

การเผาไหม้เสกเซนและพาทาลิกแอนไฮไดรด์บนตัวเร่งปฏิกิริยา  $V_2O_5/TiO_2$  ที่ได้รับการเคลือบผิว

ด้วยออกไซด์ของโลหะทรานซิชันและแมกนีเซียมออกไซด์ในเครื่องปฏิกรณ์

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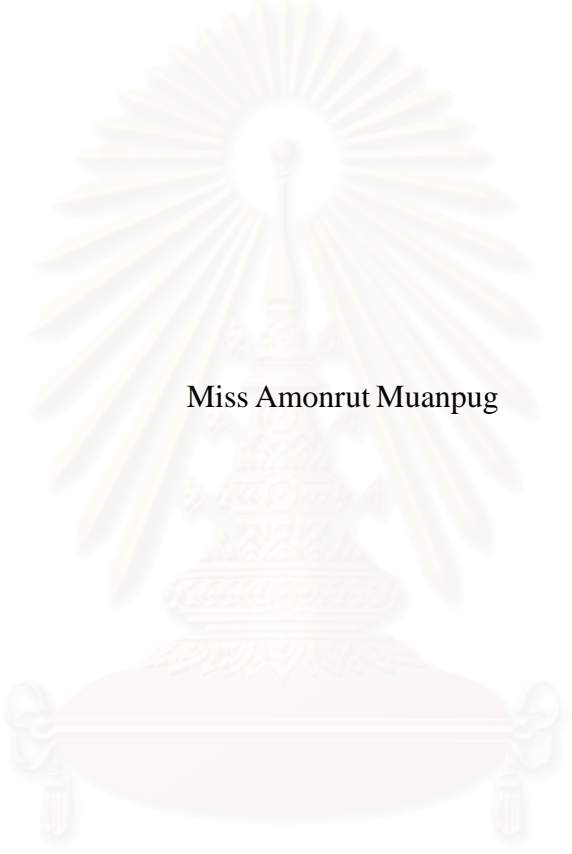
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COMBUSTION OF HEXANE AND PHTHALIC ANHYDRIDE OVER  
 $V_2O_5/TiO_2$  CATALYSTS IMPREGNATED WITH TRANSITION METAL  
OXIDE AND MAGNESIUM OXIDE IN A NONISOTHERMAL  
NONADIABATIC FIXED-BED REACTOR



Miss Amonrut Muanpug

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  REACTOR

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งานวิจัยนี้ได้ทำการศึกษาปฏิกิริยาการเผาไหม้ของเฮกเซนและสารประกอบพาทาลิกแอนไฮไดรด์บนตัวเร่งปฏิกิริยาวานาเดียมออกไซด์บนตัวรองรับไททานีอัม ที่ได้รับการเสริมด้วยโลหะทรานซิชัน (ทองแดง เหล็ก โมลิบดีนัม และ สังกะสี) และแมกนีเซียมออกไซด์ในเครื่องปฏิกรณ์ชนิดเบดนิ่งสภาวะความร้อนและอุณหภูมิไม่คงที่ ได้ทดลองเพิ่มความสูงของเบดตัวเร่งปฏิกิริยาและลดปริมาณความร้อนที่ต้องป้อนเพิ่มเติมในปฏิกิริยาจากงานวิจัยก่อนหน้านี้ ผลการทดลองแสดงให้เห็นว่า ปฏิกิริยาการเผาไหม้ด้วยตัวเร่งปฏิกิริยาสามารถเกิดขึ้นได้ที่อุณหภูมิของเครื่องปฏิกรณ์ที่ต่ำลงและมีค่าการเปลี่ยนของสารตั้งต้นเพิ่มขึ้นที่อุณหภูมิเริ่มต้นปฏิกิริยา การเติมเฮกเซนความเข้มข้นต่ำ (0.56% โดยปริมาตร) และความเข้มข้นสูง (1.34% โดยปริมาตร) ไม่มีผลต่อค่าการเปลี่ยนของพาทาลิกแอนไฮไดรด์สำหรับตัวเร่งปฏิกิริยาทองแดงและสังกะสี แสดงให้เห็นว่าปฏิกิริยาการเผาไหม้ของพาทาลิกแอนไฮไดรด์และเฮกเซนเกิดบนตำแหน่งที่ว่องไวของตัวเร่งปฏิกิริยาต่างกัน และยังพบว่าสำหรับตัวเร่งปฏิกิริยาเหล็กและ โมลิบดีนัม การเติมเฮกเซนความเข้มข้นต่ำ (0.56% โดยปริมาตร) ทำให้ค่าการเปลี่ยนของพาทาลิกแอนไฮไดรด์และเฮกเซนเพิ่มขึ้นเมื่อเปรียบเทียบกับกรณีเติมเฮกเซนความเข้มข้นสูง (1.34% โดยปริมาตร) แสดงให้เห็นว่าเกิดการแย่งกันดูดซับบนตำแหน่งที่ว่องไวของสารตั้งต้นเมื่อเพิ่มความเข้มข้นของเฮกเซนปฏิกิริยา

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AMONRUT MUANPUG: COMBUSION OF HEXANE AND PHTHALIC  
ANHYDRIDE OVER  $V_2O_5/TiO_2$  CATALYSTS IMPREGNATED WITH  
TRANSITION METAL OXIDE AND MAGNESIUM OXIDE IN A  
NONISOTHERMAL NONADIABATIC FIXED-BED REACTOR

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A  $V_2O_5/TiO_2$  catalyst with different transition metals (Cu, Fe, Mo and Zn) and magnesium oxide loading has been used to investigate the combustion of phthalic anhydride in the presence of hexane in a nonisothermal nonadiabatic fixed bed reactor. The results showed that the catalytic combustion reaction could start up at a lower reactor temperature with increase in reactant conversion. The concentration of hexane did not affect the combustion of phthalic anhydride on Cu and Zn promoted catalysts, indicating that the combustion of phthalic anhydride and hexane occurred on different active sites. Fe and Mo catalysts showed different results. It was found that the lower concentration of hexane leading to better combustion of phthalic anhydride. This is possibly due to the added hexane competitively adsorbed with phthalic anhydride.

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สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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# CHAPTER I

## INTRODUCTION

Phthalic anhydride is an important organic chemical used mainly in the preparation of plasticizers for PVC. The first phthalic production process was based on the liquid-phase oxidation of naphthalene. The main process employed base on the gas-phase air oxidation process of o-xylene. Among the various catalysts used for the oxidation of o-xylene those containing  $V_2O_5$  supported on titania ( $TiO_2$ ) show the best performance [Dias et al. 1995].

In the oxidation process, the aromatic reactant was vapourised and mixed with air in gaseous phase. The concentration of the aromatic was limited by the lower explosive limit of the gas mixture. The gas mixture then flowed to a reactor containing several thousands of catalyst tubes. The products formed, the anhydrides, were recovered by cooling the product gas stream using a condenser.

At the condenser, it was known that the lower coolant temperature, the higher product recovery. In practice, the temperature at the condenser was limited by the concentration of water in the product gas stream. If water was allowed to condense, corrosion will occur. The effluent gas leaving the condenser, therefore, still contained traces of organic compounds including the hydrocarbon reactant and the anhydride product.

Eliminating the remaining organic compounds from the effluent gas was necessary. At present, the removal could be carried out by sending the effluent gas which still contained high oxygen concentration to a furnace. This method, however, may cause problem concerning the energy balance of the plant and  $NO_x$  forming from high temperature combustion. Catalytic combustion was an alternative for controlling volatile organic compounds (VOCs) emissions is a well-known technology that is being used in a variety of industrial applications. There were two catalyst families that could completely oxidize organic compounds. One was the Pt-based catalysts and the other one was the acidic metal oxide based catalysts.

The Pt-based catalysts could initiate the combustion of the organic compounds at a lower temperature than the acidic metal oxide-based catalysts, typically 100-200°C lower. But the Pt-based catalysts could not withstand prolong operation in a high oxygen concentration atmosphere. The acidic metal oxide-based catalysts worked better in the latter case.

An important nature of the acidic metal oxide catalyst is its capability to adsorb acidic organic compounds. On the acidic surface, the acidic organic compounds are less likely to be adsorbed. The further oxidation of the acidic compounds to combustion products, therefore, is low. Because of this reason, the acidic metal oxide catalyst becomes a selective oxidation catalyst for the production of anhydrides because it has low ability to further oxidise the anhydride products formed. On the contrary, this behavior causes problem when one has to use it as a combustion catalyst.

In order to overcome the aforementioned problem, it was proposed to dope a MgO to an acidic metal (Cr, Mn, Fe, Co, Ni, Cu, Zn Mo and W) oxide catalyst to enhance the adsorption of the acidic organic compounds. Previous studies discovered that magnesium oxide promoted the adsorption of phthalic anhydride leading to better combustion of the phthalic anhydride for the acidic and amphoteric metal oxides [Tongsang (2001), Umpo (2001) and Nugoolchit (2002)]. The loading sequence of Cr, Mn, Mo, W, Fe and Zn promoted MgO on Al<sub>2</sub>O<sub>3</sub> supported catalysts on the combustion of phthalic anhydride affected the catalytic activity by changing the number of surface basic sites and depended on the amount of the magnesium selected [Nuampituk (2002)]. Next research has aim to study the possibility to improve the spent V<sub>2</sub>O<sub>5</sub> catalysts, normally removed after deactivation, for being used as catalysts in combustion of phthalic anhydride. In the present work, the spent catalyst is simulated by preparation the V<sub>2</sub>O<sub>5</sub> /TiO<sub>2</sub> catalyst which has the same composition as the industrial catalyst for the production of phthalic anhydride. Then promoting the prepared catalyst with transition metal and magnesium oxide and used as catalysts for the combustion of phthalic anhydride [Charoenruay (2003)]. The heat generated from the combustion of the added reactant could make the overall combustion reaction self maintain. The combustion for phthalic anhydride in presence of hexane could

maintain the combustion reaction after the effluent gas was heated up to a temperature which could initiate the combustion reaction [Punjasamud (2003)].

In this study the V-Mg-O/TiO<sub>2</sub> catalyst with different transition metal (Zn, Cu, Mo and Fe) loading had been used to investigate the combustion for phthalic anhydride in presence of hexane in an nonisothermal nonadiabatic fixed-bed reactor.

This present work is organized as follows:

Chapter II contains literature reviews of phthalic anhydride process, transition metal oxide, supported transition metal oxide catalysts on various reactions and effect of mixture on nonoxidation catalyst reaction.

The theory of this research, studies about the oxidation reaction and its possible mechanisms, the reaction of anhydrides, and the properties of transition metal oxides are presented in chapter III.

Description of experimental systems and the operational procedures are described in chapter IV.

Chapter V reveals the experimental results of the characterization of Fe-V-Mg-O/TiO<sub>2</sub>, Zn-V-Mg-O/TiO<sub>2</sub>, Mo-V-Mg-O/TiO<sub>2</sub> and Cu-V-Mg-O/TiO<sub>2</sub> catalysts and the oxidation reaction of phthalic anhydride over these catalysts.

Chapter VI contains the overall conclusion emerged from this research.

Finally, the sample of calculation of catalyst preparation, external and internal diffusion limitations, calibration curves from area to mole of phthalic anhydride, hexane and carbon dioxide, and data of the experiments which had emerged from this study are included in appendices at the end of this thesis.



