a mixture thereof*, United States Patent 5684188.

Higgins, R & Hayden, P 1976, 'Selective oxidation of hydrocarbons over mixed oxide catalysts', *Catalysis*, vol. 1, pp. 168-203.

Hildenbrand, HH & Lintz, HG 1990, 'Phase-composition and selectivity: solid electrolyte potentiometry aided study of the oxidation of propene on copper oxides', *Applied Catalysis*, vol. 65, pp. 241-252.

Jinno, K, Ogawa, Y, Suzuki, Y & Yada, S 2009, *Process for producing (meth)acrolein or (meth)acrylic acid*, United States Patent 7544836.

Joshi, VV & Chanda, M 1978, 'Vapour phase oxidation of propylene over bismuth molybdate', *Journal of Applied Chemistry and Biotechnology*, vol. 28, pp. 1.

Jo, BY, Kim, EJ & Moon, SH 2007, 'Performance of Mo-Bi-Co-Fe-K-O catalysts prepared from a sol-gel solution containing a drying control chemical additive in the partial oxidation of propylene', *Applied Catalysis A: General*, vol. 332, no. 2, pp. 257-262

Jo, BY, Kim, EJ & Moon, SH 2009, 'Performance of $Mo_{12}Bi_{1.0}Co_{4.4}Fe_{1.0}K_{0.07}O_x$ catalysts prepared from a sol-gel solution containing added ethylene glycol in the partial oxidation of propylene to acrylic acid', *Applied Catalysis A: General*, vol. 358, no. 2, pp. 180-185.

Kaddouri, A, Mazzocchia, C & Tempesti, E 1999, 'The synthesis of acrolein and acrylic acid by direct propane oxidation with Ni-Mo-Te-P-O catalysts', *Applied Catalysis A: General*, vol. 180, no. 1-2, pp. 271-275.

Kang, JH, Lee, WH, Kil, MH, Shin, HJ, Choi, BY, Yoo, YS, Choe, YH & Park, JY 2008, *Method for preparing a catalyst for partial oxidation of propylene*, United States Patent 7341974B2.

Kang, JH, Lee, WH, Kil, MH, Moon, SH & Jo, BY 2009, *Catalyst for partial oxidation and preparation method thereof*, United States Patent 7544633.

Kirk, RE, Othmer, DF, Kroschwitz, JI & Howe-Grant, M 1991, 'Acrolein and derivatives', in *Encyclopaedia of Chemical Technology*, 4th ed., vol. 1, John Wiley & Sons, New York, pp. 232-251.

Kishimoto, N & Matsunami, E 2004, *Lower alkane oxidative dehydrogenation catalysts and a process for producing olefins*, United States Patent 6756517.

Keulks, GW & Lo, MY 1986, 'Catalytic oxidation of propylene: an investigation of the kinetics and mechanism over iron-antimony oxide', *Journal of Physical Chemistry*, vol. 90, pp. 4768-4775.

Keulks, GW, Rosyneck, MP & Daniel, C 1971, 'Bismuth molybdate catalysts. Kinetics and mechanism of propylene oxidation', *Industrial Engineering Chemical Product: Research and Development*, vol. 10, no. 2, pp. 138-142.

Klanner, C, Dieterle, M, Schindler, GP, Cheng, TC & Mueller-Engel, KJ 2008, *Process for preparing acrolein or acrylic acid or a mixture thereof from propane*, United States Patent 7388106.

Kochloefl, K 2001, 'Review: Development of Industrial Solid Catalysts', *Chemical Engineering and Technology*, vol. 24, no. 3, pp. 229-234.

Kremenic, G, Nieto, JML, Tascon, JMD & Tejuca, LG 1987, 'Selective oxidation of propene on a Mo-Pr-Bi catalysts', *Industrial Engineering Chemical Product: Research and Development*, vol. 26, no. 7, pp. 1419-1424.

Krenzke, LD 1977, 'The kinetics and mechanism of propylene oxidation over $Bi_2Mo_3O_{12}$, Bi_2MoO_6, $Bi_3FeMo_2O_{12}$, and USb_3O_{10}', PhD thesis, University of Wisconsin.

Krenzke, LD & Keulks, GW 1980, 'The catalytic oxidation of propylene: An investigation of the kinetics over $Bi_2Mo_3O_{12}$, Bi_2MoO_6, and $Bi_3FeMo_2O_{12}$', *Journal of Catalysis*, vol. 64, pp. 295-302.

Larsen, JB 2003, *Run in of a plug flow reactor using the selective oxidation of propene to acrolein over β-$Bi_2Mo_2O_9$*, Aalborg Universitet Esbjerg.

Le, MT, Van Craenenbroeck, J, Van Driessche, I & Hoste, S 2003, 'Bismuth molybdate catalysts synthesized using spray drying for the selective oxidation of propylene, *Applied Catalysis A: General*, vol. 249, no. 2, pp. 355-364.

Leib, TM, Mills, PL & Lerou, JJ 1996, 'Fast response disturbed parameter fluidized bed reactor model for propylene partial oxidation using feed-forward neural network methods', *Chemical Engineering Science*, vol. 51, no. 10, pp. 2189-2198.