## CHAPTER II

### LITERATURE REVIEW

The heterogeneous catalytic oxidation on transition metal oxides of organic compounds was extensively used in catalysis for selective and total oxidation processes. This review focused on application to control VOC by complete catalytic oxidation. The complete catalytic oxidation is an alternative method for eliminating organic pollutants in gaseous streams to CO<sub>2</sub> and water.

This chapter reviews research works relate to the combustion of phthalic anhydride on Cr, Mn, Fe, Ni, Cu, Zn, Mo and W promoted MgO on Al<sub>2</sub>O<sub>3</sub> supported catalysts and V-Mg-O/TiO<sub>2</sub>, the deactivation of industrial V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts for the oxidation of o-xylene into phthalic anhydride, the transition metal oxide, supported transition metal oxide catalysts in the various reactions, the catalytic combustion of other relate VOCs, infrared studies of the reactive adsorption of organic molecules over metal oxides and catalytic combustion of VOCs in mixtures.

#### 2.1 Literature reviews

Toyada and Teraji (1980) invented a process that allows the treatment of byproducts obtained in the preparation of phthalic anhydride without creating secondary pollution. The byproducts may be low boiling point and/or high boiling point fractions obtained in the purification step by distillation of crude phthalic anhydride produced by the partial oxidation of o-xylene or naphthalene. Byproducts were treated by heating the byproducts to a temperature sufficient to maintain the byproducts in a molten state and thereafter atomizing air having a temperature of at 60°C for combustion. The byproducts may be low boiling point and/or high boiling point fractions obtained in the purification step by distillation of crude phthalic anhydride produced by the partial oxidation of o-xylene or naphthalene.

Keuneche *et al.* (1981) invented a process for continuously separating phthalic anhydride from the reaction gases of the catalytic oxidation of o-xylene and/or

naphthalene by treating reaction gas mixture with a maleic anhydride absorbent. Even though pure maleic anhydride could be used as an absorbent, maleic anhydride containing phthalic anhydride was usually used so as to keep the costs of regenerating the absorbent within economical bounds. Thus, maleic anhydride could contain up to 85% by weight phthalic anhydride. Absorption could be performed in two or more stages, preferably in two stages. The reaction gas, with a temperature from 135-150°C, was introduced into the absorption zone, and withdrawn at a temperature from 45-80°C from the absorption zone. The maleic anhydride, which was loaded with phthalic anhydride, was separated through distillation into raw phthalic anhydride as a bottoms product and an overhead product primarily containing maleic anhydride. The overhead product was then returned into the absorption zone. The raw phthalic anhydride was treated and then purified through distillation, e.g. in a continuous, two stage distillation in which light, volatile impurities, such as residual maleic anhydride and benzoic acid, were distilled off in the first stage and the pure phthalic anhydride was distilled in the second as an overhead product. The gas leaving the absorption zone and containing small amounts of maleic anhydride was scrubbed with water. The maleic acid solution recovered from this scrubbing was evaporated, the maleic acid was dehydrated and distilled, and a part of the maleic anhydride distillate was returned into the absorption zone.

Way and Peter (1981) invented an apparatus for recovery of vaporized phthalic anhydride from the gas streams. Phthalic anhydride was recovered from gases in a multiple heat-pipe exchanger system, one or more for condensing phthalic anhydride from gases containing vapors thereof and one or more simultaneously melting out the condensed phthalic anhydride solids. The exchangers being switched in alternate cycles to melt out from the surfaces of the exchanger tube ends on which the phthalic anhydride solids were first accumulated, and to condense phthalic anhydride solids in the exchanger from which melting out cleared the phthalic anhydride. The cooling to recover phthalic anhydride was carried out with ambient air, and the heating to melt out accumulated phthalic anhydride was performed with hot gases, such as combustion gases, produced by incineration of residual phthalic anhydride tail gas from which phthalic anhydride was condensed, or other hot combustion gases.



Spivey (1987) reviewed the complete catalytic oxidation of volatile organics. The paper reviewed that both metal oxides and supported noble metals were active for many deep oxidations. Metal oxide catalysts were generally less active than were supported noble metals, but they were more resistant to poisoning. This poisoning resistance was suggested to be due to the high active surface area of metal oxides compared to supported noble metals. The most active single metal oxide catalysts for complete oxidation for a variety of oxidation reactions were usually found to be oxides of V, Cr, Mn, Fe, Co, Ni and Cu. The mechanism of oxidation on these oxide catalysts was generally thought to involve strong adsorption of the organic compound at an anionic oxygen site in the oxide lattice leading to the formation of an activated complex. This complex could then react further to yield products of complete combustion.

Gangwal *et al.* (1988) studied complete low-temperature deep oxidation of n-hexane and benzene over a 0.1% Pt, 3% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. These VOCs were subjected to oxidation as single components and as a binary mixture at temperatures ranging from 160 to 360°C. They found that n-hexane oxidation was significantly inhibited in the mixtures. An approach based on the Mars-Van Krevelen rate model was used to explain the results. Kinetic parameters were developed for the individual VOCs based on single component differential reactor data. These kinetic parameters were then incorporated into a proposed multicomponent Mars-Van Krevelen rate model to predict the experimental conversions in the binary mixture. The model was found to be reasonably successful in predicting the conversion of benzene and n-hexane in their binary mixture.

Hess *et al.* (1993) studied catalysts containing metal oxides for use in the degenerative oxidation of organic compounds presented in exhaust gases from combustion plants. Metal oxide containing catalysts, which contained oxides of titanium and/or zirconium, oxides of vanadium and/or niobium, and oxides of molybdenum, tungsten, and chromium were investigated. It was reported that the adding of alkaline earth metal sulfates produced a catalyst, which was clearly superior to catalysts composed only of the metal oxides. They also proposed that the preferred catalyst should contain the following components: titanium dioxide, especially in the

form of anatase, vanadium oxide in the form of  $V_2O_5$  and tungsten oxide in the form of  $WO_3$ .

Kang and Wan (1994) studied the effects of acid or base additives on the catalytic combustion activity of chromium and cobalt oxides. It was found that the base additive could enhance the catalytic activity of Cr, Co oxides for carbon monoxide oxidation, but the acid additive reduced the activity. For ethane combustion, the addition of a base additive to the catalysts could reduce the ethane conversion. The selectivity of carbon dioxide, however, was increased to 100% because the rate of carbon monoxide oxidation was enhanced. On the other hand, the addition of acid additive to the catalyst gave an increase in ethane conversion, but the selectivity to carbon dioxide was reduced.

Busca *et al.* (1997) studied the transition metal mixed oxides as combustion catalysts. The catalysts have been tested in the catalytic combustion of methane, CO and  $H_2$  (perovskites), of propane and of phenanthrene. FT-IR experiments allowed to obtain a quite complete picture of the mechanism of catalytic combustion of  $C_3$  organic compounds on spinel-type oxides  $MgCr_2O_4$  and  $Co_3O_4$ . Nucleophilic oxygen species (lattice oxygen) is thought to be involved in both partial and total oxidation.

Larsson *et al.* (1997) investigated supported metal oxides for catalytic combustion of CO and VOCs.  $TiO_2$  (anatase),  $SiO_2$  and  $\gamma-Al_2O_3$  were used as supports for Co-, Cu-, Fe- and Mn-oxide with a loading of active phase corresponding to one theoretical layer. The catalysts were tested for the combustion of CO and toluene, and the best combinations with active phase and support they found were submitted to a deactivation test in a waste gas incinerator for 50 days. The catalyst screening showed that  $CuO_x/TiO_2$  was the most promising system. To design a catalyst with good activity and transport properties, they proposed to coat a macroporous substrate with  $TiO_2$  for use as a support for Cu-oxide. Titania overlayers were prepared by precipitation from oxychloride, tetrachloride and alkoxide, and stabilisation with  $ZrO_2$  and  $SiO_2$  was tried. The results showed that precipitation from oxychloride gives the best properties and that addition of  $ZrO_2$  gives enhanced activity to the catalyst, while  $SiO_2$  addition produces increased stability.

Ozkan *et al.* (1997) investigated the partial oxidation of C<sub>5</sub> hydrocarbons over unpromoted and alkali-promoted V<sub>2</sub>O<sub>5</sub> catalysts. Products of this mild oxidation reaction include both maleic and phthalic anhydride. The apparent effect of alkali promotion was to facilitate the loss of surface oxygen species which were important in the activation of alkanes and the complete oxidation of intermediate species. Studies performed using 1-pentene as feed have indicated that once the first oxidative dehydrogenation step is eliminated, pentene oxidation proceeds readily towards maleic and phthalic anhydride formation.

Leklertsunthon (1998) investigated the oxidation property of a series of V-Mg-O/TiO<sub>2</sub> catalyst in the oxidation reaction of propane, propene, 1-propanol and carbon monoxide. It had been found that the catalytic behavior of the catalyst depended on the reactants. Propene and CO<sub>2</sub> were the major products in the propane oxidation reaction. The vanadium and magnesium contents affected the catalytic property of the V-Mg-O/TiO<sub>2</sub> catalyst in the reaction. The sequence of magnesium loading also affected the structure and catalytic performance of this catalyst. In addition, this catalyst was inactive for propene oxidation, from which it could be indicated that propene formed in propane oxidation reaction was not further oxidized to CO<sub>2</sub>. According to 1-propanol oxidation, propionaldehyde was the main observable product at low reaction temperatures, and it was oxidized rapidly to CO<sub>2</sub> when the reaction temperature was increased. Moreover, the dehydration of 1-propanol became significant at high temperatures. It was found that the sequence of magnesium loading and magnesium content had no effect on the catalytic performance of the catalyst. On the other hand, increasing vanadium content improved the propene selectivity and decreased the CO<sub>2</sub> selectivity. Finally, in CO oxidation, this catalyst was rather inactive. Since CO was an unobservable product in propane, propene and 1-propanol reactions, on the V-Mg-O/TiO<sub>2</sub> catalysts, CO was not produced in these three reactions.

Mongkhonsi and Kershenbaum (1998) studied the effect of deactivation of a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (anatase) industrial catalyst on reactor behavior during the partial oxidation of o-xylene to phthalic anhydride. Elemental C-H-N analysis of the results for catalyst pellets aged under a variety of operating conditions showed that some carbonaceous materials could deposit on the catalyst surface at most high reaction

temperature, especially at high hydrocarbon concentration. The XRD and XPS results did not reveal the presence of vanadium oxides of V valency  $< 5+$ . The presence of carbon on the used catalyst pellet and the absence of any low oxidation state of vanadium from the XRD and XPS analyses indicated that the deposition of some carbonaceous materials was likely to be a major cause of catalyst deactivation when it was used in regions high hydrocarbon concentration. This deposited carbon compounds may slow down the reaction rate by a fouling process which reduced the effective activity surface area of the catalyst for further hydrocarbon adsorption. To effectively removed all the adsorbed compounds, the catalyst required reaction in an air stream at a temperature not less than  $400^{\circ}\text{C}$  over several hours, depending upon the past history of the catalyst.

Amiridis *et al.* (1999) studied the effect of metal oxide additives on the activity of  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts for the selective catalytic reduction of nitric oxide by ammonia. The results showed the presence of the second metal oxide phase had different effects on the selective catalytic reduction activity of the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst depending on the nature of the additive. They observed that  $\text{MoO}_3$ ,  $\text{WO}_3$  and  $\text{Nb}_2\text{O}_5$  additive promoted the selective catalytic reduction activity, while  $\text{GeO}_2$ ,  $\text{FeO}_3$  and  $\text{CeO}_2$  had no significant effect on it, and  $\text{MnO}_2$ ,  $\text{Ge}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{SnO}_2$  and  $\text{ZnO}$  appeared to poison it. The results of this effort indicated that the presence of the additive metal oxides may affect a variety of catalyst properties, including the structure and reducibility of vanadia, and the overall amount and type of surface acidity. Among these factors the only one that correlated with selective catalytic reduction reactivity was the amount of surface Brönsted acid sites on the catalyst surface results in an increase in the selective catalytic reduction rate.

Brink *et al.* (1999) studied the catalytic combustion of chlorobenzene on a 2%  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  catalyst. Considerable amounts of polychlorinated benzenes were formed as by-products. They noted that the co-feeding of heptane practically eliminates this unwanted side-reaction. Moreover, the conversion of chlorobenzene occurs at much lower temperatures (the temperature at which 50% conversion drops from  $305$  to  $225^{\circ}\text{C}$ ). Simultaneously, the conversion of heptane was retarded. The additions of other hydrocarbons had a similar effect. Water and heat produced by the combustion

of the added hydrocarbon could not explain the increase in the destruction rate of chlorobenzene. Removal of chlorine from the surface by the alkane appears to be the ruling factor.

Lietti *et al.* (1999) studied the characterization and reactivity of  $V_2O_5$ - $MoO_3/TiO_2$  de- $NO_x$  SCR catalysts. The results showed that the  $V_2O_5$ - $MoO_3/TiO_2$  catalysts were very active in the reduction of NO by  $NH_3$ , and exhibited a higher reactivity with respect to the corresponding binary  $V_2O_5/TiO_2$  and  $MoO_3/TiO_2$  samples having the same V and Mo loading. The addition of Mo and V caused the formation of Brønsted sites and of stronger Lewis acid sites, if compared to  $TiO_2$ .

O'Malley and Hodnett (1999) studied the reactivity of a range of volatile organic compounds with differing functional groups over platinum catalysts supported on  $\beta$ -zeolite, mordenite, silica or alumina. Alcohols, ketones, carboxylic acids, aromatics and alkanes were used in the study. The reactivity pattern observed by them was alcohols > aromatics > ketones > carboxylic acids > alkanes, although some overlap was observed in that the more reactive alkanes were more readily oxidized than the less reactive carboxylic acids. The same order of reactivity was observed for all the catalysts studied here. A kinetic isotope effect was observed when deuterated acetone was compared to normal acetone, consistent with C–H bond cleavage being the slow step in the catalytic oxidation of this substrate. A correlation was found between the reactivity of the individual substrates and the strength of the weakest C–H bond in the structure. A single weak C–H bond in the substrate led to a high reactivity. It is postulated that catalytic oxidation on platinum catalysts proceeds via initial rupture of the weakest C–H bond in the substrate followed by further reaction steps which involves free radical chemistry.

Chaiyasit (2000) investigated the selective oxidation reaction of 1-propanol and 2-propanol over Co-Mg-O/ $TiO_2$  (8wt%Co, 1wt%Mg) catalyst. It was found that the oxidation property of Co-Mg-O/ $TiO_2$  catalyst depended on type of the reactants. Propionaldehyde was the main product for selective oxidation of 1-propanol. In case of 2-propanol oxidation reaction, it was found that Co-Mg-O/ $TiO_2$  catalyst was an active catalyst for the selective oxidation reaction. The main product at low reaction temperature was propylene while at high reaction temperature the main reaction



products were propylene and propionaldehyde. From the result of propylene oxidation, it could be indicated that propionaldehyde was produced directly from propylene. In addition, the sequence of cobalt and magnesium loading had no effect on the structure and catalytic performance of this catalyst. While the type of support affected the selectivity of supported cobalt catalyst.

Brink *et al.* (2000) studied the catalytic combustion of chlorobenzene on a 2 wt.% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in binary mixtures with various hydrocarbons (toluene, benzene, cyclohexane, cyclohexene, 1,4-cyclohexadiene, 2-butene, and ethene) and with carbon monoxide. For all binary mixtures used they reported that the excess of added hydrocarbon increased the rate of conversion of chlorobenzene. With 2-butene, temperature at which 50% conversion and temperature at which 100% conversion for chlorobenzene were reduced by 100 and 200°C, respectively. Toluene and ethene were almost equally efficient as 2-butene. Co-feeding benzene or carbon monoxide resulted in a much smaller decrease of temperature at which 50% conversion. The additional heat and water production in hydrocarbon combustion may contribute to some extent to the observed rate acceleration, but removal of Cl from the surface due to the hydrocarbon appears to be the major factor. The co-feeding of hydrocarbons invariably reduced the output of polychlorinated benzenes, which are formed as byproducts in the combustion of chlorobenzene on Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Again, especially toluene, ethene, and 2-butene were very efficient. Benzene as well as cyclohexane, cyclohexene, and 1,4-cyclohexadiene, which were converted in situ into benzene was much less effective, due to chlorination of the aromatic nucleus. In chlorobenzene-CO mixtures the levels of polychlorinated benzenes were almost as high as with chlorobenzene per se. Removal of Cl from the surface (mainly in the form of HCl) by (non-aromatic) hydrocarbons is responsible for reducing the formation of byproducts.

Deutschmann *et al.* (2000) studied hydrogen assisted catalytic combustion of methane on platinum experimentally and numerically. In their experiment, they measured the exit temperatures of methane/hydrogen/air mixtures flowing at atmospheric pressure through platinum coated honeycomb channels. A single channel of this monolith was investigated numerically by a two-dimensional Navier–Stokes simulation including an elementary-step surface reaction mechanism. Furthermore, a

one-dimensional time-dependent simulation of a stagnation flow configuration was performed to elucidate the elementary processes occurring during catalytic ignition in the mixtures studied. The dependence of the hydrogen assisted light-off of methane on hydrogen and on methane concentrations was discussed. The light-off was primarily determined by the catalyst temperature that was a result of the heat release due to catalytic hydrogen oxidation. Increasing hydrogen addition ensured light-off, decreasing hydrogen addition required an increasing methane feed for light-off.

Minicò *et al.* (2000) investigated catalytic oxidation of 2-propanol, methanol, ethanol, acetone and toluene on coprecipitated Au/Fe<sub>2</sub>O<sub>3</sub> catalysts in the presence of excess of oxygen. Gold catalysts have been found to be very active in the oxidation of tested volatile organic compounds. The high activity of these systems has been related to the capacity of highly dispersed gold to weaken the Fe–O bond thus increasing the mobility of the lattice oxygen which is involved in the VOCs oxidation probably through a Mars–van Krevelen reaction mechanism.

Tongsang (2001) studied the oxidation property of the V-Mg-O/TiO<sub>2</sub> catalysts on the combustion of phthalic anhydride and maleic anhydride. From the results, the MgO modified V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts could better oxidize the anhydride ring than the unmodified one. Additionally, the appropriate ratio of vanadium per magnesium led to a balance between the adsorption of the anhydrides and the catalytic activity of vanadium and titania support.

Umpon (2001) investigated the oxidation property of the Co-Mg-O/Al<sub>2</sub>O<sub>3</sub> catalyst on the combustion of phthalic anhydride and maleic anhydride. The results showed that magnesium promoted the adsorption of anhydride leading to better combustion of the anhydrides. The research also found that the ratio of cobalt per magnesium should be at an appropriate ratio to keep a balance between the adsorption of the anhydrides and the catalytic activity of cobalt and alumina support.

Centeno *et al.* (2002) investigated the catalytic oxidation of n-hexane, benzene and 2-propanol on Au/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Au/Al<sub>2</sub>O<sub>3</sub> catalysts. It was shown that ceria enhanced the fixation and final dispersion of gold particles, leading to stabilize them in lower crystallite size. Catalytic results showed that ceria improved the activity of

gold particles in the oxidation of the tested volatile organic compounds probably by increasing the mobility of the lattice oxygen and controlling and maintaining the adequate oxidation state of the active gold particles.

Dias *et al.* (2002) investigated the selective oxidation of *o*-xylene to phthalic anhydride on a series of ternary V-Ti-Si oxides. Fresh and used catalysts, containing one monolayer of V<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub>-SiO<sub>2</sub> supports with 0.5, 1, 2 and 3 monolayers of TiO<sub>2</sub> on SiO<sub>2</sub>, were characterised by Raman spectroscopy, X-ray diffraction (XRD) and temperature-programmed reduction (TPR). The characteristics and catalytic behaviour of these catalysts were compared with those of catalysts containing one monolayer of V<sub>2</sub>O<sub>5</sub> supported on SiO<sub>2</sub> and on TiO<sub>2</sub>. In the ternary V-Ti-Si catalysts, the presence of V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> (anatase) was detected, TiO<sub>2</sub> (rutile) being also found in those with two and three monolayers of TiO<sub>2</sub>. The formation of TiO<sub>2</sub> (rutile) due to exposure to reaction conditions was not observed. A moderate rearrangement of surface vanadium oxide species into crystalline V<sub>2</sub>O<sub>5</sub> was observed. In addition, the formation of V<sub>2</sub>O<sub>4</sub> was detected by XRD in the used catalyst containing one monolayer of V<sub>2</sub>O<sub>5</sub> on the support with one monolayer of TiO<sub>2</sub> on silica. The TPR of used and fresh samples showed that the reduction of vanadium occurred during reaction, such reduction being partially reversible after reoxidation in air flow at high temperature. This partial reduction may favour the aggregation of dispersed vanadia species into crystalline V<sub>2</sub>O<sub>5</sub>. The catalytic behaviour of ternary systems in the selective oxidation of *o*-xylene depended strongly on the characteristics of the support. An increase in the content of TiO<sub>2</sub> led to a decrease in the temperature required to achieve total conversion. The use of SiO<sub>2</sub> as support caused formation of large amounts of undesirable C<sub>8</sub> products, whereas the presence of TiO<sub>2</sub> deposited on SiO<sub>2</sub> led generally to the formation of lower amounts of such products. The formation of both CO<sub>2</sub> and tar was strongly favoured on the support composed of two monolayers of TiO<sub>2</sub> on SiO<sub>2</sub>.

Gervasini *et al.* (2002) investigated the catalytic combustion with and without pre-catalytic actions (i.e., ionisation/ozonisation) of tetrachloromethane over alumina-supported copper-chromite and manganese oxide catalysts with and without the presence of hydrogen-rich compounds, i.e. *n*-hexane and toluene. Experiments were performed at conditions of lean carbon tetrachloride concentration (from 500 to 3000



ppmV) in excess air, between 100 and 500°C in a continuous reaction line at laboratory scale. n-Hexane and toluene were added to the feedstream in variable concentration, between 100 and 500 ppmV. Ionisation/ozonisation of pure CCl<sub>4</sub> streams and of streams of hexane or toluene admixtures showed the efficiency of the hydrogen donor role of the hydrocarbons on CCl<sub>4</sub> conversion. The tests of ionisation/ozonisation were performed at different residence times in the ionisation reactor and a rate equation with second-order in CCl<sub>4</sub> concentration was found to represent the ionisation process. Over Cu-Cr and Mn catalysts, both n-hexane and toluene improved the CCl<sub>4</sub> combustion when added at low concentration (ca. 300°C) but inhibited it when they were present at high concentration (ca. 350°C). Catalytic combustion assisted with ionisation process enhanced CCl<sub>4</sub> conversion at low temperatures in comparison with conventional catalytic combustion (e.g. 90% of 1000 ppmV of CCl<sub>4</sub>-hexane mixture was converted on Cu-Cr at 250°C and 5000 h<sup>-1</sup> by the combined actions of catalytic and ionisation processes). Selectivity to CO<sub>2</sub> was controlled on the two catalysts. Mn was more active but less selective than Cu-Cr catalyst. Various oxygenated and chlorinated by-products, in particular COCl<sub>2</sub>, were formed during ionisation of CCl<sub>4</sub> streams. By-products were greatly reduced and COCl<sub>2</sub> disappeared at 250°C on catalysts.