Lin, M, Desai, TB, Kaiser, FW & Klugherz, PD 2000, 'Reaction pathways in the selective oxidation of propane over a mixed metal oxide catalyst', *Catalysis Today*, vol. 61, no. 1-4, pp. 223-229.

LoJacono, M, Notermann, T & Keulks, GW 1975, 'The catalytic oxidation of propylene. V. X-ray characterisation of iron-containing bismuth molybdate catalysts', *Journal of Catalysis*, vol. 40, no. 1, pp. 19-33.

Machhammer, O, Adami, C, Hechler, C & Zehner, P 2008a, *Method for producing acrolein and/or acrylic acid*, United States Patent 7321058B2.

Machhammer, O, Schindler, GP, Adami, C, Hechler, C & Dieterle, M 2008b, *Preparation of acrolein or acrylic acid or a mixture thereof from propane*, United States Patent 7388109.

Matsuura, I, Mizuno, S & Hashiba, H 1986 'Acidic properties of molybdate-based catalysts for propylene oxidation', *Polyhedron*, vol. 5, no. 1-2, pp. 111-117.

Martan, H, Schwarzmann, M, Boehning, KH & Dreyer, H 1990, *Preparation of a catalytically active composition for the gas phase oxidation of propylene to acrolein and acrylic acid*, United States Patent 4916103.

Martin-Arranda, RM, Portela, Madeira, LM, Freire, F & Oliveira, M 1995, 'Effect of alkali metal promoters on nickel molybdate catalysts and its relevance to the selective oxidation of butane', *Applied Catalysis A: General*, vol. 127, no. 1-2, pp.201-217.

Millet, JMM, Ponceblanc, H, Coudurier, G, Herrmann, JM & Vedrine, JC 1993, 'Study of multiphasic molybdate-based catalysts: II. Synergy effect between bismuth molybdates on mixed iron and cobalt molybdates in mild oxidation of propene', *Journal of Catalysis*, vol. 142, no. 2, pp. 381-391.

Nieto, JML, Tascon, JMD & Kremenic, G 1988, 'Reaction network for selective oxidation of propene on a (Mo-Pr-Bi)O/SiO$_2$ catalyst', *Bulletin of the Chemical Society of Japan*, vol. 61, no. 4, pp. 1383-1389.

Neher, A, Haas, T, Arntz, D, Klenk, H & Girke, W 1995, *Process for the production of acrolein*, United States Patent 5387720.

Notermann, T, Keulks, GW, Skliarov, A, Maximov, Y, Margolis, LY & Krylov, OV 1975, 'The physicochemical properties of the bismuth iron molybdate system', *Journal of Catalysis*, vol. 39, no. 2, pp. 286-293.

Ogawa, Y, Yada, S, Suzuki, Y, Takasaki, K & Jinno, K 2009, *Process for producing (meth)acrylic acid or (meth)acrolein*, United States Patent 7563927.

Ohara, T, Sato, T, Shimizu, N, Prescher, G, Schwind, H & Weiberg, O 1985, 'Acrolein and methacrolein' in *Ullmann's Encyclopedia of Chemical Technology*, vol. A1, eds W. Gerhartz, VCH Verlagsgesellschaft, Weinheim, pp. 149-160.

Olbert, G & Hechler, C 2007, *Preparation of (meth)acrolein and/or (meth)acrylic acid by heterogenelusly catalysed partial oxidation of C3 and/or C4 precursor compounds in a reactor having thermoplate modules*, United States Patent 7268254.

Patience, GS & Mills, PL 1994, 'Modelling of propylene oxidation in a circulating fluidized-bed reactor', *Studies in Surface Science and Catalysis*, vol. 82, pp. 1-18.

Pham, GH 2003, 'Progress report on the acrolein pilot plant' in *Chemeq Confidential Progress Report*, February 2003.

Ponceblanc, H, Millet, JMM, Coudurier, G, Herrmann, JM & Vedrine, JC 1993, 'Study of multiphasic molybdate-based catalysts: I. Electrical conductivity study of valence states and solubility limits in mixed iron and cobalt molybdates', *Journal of Catalysis*, vol. 142, no. 2, pp. 373-380.

Petzold, J & Mueller-Engel, KJ 2007a, *Preparation of acrolein by heterogeneously catalysed partial gas phase oxidation of propene*, United States Patent 7208636.

Petzoldt, J, Dieterle, M, Arnold, H, Ruppel, W & Mueller-Engel, KJ 2007b, *Heterogeneously catalysed partial gas phase oxidation of propene to acrolein*, United States Patent 7211691.

Pichat, P, Herrmann, JM, Disdier, J & Mozzanega, MN 1979, 'Photocatalytic oxidation of propene over various oxides at 320K selectivity', *The Journal of Physical Chemistry*, vol. 83, no. 24, pp. 3122-3126.

Qiu, FY, Weng, LT, Sham, E, Ruiz, P & Delmon, B 1989a, 'Effect of added Sb_2O_4, $BiPO_4$ or SnO_2 on the catalytic properties of $ZnFe_2O_4$ in the oxidative dehydrogenation of butane to butadiene', *Applied Catalysis*, vol. 51, pp. 235-253.