Kim (2002) studied the catalytic oxidation of aromatic hydrocarbons over supported metal oxide. The catalytic activity of metal (Cu, Mn, Fe, V, Mo, Co, Ni, Zn)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was investigated to bring about the complete oxidation of benzene, toluene and xylene. Among them, Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was found to be the most promising catalyst from the viewpoint of activity. Increasing the calcination temperature resulted in decreasing the specific surface areas of catalysts, subsequently the catalytic activity. The copper loadings on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> had a great effect on catalytic activity, and 5 wt% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was observed to be the most active. The activity of 5 wt% Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with respect to the VOC molecule was observed to follow the sequence: toluene > xylene > benzene, indicating that the combination of the catalyst property and the physicochemical property of the reactant plays an important role in activity.

Nuampituk (2002) investigated the oxidation property of the Cr, Mn, Mo, W, Fe and Zn promoted MgO on Al<sub>2</sub>O<sub>3</sub> supported catalysts on the combustion of phthalic

anhydride. It was found that the loading sequence of the metal affected the catalytic activity by changing the number of the surface basic sites. The effects would be positive or negative depended on the type of transition metal and the amount of the magnesium selected. If the amount of magnesium selected was lower than the optimum amount, the procedure that resulted in a larger number of the surface basic site would yield a catalyst with higher catalytic activity. On the other hand, if the amount of magnesium selected was higher than the optimum amount, the procedure that resulted in a larger number of the surface basicity would decrease the catalytic activity.

Nugoolchit (2002) investigated the effects of MgO on the oxidation property of the transition metal oxide catalysts on the combustion of phthalic anhydride. The results showed that magnesium oxide promoted the adsorption of phthalic anhydride leading to better combustion of the phthalic anhydride for the acidic and amphoteric metal oxides. For the basic metal oxides, the magnesium oxide addition would decrease the combustion of phthalic anhydride. The research also found that the ratio of transition metal oxide per magnesium oxide should be at an appropriate ratio to keep a balance between the adsorption of the phthalic anhydride and the catalytic activity of the transition metal oxides.

Ordóñez *et al.* (2002) investigated the catalytic oxidation of benzene, toluene and *n*-hexane in air, both alone and in binary mixtures, over a commercial Pt on  $\gamma$ -alumina catalyst. Studies have been carried out at concentrations of up to 4200 ppmV, in a laboratory fixed-bed catalytic reactor. Results for single compounds showed that temperature at which 50% conversion was attained increased as concentration increased for benzene and toluene, while the opposite behavior was observed for *n*-hexane. Results for mixtures showed that, while the presence of *n*-hexane did not affect the conversion of benzene and toluene, the presence of benzene or toluene inhibited the combustion of hexane, and the aromatic compounds inhibits each other when are reacted together.

Anastasov (2003) studied the deactivation of an industrial V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst for the oxidation of *o*-xylene into phthalic anhydride. The industrial reactor investigated contained 10550 tubes of 26 mm inner diameter and 3250 mm length.

The catalyst was loaded in the tubes, while a molten salt  $\text{NaNO}_2/\text{KNO}_3$  circulating in the shell-side removed the heat generated by the reactions. The catalyst was a  $\text{V}_2\text{O}_5$ - $\text{TiO}_2$  (anatase) supported catalyst. The weight ratio  $\text{V}_2\text{O}_5/\text{TiO}_2$  was 0.06, the catalyst being promoted by rubidium and phosphorus. The active substance (0.1 mm thick) was laid over porcelain ring in order to increase the contact surface. The sizes of a ring were height 6 mm, outside and inside diameters 8.4 and 4.6 mm, respectively. There were three to four pellets on a tube diameter. The length of the bed was 280 cm, while its bulk density was about  $1500 \text{ kg/m}^3$ . From the results, the very low activity of a catalyst being 60.5 months old in the region after 100 cm. of the bed, was most probably due to a reversible deactivation caused by tar products blocking the active site. Therefore, the catalyst must be removed after 5 years use.

Charoenruay (2003) investigated the oxidation property of  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst unpromoted and promoted with transition metal (Fe, Cu, Zn and Mo) and magnesium oxide on the combustion of phthalic anhydride. The result showed that the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst was not active for the combustion of phthalic anhydride. After adding both transition metal and magnesium oxide to the  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst, it was found that metal-V-Mg-O/ $\text{TiO}_2$  catalysts showed the phthalic anhydride combustion activity higher than the unpromoted  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst, indicating that the added transition metal and magnesium were able to catalyze the reaction. This is due to the addition of metal oxide to  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst would increase the active sites on the surface of catalysts. Moreover, the addition of magnesium oxide would increase the numbers of the basic sites on surface of  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst and increased the adsorption of phthalic anhydride, thus, provided more opportunity to react with metal.

Cimino *et al.* (2003) studied effect of the addition of a second fuel such as CO,  $\text{C}_3\text{H}_8$  or  $\text{H}_2$  on the catalytic combustion of methane over ceramic monoliths coated with  $\text{LaMnO}_3/\text{La-}\gamma\text{Al}_2\text{O}_3$  catalyst. Results of autothermal ignition of different binary fuel mixtures characterised by the same overall heating value showed that the presence of a more reactive compound reduces the minimum pre-heating temperature necessary to burn methane. The effect was more pronounced for the addition of CO and very similar for  $\text{C}_3\text{H}_8$  and  $\text{H}_2$ . Order of reactivity of the different fuels established in isothermal activity measurements was:  $\text{CO} > \text{H}_2 \geq \text{C}_3\text{H}_8 > \text{CH}_4$ . Under autothermal conditions, nearly complete methane conversion was obtained with

catalyst temperatures around 800°C mainly through heterogeneous reactions, with about 60–70 ppm of unburned CH<sub>4</sub> when pure methane or CO/CH<sub>4</sub> mixtures were used. For H<sub>2</sub>/CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>/CH<sub>4</sub> mixtures, emissions of unburned methane were lower, probably due to the proceeding of CH<sub>4</sub> homogeneous oxidation promoted by H and OH radicals generated by propane and hydrogen pyrolysis at such relatively high temperatures. Finally, a steady state multiplicity was found by decreasing the preheating temperature from the ignited state. This occurrence was successfully employed to pilot the catalytic ignition of methane at temperatures close to compressor discharge or easily achieved in regenerative burners.

Graham *et al.* (2003) studied the effects of V/Ti mass ratios in nanostructured V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts on catalyst characteristics and catalyst activities were investigated. The destruction of monochlorobenzene was used as a measure of catalyst activity. The V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts, which have been traditionally used as de-NO<sub>x</sub> catalysts and selective oxidation catalysts (e.g. in the production of phthalic anhydride), were made by the wet incipient method. They reported that the catalyst synthesis method used by them provided nanostructured V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts with the vanadium species on the surface of the TiO<sub>2</sub>. The catalysts were characterized using X-ray diffraction (XRD), BET surface area, and Raman spectroscopy. The performance of the catalysts for the destruction of organic pollutants was assessed in a differential tube flow reactor for gas-phase thermal oxidation reactions. It was found that the presence of crystalline V<sub>2</sub>O<sub>5</sub> on the surface of TiO<sub>2</sub> (V/Ti mass ratio 0.05 and 0.1) is necessary for the oxidation of monochlorobenzene at temperatures <300°C.

López-Fonseca *et al.* (2003) studied the complete oxidation of 1,2-dichloroethane (DCE), dichloromethane (DCM) and trichloroethylene (TCE) as individual chlorohydrocarbons and of their binary mixtures over protonic zeolites (H-ZSM-5, H-MOR and chemically dealuminated H-Y zeolite) using a conventional fixed bed flow reactor. Its catalytic performance was associated with the presence of strong Brönsted acidity. Both H-MOR and chemically dealuminated H-Y zeolites exhibited the highest destruction activity for the abatement of single and binary mixtures. The destruction of chlorinated mixtures induced an inhibition of the reactivity of each compound leading to a significant increase in the ignition

temperature, which varied from one compound to other. On the other hand, a moderate decrease in chlorinated intermediates/by-products formation was noted. Likewise, the presence of hydrogen, either as a part of the additional chlorinated molecule or as a part of water generated as a reaction product, was determined to be important for efficient combustion of the chlororganics to HCl.

Punjasamud (2003) investigated the effect of addition hexane on the combustion of phthalic anhydride over  $V_2O_5/TiO_2$  catalyst promoted with transition metal (Cu, Fe, Mo and Zn) and magnesium oxide. The results show that there are competitive adsorption of phthalic anhydride and hexane on the catalyst. For Cu Mo and Zn, catalyst phthalic anhydride and hexane competitively adsorbed and reacted on same active sites. Therefore, the combustion of phthalic anhydride or hexane hindered each other depended on the adsorption ability on each catalyst. The Fe catalyst showed the different result i.e. the combustion of phthalic anhydride and hexane was promoted when both reactants were feul together.

Jiménez-Jiménez (2004) studied the selective oxidation of *o*-xylene on catalysts based on mesoporous titanium phosphate-supported vanadium oxide. The catalysts were characterized by different physico-chemical techniques (XRD, XPS,  $N_2$  isotherms, TPD of chemisorbed  $NH_3$  and Raman spectroscopy). The conversion and yield to phthalic anhydride increased with vanadium oxide loading up to one theoretical monolayer. Moreover, a significant improvement in the yield of phthalic anhydride, coinciding with a decrease in the formation of carbon oxides, was observed when potassium was incorporated to the vanadium catalysts. The enhancement of the phthalic anhydride yield was correlated with the neutralization of the stronger surface acid centers by the  $K^+$  ions, providing evidence for the hypothesis that stronger acid sites were involved in the formation of total oxidation products (carbon oxides).

Lichtenberger (2004) studied kinetic and in situ infrared spectroscopic were conducted to investigate the oxidation of different chlorinated benzenes (i.e., chlorobenzene, 1,2- 1,3-, and 1,4-dichlorobenzene) over  $V_2O_5/TiO_2$  catalysts. The oxidation of cyclohexyl chloride and that of benzene were also examined for comparison. Observed differences in the reaction rates and activation energies can be



correlated to the structural differences of these compounds, in light of a common reaction mechanism. This mechanism was supported by the results of in situ FTIR studies, which indicate the presence of similar surface intermediates on the catalyst surface under reaction conditions for all the aromatic compounds examined. The results further suggested that the following two were the important mechanistic steps in the oxidation of chlorinated benzenes: (1) the adsorption of the aromatic compound on the catalyst via a nucleophilic attack on the chlorine position in the aromatic ring and (2) the subsequent oxidation of the remaining aromatic ring.