Qiu, FY, Weng, LT, Ruiz, P & Delmon, B 1989b, 'Effect of antimony (IV) oxide, bismuth phosphate and tin (IV) oxide on the catalytic properties of compound oxide catalysts in the oxidative dehydrogenation of n-butene', *Applied Catalysis*, vol. 47, pp. 115-123.

Redlingshöfer, H, Kröcher, O, Böck, W, Huthmacher, K & Emig, G 2002, 'Catalytic wall reactor as a tool for isothermal investigations in the heterogeneously catalysed oxidation of propene to acrolein', *Industrial & Engineering Chemistry Research*, vol. 41, pp. 1445-1453.

Redlingshöfer, H, Fischer, A, Weckbecker, C, Huthmacher, K & Emig, G 2003, 'Kinetic modelling of the heterogeneously catalysed oxidation of propene to acrolein in a catalytic wall reactor', *Industrial & Engineering Chemistry Research*, vol. 42, no. 22, pp. 5482-5488.

Reitz, JB & Solomon, EI 1998, 'Propylene oxidation on copper oxide surfaces: electronic and geometric contributions to reactivity and selectivity', *Journal of the American Chemical Society*, vol. 120, no. 44, pp. 11467-11478.

Schaal, GE 1973, 'Make acrolein from propylene', *Hydrocarbon Processing*, vol. 52, no. 9, pp. 218-220.

Sinev, MY, Udalova, OV, Tulenin, YP, Margolis, LY, Vislovskii, VP, Valenzuela, RX & Cortes Corberan, V 2000, 'Propane partial oxidation to acrolein over combined catalysts', *Catalysis Letters*, vol. 69, no. 3-4, pp. 203-206.

Tan, HS 1986, 'Analysis of the reaction network for the catalytic oxidation of propylene', PhD thesis, Queen's University.

Tan, HS, Downie, J & Bacon, DW 1988, 'The kinetics of the oxidation of propylene over a bismuth molybdate catalyst', *The Canadian Journal of Chemical Engineering*, vol. 66, pp. 611-618.

Tan, HS, Downie, J & Bacon, DW 1989, 'The reaction network for the oxidation of propylene over a bismuth molybdate catalyst', *The Canadian Journal of Chemical Engineering*, vol. 67, pp. 412-417.

Tanimoto, M, Nakamura, D & Kawajiri, T 2003, *Method for production of acrolein and acrylic acid from propylene*, United States Patent 6545178.

Teng, Y & Kobayashi, T 1998, 'Reaction pathways for the oxygenates formation from propane and oxygen over potassium-modified Fe/SiO2 catalysts', *Catalysis Letters*, vol. 55, pp. 33-38.

Uda, T, Lin, TT & Keulks, GW 1980, 'The catalytic oxidation of propylene VII. The use of temperature programmed reoxidation to characterize γ-bismuth molybdate', *Journal of Catalysis*, vol. 62, pp. 26-34.

Udalova, OV, Shashkin, DP, Shibanova, MD & Krylov, OV 2005, 'Action of Co-Mo-Bi-Fe-Sb-K catalysts in the partial oxidation of propylene to acrolein: 1. The composition dependence of activity and selectivity', *Kinetics and Catalysis*, vol. 46, no. 4, pp. 569-579.

Vitry, D, Dubois, JL & Ueda, W 2004, 'Strategy in achieving propane selective oxidation over multi-functional Mo-based oxide catalysts', *Journal of Molecular Catalysis A: Chemical*, vol. 220, no. 1, pp. 67-76.

Watanabe, S, Oh-Kita, M & Sato, T 2007, *Process for producing (meth)acrolein and/or (meth)acrylic acid*, United States Patent 7217836.

Weng, LT, Cadus, L, Ruiz, P & Delmon, B 1992, 'Protection against deactivation of selective oxidation catalysts due to spillover oxygen', *Catalysis Today*, vol. 11, pp. 455-464.

Wong, BJ, Wise, H & Yolles, RS 1969, 'Selectivity and stoichiometry of copper oxide in propylene oxidation', *Journal of Catalysis*, vol. 15, no. 4, pp. 355-362.

Yada, S, Ogawa, Y, Suzuki, Y, Hosaka, H & Samura, Y 2008, *Oxidation reactor, process for producing (meth)acrylic acid, and method for analysing easily-polymerizable compounds*, United States Patent 7388108.

You, Y, Lamola, AA, Gore, RH, Gallagher, MK & Annan, N 2001, *Porous materials*, United States Patent 6271273.

Yunoki, H & Tanimoto, M 2005, *Catalyst for catalytic gas phase oxidation of acrolein and process for producing acrylic acid by catalytic gas phase oxidation using said catalyst*, United States Patent 7220698.

Zehner, P, Machhammer, O, Arnold, P & Muller-Engel, KJ 2002, *Method for producing acrolein by heterogeneous catalytic gas-phase partial oxidation of propene*, United States Patent 6410785.