Routray (2004) studied the oxide support for supporting the vanadium oxide phase by estimating the reaction parameters for the oxidative dehydrogenation of propane. Several  $V_2O_5/Al_2O_3$  and  $V_2O_5/TiO_2$  catalysts were synthesized by an incipient-wetness-impregnation technique. The supported vanadium oxide catalysts were characterized and the surface area, monolayer coverage and reducibility were determined. The surface area of the catalyst samples was not significantly affected with supported vanadium oxide loading. It was observed that the catalysts contain only molecularly dispersed vanadium oxide species below monolayer coverage, and molecularly dispersed and crystalline  $V_2O_5$  above monolayer coverage. TPR studies revealed that the  $V_2O_5/Al_2O_3$  samples were more difficult to reduce relative to the  $V_2O_5/TiO_2$  samples. The monolayer or near-monolayer catalysts, 10%  $V_2O_5/Al_2O_3$  and 4%  $V_2O_5/TiO_2$ , were selected for detailed kinetic analysis. A Mars–van Krevelen (MVK) model containing eight parameters was chosen for this purpose. The parameters were estimated using a generic algorithm, which optimizes a suitable objective function for a non-linear multi-response system. It was determined that a similar catalytic cycle occurred independent of the oxide support. The rate at which the catalytic cycle occurred appeared to be much faster on the more reducible titania support compared to the rate on the less reducible alumina support. The degree of reduction varied along the length of the reactor and depended on the support. Thus, they reported that the support had a significant effect on the reaction parameters for the oxidative dehydrogenation of propane over supported vanadium oxide catalysts.

## 2.2 Comment on previous works

### - $V_2O_5$ - $TiO_2$ catalyst

The reviewed literatures show that vanadium oxide supported on titanium oxide is widely employed in selective oxidation reactions, such as partial oxidation of o-xylene to phthalic anhydride and selective catalytic reduction of nitric oxide. Several studies have aim to improve activity and selectivity of catalysts [Dias *et al.* 2002, Amiridis *et al.* 1999 and Lietti *et al.* 1999]. Several studies deactivation of an industrial  $V_2O_5$ - $TiO_2$  catalyst [Mongkhonsi and Kershenbaum 1998, Anastasov 2003]. Some work also found that the  $V_2O_5$ - $TiO_2$  catalyst can be used for the destruction of organic pollutants [Graham *et al.* 2003].

### - Catalytic combustion of VOC and phthalic anhydride

From the above reviewed literature, it could be seen that the transition metal oxides showed the high activity of oxidation the organic compounds [Spivey 1987, Busca *et al.* 1997, Larsson *et al.* 1997 and Kim 2002]. Furthermore, the result of the combustion of phthalic anhydride on Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo and W promoted MgO on  $Al_2O_3$  supported catalysts [Nugoolchit 2002] and V-Mg-O/ $TiO_2$  [Tongsang 2001] showed that MgO could promote the adsorption of phthalic anhydride leading to better phthalic anhydride combustion for the acidic and amphoteric metal oxides. For the basic metal oxides, the magnesium oxide addition would decrease the combustion of phthalic anhydride. The research also found that the ratio of transition metal oxide per magnesium oxide should be at an appropriate ratio to keep a balance between the adsorption of the phthalic anhydride and the catalytic activity of the transition metal oxides.

### - Mixture effect

Very little has been reported in the literature on research into the catalytic oxidation of mixtures as compared to the catalytic oxidation of individual component. Often, but not always, the catalytic reaction cannot be predicted solely from the behavior of the individual component [Brink *et al.* 1999, Brink *et al.* 2000,

Deutschmann *et al.* 2000, Gervasini *et al.* 2002, Ordóñez *et al.* 2002, Cimino *et al.* 2003, and López-Fonseca *et al.* 2003].

Accordingly, this thesis is interested in the effects of hexane addition on phthalic anhydride combustion over  $V_2O_5/TiO_2$  catalyst impregnated with transition metal oxide and magnesium oxide.



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## CHAPTER III

### THEORY

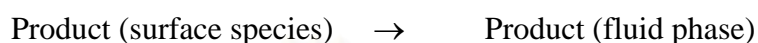
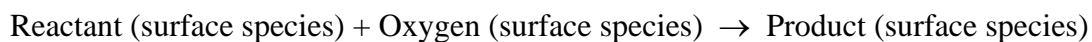
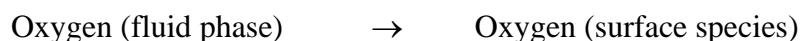
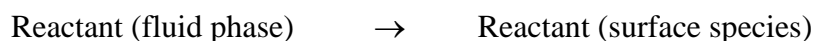
Removal of volatile organic compounds (VOCs), hazardous air pollutants (HAPs) and odors from industrial exhaust gas flows is a requirement of a large number of industries. At present, several methods for VOC removal are available. The main processes currently used are thermal and catalytic incinerations. In both processes the organic compounds are completely oxidized by oxygen to carbon dioxide and water. Previously, the combustion of VOCs was always thermal, taking place at temperatures in excess of 800°C. However, at these temperatures the harmful by-products nitrogen oxides (NO<sub>x</sub>) and carbon monoxide (CO) are often formed. The needed to achieve high temperature requires significant energy expenses, and large combustion chambers designed to operate at high temperature are costly. The completely catalytic oxidation is an alternative method for eliminating organic pollutants in gaseous streams.

Catalytic oxidation can be categorized as complete oxidation and selective oxidation. Complete oxidation is the combustion of organic compounds to the combustion products; CO<sub>2</sub> and H<sub>2</sub>O [Thammanonkul (1996)]. It is a practicable method for the elimination of organic pollutants in gaseous streams. The selective oxidation is the reaction between hydrocarbon and oxygen to produce oxygenates (such as alcohols, aldehydes, carboxylic acids which are produced from partial oxidation processes) or unsaturated hydrocarbons (such as ethane and propene which can be produced from oxidative dehydrogenation process) [Thammanonkul (1996)].

#### 3.1 Mechanism of oxidation reaction

There are 2 mechanisms of oxidation reaction on a catalyst surface depend on the reaction, one is the oxidation reaction between a reactant and an adsorbed surface oxygen species on a catalyst surface. The other one is the oxidation reaction between a reactant and lattice oxygen.

The mechanism of oxidation reaction between a reactant and an adsorbed surface oxygen species on a catalyst surface can be shown as follows:



This oxidation mechanism is name “Mars and van Krevan” type mechanism.

### 3.2 Catalytic Combustion

In studies on the oxidative catalysis, commonly great attention is attached to the state of oxygen on the catalyst surface. A relative inert oxygen molecule is activated by interacting with the surface of an oxide catalyst. The main parameter determining oxygen reactivity on the catalyst is the energy of oxygen binding with the catalyst as a thermochemical characteristic. Correlation between rates of catalytic oxidation and oxygen binding energy on oxide catalyst have been established. The weaker the oxygen binding with the catalyst surface, the more efficient is complete oxidation with this catalyst [Satterfield (1980)].

With oxide catalysts, chemisorbed surface oxygen as well as lattice oxygen may play a role. The oxidation of propylene to acrolein on a BiMo/SiO<sub>2</sub> catalyst in a pulsed reactor showed that surface chemisorbed oxygen as well as lattice oxygen could contribute to the overall reaction. It seemed plausible that in many other cases chemisorbed oxygen would lead to a different set of products than lattice oxygen and both mechanisms could be significant. On the basis of other studies advanced the hypothesis that surface-adsorbed oxygen may in general lead to products of complete oxidation and the lattice oxygen is needed for partially oxidized products [Satterfield (1980)].

Transition metal oxides were interesting materials in the field of heterogeneous catalysis. The most active single metal oxide catalysts for complete oxidation for a variety of oxidation reactions were usually found to be oxides of V,

Cr, Mn, Fe, Co, Ni, and Cu. For the complete oxidation of methane, methanol, ethanol, acetaldehyde, and ethanol/methanol mixture, the transition metal oxide catalysts exhibited high activity. The  $\text{CuMn}_2\text{O}_4/\text{Al}_2\text{O}_3$  catalyst was more active than the  $\text{CuO}_x/\text{Al}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst for the complete oxidation of CO, ethyl acetate, and ethanol. The  $\text{MoO}_3/\text{SiO}_2$  was the most active catalysts among the  $\text{MoO}_3/\text{support}$  catalysts for the diesel soot oxidation. For the photo-oxidation of benzoic acid,  $\text{TiO}_2/\text{W}$  was the most efficient catalyst.

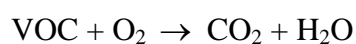
MgO was white powder that usually obtained by dehydration of magnesium dihydroxide. Its catalytic interest lied in its essentially basic surface character, which made it an effective catalyst support. Magnesium oxide was interesting because it had the ability to stabilize metals in unusual oxidation states and to avoid sintering and evaporation of the metal atoms [Aramendia *et al.* (1999)].

Several studies deactivation of an industrial  $\text{V}_2\text{O}_5\text{-TiO}_2$  catalyst [Mongkhonsi and Kershenbaum 1998, Anastasov 2003]. Some work also found that the  $\text{V}_2\text{O}_5\text{-TiO}_2$  catalyst can be used for the destruction of organic pollutants [Graham *et al* 2003]. The catalytic property of  $\text{V}_2\text{O}_5/\text{TiO}_2$  promoted with transition metals (Cu, Fe, Zn, and Mo) and MgO on the combustion was more active than un promoted catalyst [Punjasamud and Charoenruay 2003].

### 3.2.1 Catalytic combustion of volatile organic compounds

Catalytic combustion is an alternative for controlling VOCs emissions. In this process, very high destructive can be achieved at relatively low operating temperature resulting in considerable environmental and economic benefits in comparison to the case of the more conventional thermal combustion.

The oxidation reaction between VOCs and oxygen on a catalyst surface can be shown as follows:



In the real catalytic combustion process, the concentration of VOCs in the effluent gas and the gas temperature are so low that the combustion reaction can not self initiate and maintain the reaction combustion after the effluent gas was heat up to the temperature which could initiate the combustion reaction. Therefore, additional energy source for this reaction heat must be supplied to the system. The heat generate from the combustion of the added reactant co-feed could make the overall combustion reaction self maintain [Punjasamud (2003)].

The reaction temperature and residence time depend on the VOC species that undergo oxidation, and on the type of catalyst used. As the catalytic reaction accelerates with increasing temperature, less catalyst is required as the oxidation temperature goes up, thus creating a window for process optimization. Reduced energy consumption and lower demands to the reaction chamber insulation offset the added cost of loading, periodically replacing the catalyst and making catalytic oxidation competitive with thermal process.

In addition to process temperature, another route to process optimization is selection of the gas velocity to the bed. High velocity means a deeper catalyst bed with a smaller cross-section. This is advantageous from a capital cost point of view, but increase pressure drop and consumption of energy need to pump gas through the bed. Wide and thin beds lead to more costly equipment and make it difficult to uniformly distribute the catalyst and the gas flow throughout the bed cross-section, that is needed to achieve require performance.

## CHAPTER IV

### EXPERIMENTAL

The experimental systems and procedures used in this work are divided into three parts:

1. The preparation of catalysts.
2. The characterization of catalysts.
3. The catalytic activity measurements.

The details of the experiments are described as the following.

#### The scope of this study

The reaction conditions are chosen as follows:

Catalysts	:	Fe- V-Mg-O/TiO <sub>2</sub> , Cu- V-Mg-O/ TiO <sub>2</sub> , Zn-V-Mg-O/ TiO <sub>2</sub> , Mo- V-Mg-O/ TiO <sub>2</sub>
Reactant	:	0.06 vol% C <sub>8</sub> H <sub>4</sub> O <sub>3</sub> , 1.34 vol% C <sub>6</sub> H <sub>14</sub> and 0.56 vol% C <sub>6</sub> H <sub>14</sub>
Flow rate of reactant	:	150 ml/min
Reaction temperature	:	150-300°C
Space velocity	:	15000 ml/g/h

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## 4.1 Preparation of catalysts

### 4.1.1 Chemicals

The details of chemicals used in this experiment are shown in Table 4.1.

**Table 4.1** The chemicals used in this experiment.

Chemical	Grade	Supplier
Ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ )	Analytical	Univar, Australia
Cupric nitrate trihydrate ( $\text{CuN}_2\text{O}_6\cdot 3\text{H}_2\text{O}$ )	Analytical	Fluka, Switzerland
Ferric nitrate nonahydrate ( $\text{FeN}_3\text{O}_9\cdot 9\text{H}_2\text{O}$ )	Analytical	Fluka, Switzerland
Magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ )	Analytical	Fluka, Switzerland
Zinc nitrate hexahydrate ( $\text{ZnN}_2\text{O}_6\cdot 6\text{H}_2\text{O}$ )	Analytical	Fluka, Switzerland
Titanium oxide ( $\text{TiO}_2$ )	JRC-TIO1	Department of Material Science, Shimane University
Ammonium metavanadate ( $\text{NH}_4(\text{VO}_3)$ )	Analytical	Carlo Erba, Italy
Phthalic Anhydride ( $\text{C}_8\text{H}_4\text{O}_3$ )	Analytical	Fluka, Switzerland
Hexane ( $\text{C}_6\text{H}_{14}$ )	Analytical	Univar, Australia



#### **4.1.2 Preparation of catalyst**

Each catalyst was prepared by 2 step. In the first step  $V_2O_5/TiO_2$  was prepared by wet impregnation.  $TiO_2$  powder was added to an aqueous solution of ammonium metavanadate ( $NH_4VO_3$ ) at  $70^\circ C$ . The suspension was evaporated at  $80^\circ C$ , then dried in the oven at  $110^\circ C$  in air over night. The resulting solid was calcined in air at  $550^\circ C$  for 6 hours. Then the desired metal (Fe, Cu, Zn and, Mo) and magnesium was introduced into the calcined solid by co-impregnation from an aqueous solution containing both salt of a desired metal and magnesium nitrate  $Mg(NO_3)_2$ , evaporated at  $80^\circ C$  and dried at  $110^\circ C$  in air overnight. After drying the catalyst was calcined in air at  $550^\circ C$  for 6 hours.

### **4.2 The characterization of catalysts**

#### **4.2.1 Determination of composition content of catalysts**

The actual composition contents of all the catalysts were determined by atomic absorption spectroscopy (AAS) at the Department of Science Service Ministry of Science Technology and Environment. The calculation of the sample preparation is shown in Appendix A.

#### **4.2.2 BET Surface area measurement**

##### **- Apparatus**

The apparatus consisted of two gas feed lines for helium and nitrogen. The flow rate of gas was adjusted by means of a fine-metering valve. The sample cell was made from pyrex glass. The operation conditions of the gas chromatograph (GOW-MAC) is shown in Table 4.2.

**Table 4.2** Operation conditions of gas chromatograph (GOW-MAC)

Model	GOW-MAC
Detector	TCD
Helium flow rate	30 ml/min
Detector temperature	80°C
Detector current	80 mA

### - Procedure

The mixture of helium and nitrogen gas flowed through the system at the nitrogen relative gauge pressure of 0.3. The sample was placed in the sample cell, which was then heated up to 150°C and held at this temperature for 2 h. The sample was cooled down to room temperature and ready to measure the surface area. There were three steps to measure the surface area.

#### (1) Adsorption step

The sample cell was dipped into the liquid nitrogen. Nitrogen was adsorbed on the surface of the sample until equilibrium was reached.

#### (2) Desorption step

The nitrogen-adsorbed sample was dipped into the water at room temperature. The adsorbed nitrogen was desorbed from the surface of the sample. This step was completed when the recorder line return back to the base line.

#### (3) Calibration step

1 ml of nitrogen gas at atmospheric pressure was injected at the calibration port and the area was measure. The area was the calibration peak. The BET surface area was calculated using procedures described in Appendix C.



### 4.2.3 X-ray diffraction (XRD)

The phase structures of the samples were determined by X-ray diffraction, Siemens D 5000 X-ray diffractometer using CuK $\alpha$  radiation with Ni filter in the  $2\theta$  range of 10-80°. The sample was placed into XRD plate before placing on the measured position of XRD diffractometer.

### 4.2.4 Pyridine Adsorption

The acid site of the samples were determined by the pyridine adsorption. The apparatus consisted of the tube connected to the gas chromatograph (GC9A). The condition of the gas chromatograph is shown in Table 4.3.

**Table 4.3** Operation conditions of gas chromatograph (GC9A) for pyridine adsorption

Model	GC9A
Detector	FID
Nitrogen flow rate	30 ml/min
Column temperature	150°C
Detector temperature	180°C
Injector temperature	180°C

0.02 g of sample was placed in the tube. 0.1  $\mu$ l of pyridine was injected to the gas chromatograph and the peak area was measured. The pyridine was injected until the sample was saturated. The amount of acid site of the sample was calculated from the total peak area of the pyridine adsorbed. The pyridine adsorption was calculated using the procedures described in Appendix G.

### 4.2.5 Maleic anhydride Adsorption

The amount of basic site of the samples was determined by the maleic anhydride adsorption. The apparatus consisted of the tube connected to the gas chromatograph (GC9A). The condition of the gas chromatograph is shown in Table 4.4.

**Table 4.4** Operation conditions of gas chromatograph (GC9A) for maleic anhydride adsorption

Model	GC9A
Detector	FID
Nitrogen flow rate	30 ml/min
Column temperature	280°C
Detector temperature	300°C
Injector temperature	300°C

0.03 g of sample was placed in the tube. 0.3  $\mu$ l of maleic anhydride aqueous solution of known concentration (0.104 g/ml) was injected to the gas chromatograph and the peak area was measured. The maleic anhydride was injected until the sample was saturated. The basic site of the sample was calculated from the total peak area of the maleic anhydride adsorbed. The maleic anhydride adsorption was calculated using the procedures described in Appendix G.

### 4.2.6 FT-IR pyridine adsorption

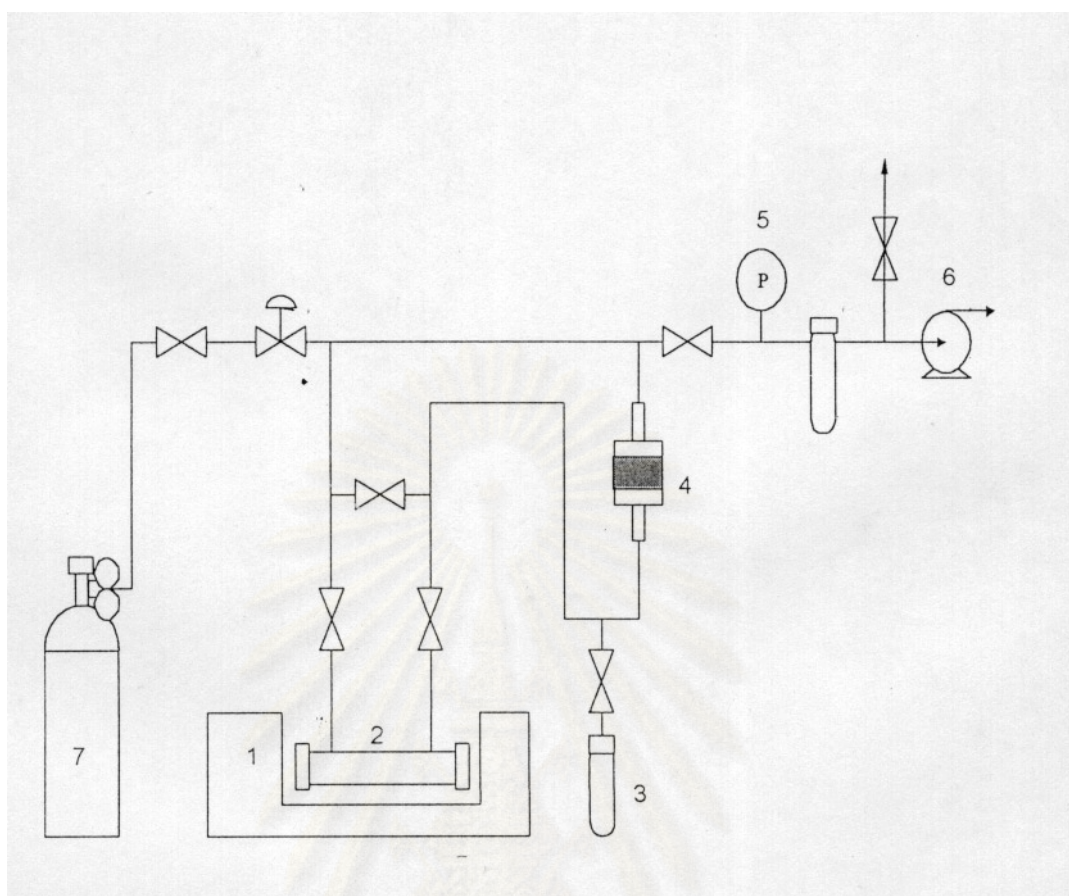
#### 4.2.6.1 Chemicals and reagents

Ultra high purity (99.99%) nitrogen supplies by TIG Ltd. and pyridine, analytical grade supplied by Univax or Ajax chemical were used in these experiment.

#### 4.2.6.2 Instruments and apparatus

##### Flow diagram

The schematic diagram of the *in situ* FT-IR apparatus is depicted in Figure 4.1. All gas lines, valves and fittings in this apparatus were made of pyrex glass except the IR gas cell and the sample disk holder, which were made of quartz glass in order to avoid the adsorption of any glass species which may remain on the inner surface of glass tube while the system was evacuated. Nitrogen was used for purging before starting the experiment. Pyridine was added to a glass tube connected which a valve which can open to the glass line system. A home made electro-magnetic pump, fixed in the gas line, was used for circulating the gas (including the pyridine vapour) through the sample in order to accomplish the adsorption of gas or pyridine species on the sample surface. A Labconco 195-500 HP vacuum pump, which theoretically had capacity at  $10^{-4}$  Torr, was used for system evacuation. Furthermore, a digital pressure indicator, attached to the gas line, measured the pressure of the system and checked leaking of the apparatus as well.



1. FT-IR Analyzer
2. IR quartz gas cell
3. Pyridine tube
4. Electro magnetic circulating pump
5. Digital pressure indicator
6. Vacuum pump
7. Nitrogen gas cylinder

**Figure 4.1** Flow diagram of instrument used for pyridine adsorption experiment

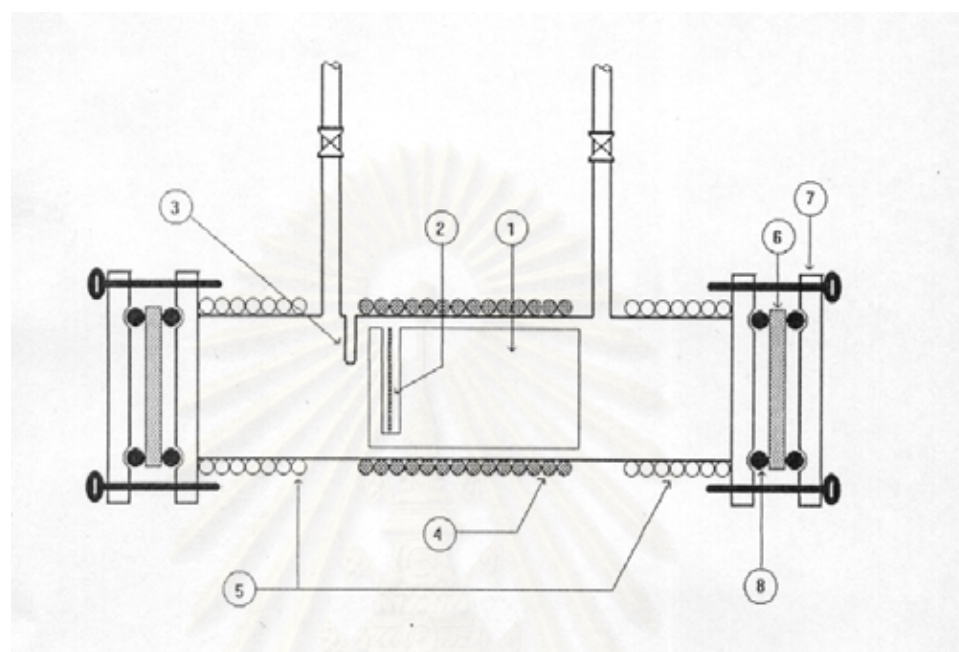
## **FT-IR**

The FTIR spectrometer was used as a detector in the experiments. A Nicolet model Impact 400 FT-IR equipped with a deuterated triglycine sulfate (DTGS) detector and connected to a personal computer with Omnic version 1.2a on Windows software (to fully control the functions of the IR analyser) were applied to this study. The analyzer was placed on a moveable table for conveniently adjustment.

## **IR gas cell**

The IR gas cell used in this experiment, shown in figure 4.2, was made of quartz and covered with 32×3 mm NaCl windows at each end of the cell. Each window was fixed with two o-rings and a stainless flange fastened by a set of screws.

The cell is roughly divided into two zones; heating and cooling respect to their temperature. The function of the heating zone at the middle of the IR cell is to increase the temperature for the sample disk. The quartz sample holder for the sample disk to keep it perpendicular to the IR beam, is arranged inside the IR cell in the heating zone. A thermocouple is used to measure the sample disk temperature. The temperature is controlled by a variable voltage transformer and a temperature controller. At both ends of the IR cell were cooled with water. Water was supplied to reduce the excessive heating, which may damage the o-ring seals and the windows.



- |                          |                |
|--------------------------|----------------|
| 1. Sample Holder         | 2. Sample Disk |
| 3. Thermocouple Position | 4. Heating rod |
| 5. Water Cooling line    | 6. KBr Window  |
| 7. Flange                | 8. O-ring      |

**Figure 4.2** IR gas cell used for pyridine adsorption experiment

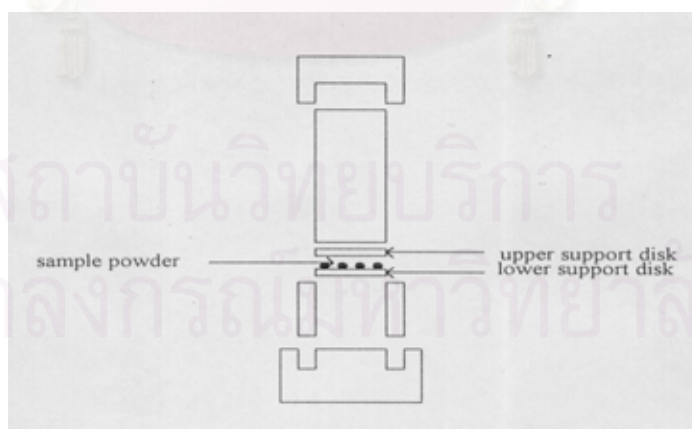
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#### 4.2.6.3 Sample disk preparation

To produce a self-supporting catalyst sample disk for an IR experiment the catalyst was milled thoroughly in a small quartz mortar to obtain a very fine powder. This minimized the scattering of infrared radiation and provided a high quality of spectrum.

The die used was made of stainless steel and is shown in figure 4.3. The most important part of this die, which is directly in contact with the sample is the so-called the support disks. The support disks are composed of upper and lower disks, each 20 mm. in diameter. The support disks are highly polished to a mirror like finish in order to overcome the sticking of sample to the surface of the die, the main problem in pressing disks. The powder sample, about 0.055-0.065 g, was spread to totally cover the surface of the lower support disk placed in the die to make the sample disk. If a thick sample disk was used, a poor IR would scan result and if too thin sample disk was employed, it would be easily cracked by thermal treating as well as broken itself. All parts of the die were put together and were pressed by a manual hydraulic press at pressure of 150-170 kg/cm<sup>2</sup> for 5 minutes. The pressure should not be too low otherwise a self-supporting disk cannot form. After pressing, the well-formed disk was carefully removed from the die and mounted in the IR cell.



**Figure 4.3** Body of the die for preparation of a self-supporting catalyst disk

#### 4.2.6.4 Experimental procedure

After a well-formed sample disk is obtained, the sample disk was placed in the sample holder and then the sample holder, including the sample disk, was placed into the middle of IR gas cell. The sample disk is located as close to the thermocouple probe hole as possible. Once the KBr windows were fixed at both ends of the IR gas cell and gas leak was not observed, the IR gas cell was evacuated by a vacuum pump through the gas line for at least 30 minutes to place the system under vacuum. The sample disk was evacuated in vacuum for 1 hour at room temperature. However, since no change of the IR spectrum of the sample was found during the pre-treatment, this step something ignored. Pyridine vapour was brought into contact with the disk at room temperature. Under vacuum, liquid pyridine evaporates from the pyridine tube in to the gas line leading to the IR gas cell. To achieve the maximum adsorption of pyridine, pyridine vapour was circulated though the system by the electro-magnetic pump for 1 hour or until the IR spectrum of pyridine peak did not change. After that, the IR cell and gas line were evacuated to remove not only pyridine vapour remaining in the cell and gas line but also the physisorbed pyridine from the catalyst surface too. The vacuum pump was operated until the IR spectra peaks of pyridine vapour and physisorbed pyridine totally vanished and there was no change in any other peaks of the spectra. This normally took around 1.5 hours then, FT-IR measurement of the spectra of the pyridine-adsorbed sample started at room temperature and was repeated at elevated temperature in 50°C steps.

The vacuum pump was kept running while the sample disk and the IR gas cell were heating to remove all species desorbed from the sample surface out of the system in order to avoid disturbing the result spectra by such species. On the other hand, since the vibration would occur and bring about bad scans, the vacuum was switched off while the temperature was held constant for IR detection. The measurement was completed when all peaks of adsorbed pyridine disappeared so that the IR spectra of the sample was identical to the one before pyridine dosing

### 4.3 The catalytic activity measurements

#### 4.3.1 Equipment

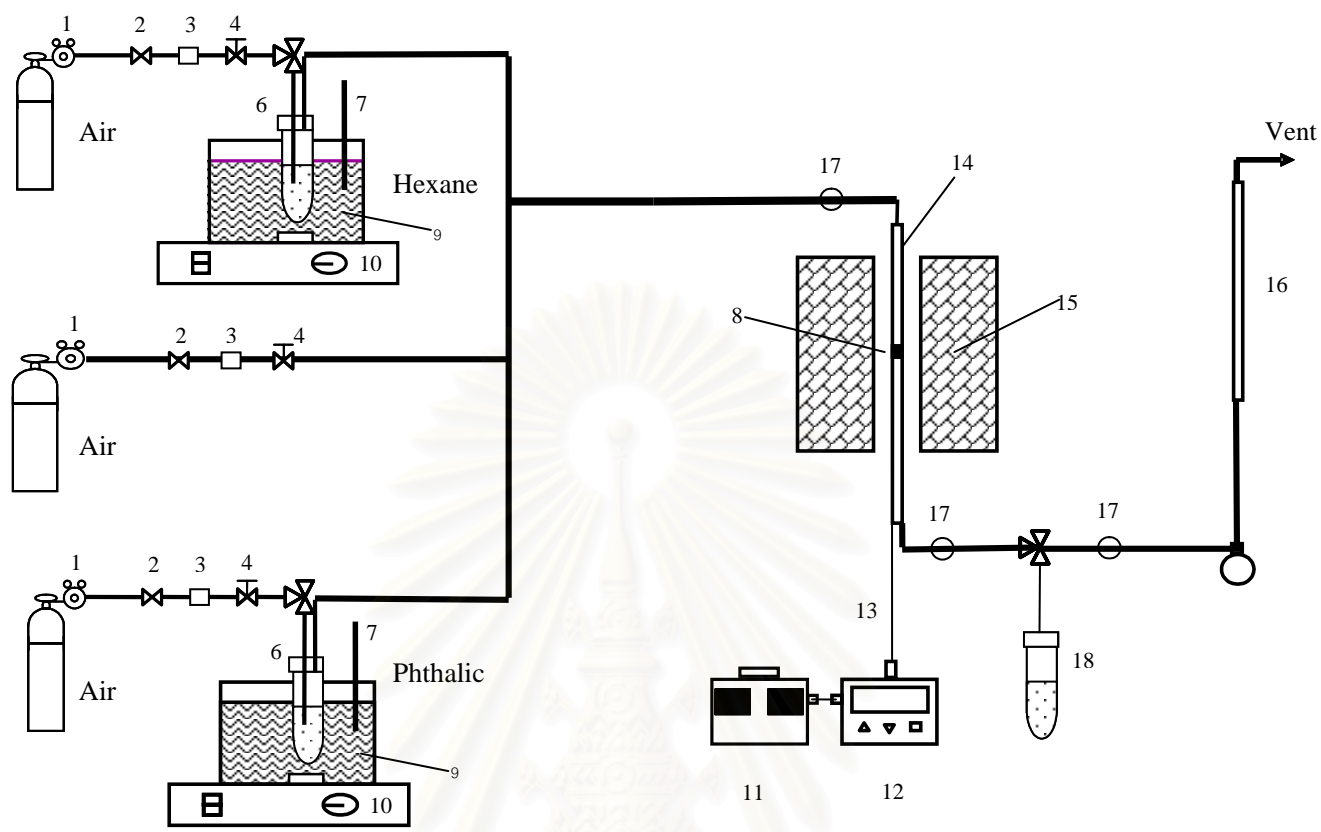
The combustion system, as shown in figure 4.4., consists of a reactor, a saturator, an automatic temperature controller, an electrical furnace and a gas controlling system.

The reactor is made from a stainless steel tube (O.D.1/4"). Three sampling points are provided above and below the catalyst bed. Catalyst is placed between two quartz wool layers.

An automatic temperature controller consists of a magnetic contactor model Telex 87114 was used to monitor and control the temperature of the reactor. The reactor temperature was measured at the bottom of the catalyst bed in the reactor. The temperature control set point is adjustable within the range of 0-800°C at the maximum voltage output of 220 volt.

The electrical furnace supplies heat to the reactor for phthalic anhydride combustion. The reactor can be operated from room temperature up to 800°C at the maximum voltage of 220 volt.

The gas supplying system consists of cylinders of air zero, each equipped with pressure regulators (0-120 psig), on-off valves and fine-meter valves used for adjusting the flow rate.



- |                         |                                  |                            |
|-------------------------|----------------------------------|----------------------------|
| 1. Pressure Regulator   | 2. On-Off Valve                  | 3. Gas Filter              |
| 4. Metering Valve       | 5. Heating Line                  | 6. Saturator               |
| 7. Thermometer          | 8. Catalyst Bed                  | 9. Oil                     |
| 10. Stirring Controller | 11. Variable Voltage Transformer | 12. Temperature Controller |
| 13. Thermocouple        | 14. Reactor                      | 15. Furnace                |
| 16. Flow Meter          | 17. Sampling Point               | 18. Tap                    |

**Figure 4.4** Flow diagram of phthalic anhydride combustion system

The compositions in the feed and product streams were analyzed by a gas chromatograph Shimadzu model GC9A equipped with a flame ionization detector .

A Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector was used to analyze permanent gases and water. Two columns, a 5A molecular sieve to separate oxygen and CO and a Porapak-Q column to separate CO<sub>2</sub> and water were operated in parallel. The operating conditions of the GC are listed in the Table 4.5.

**Table 4.5** Operating conditions for gas chromatographs

Gas chromatograph	GC8A	GC9A
Detector	TCD	FID
Column	MS-5A, Porapak-Q	Chromosorb WAW
Carrier gas	He (99.999%)	N <sub>2</sub> (99.999%)
Carrier gas flow	25 ml/min	30 ml/min
Column temperature	100°C	210°C
Detector temperature	130°C	250°C
Injector temperature	130°C	250°C
Analyzed gas	CO, CO <sub>2</sub> , H <sub>2</sub> O	C <sub>8</sub> H <sub>4</sub> O <sub>3</sub> and C <sub>6</sub> H <sub>14</sub>

#### 4.3.2 Oxidation procedure

The oxidation procedures are described in the detail below.

1. 90 mm height of catalyst was packed in the middle of the stainless steel microreactor located in an electrical furnace.
2. The total flow rate was 150 ml/min. The concentration of phthalic anhydride and hexane in air was adjusted to the required values.
3. The reaction temperature was between 150-300 °C. The effluent gas was analyzed by using the FID and TCD gas chromatograph. The chromatograph data were changed into mole of phthalic anhydride, hexane and CO<sub>2</sub> by calibration curves in Appendix D.

The operating conditions selected have been checked to confirm that there was no external and internal mass transfer resistance. The calculation was shown in Appendix B.



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## CHAPTER V

### RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two major parts including the catalyst characterization and the catalytic combustion reaction of phthalic anhydride in presence of hexane, and surface acidity and basicity, respectively.

#### 5.1 Catalyst characterization

##### 5.1.1 Determination of composition content and BET surface area of catalyst

The results of metal composition and BET surface area of all catalysts, which were analyzed by atomic absorption spectroscopy (AAS) and BET surface area are summarized in Tables 5.1.

**Table 5.1** The composition of different magnesium loading catalysts and BET surface area

Catalyst	wt% metal	wt% Mg	BET surface area (m <sup>2</sup> /g)
TiO <sub>2</sub>	-	-	47.98
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	6.1	-	8.87
8Cu- 7V-1Mg-O/TiO <sub>2</sub>	8.0	0.96	7.59
8Fe- 7V-1Mg-O/TiO <sub>2</sub>	7.7	1.00	12.43
8Mo- 7V-1Mg-O/TiO <sub>2</sub>	7.8	1.10	9.13
8Zn- 7V-1Mg-O/TiO <sub>2</sub>	8.0	1.00	7.33

It must be noted here that the amounts of the transition metals and magnesium used in this work have not been proved to be the amounts that yielded the best performance catalyst for each transition metal. The previous works [Nuampituk (2002), Nugoolchit (2002)] have showed that adding about 1wt% Mg could significantly increase the combustion activity of the catalysts. Mg loading higher than 1wt% may increase or decrease the combustion activity. In case of activity gain, the increase of Mg loading from 1wt% to 4wt% did not strongly increase of the combustion activity as the increase from 0wt% to 1wt%. Therefore, 1wt% Mg was chosen in this work. The amount of the transition metals was fixed at 8 wt% to make the obtained results comparable to the previous works [Nuampituk (2002), Nugoolchit (2002)].

### 5.1.2 X-ray Diffraction (XRD)

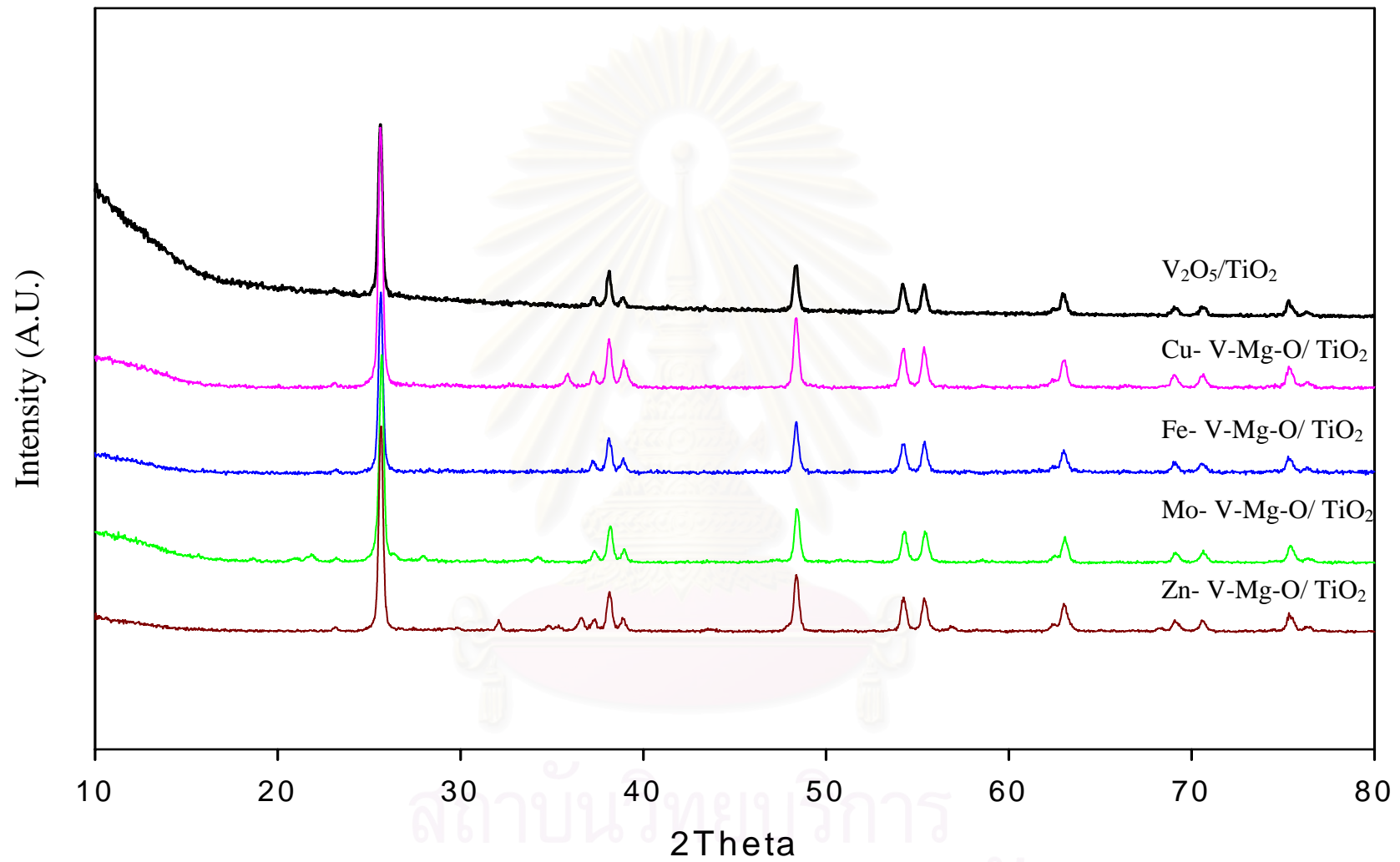
The first three strongest XRD peaks of transition metal oxides from the reference [The JCPDS (1980)] using  $\text{CuK}\alpha$  radiation are listed in Table 5.2.

**Table 5.2** The reference XRD patterns for transition metal oxides

Oxides	Position ( $2\theta$ )	Oxides	Position ( $2\theta$ )
CuO	35.4°, 35.6°, 38.8°	MoO <sub>3</sub>	9.6°, 25.8°, 29.4°
Cu <sub>2</sub> O	37°, 40.4°, 42.4°	MoO <sub>2</sub>	26°, 36.8°, 53.4°
Fe <sub>2</sub> O <sub>3</sub>	29.8°, 32.8°, 67.5°	ZnO	33.6°, 58.4°, 62.6°
FeO	61°, 61.4°, 73°	ZnO <sub>2</sub>	31.8°, 37°, 63°
MgO	37°, 43°, 62.8°		

XRD was used to determine the bulk crystalline phases in the catalysts. The diffraction patterns of all catalysts are shown in figure 5.1. The XRD pattern of TiO<sub>2</sub> showed strong diffraction peaks at 25.3°, 37.8°, 48.0°, 53.9° and 55.1° indicating the TiO<sub>2</sub> is in the anatase form.

From the XRD result of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, it was observed that only peaks of TiO<sub>2</sub> were present in the XRD pattern. The peak of vanadium oxide was not detected



**Figure 5.1** The XRD patterns of all catalysts

possibly because the XRD pattern of vanadium oxide was hidden by the XRD pattern of  $\text{TiO}_2$  support, or vanadium oxide did not form a crystal with significant size or did not form a crystal. It was also found that the  $\text{TiO}_2$  (anatase) support did not undergo structural changes during the vanadia impregnation and calcinations ( $550^\circ\text{C}$ -6 hr) in the first step because the XRD analysis only exhibited the anatase phase (rutile was not present in the XRD pattern).

After addition of Fe, Cu, Zn and Mo in the second step, different results were observed. The XRD result of Cu-V-MgO/ $\text{TiO}_2$  showed two small diffraction peaks at  $35.8^\circ$  and  $38.6^\circ$  which are belong to CuO.

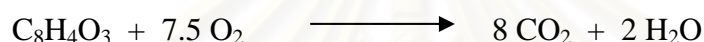
For Zn-V-MgO/ $\text{TiO}_2$ , the introduction of zinc oxide induced the appearance of small peaks of ZnO. These peaks were very weak at  $31.9^\circ$  and  $36.4^\circ$ . The relative intensity of those peaks was much lower compared to the  $\text{TiO}_2$  peaks. This observation suggested that CuO and ZnO could form crystal with significant size on the catalyst surface.

Similar diffraction patterns were obtained for Fe-V-MgO/ $\text{TiO}_2$  and Mo-V-MgO/ $\text{TiO}_2$ . The XRD results of Fe and Mo showed only the  $\text{TiO}_2$  peaks and did not show any peak of these transition metal oxides. The peaks of Fe and Mo oxides were not detected possibly because the XRD patterns of these transition metal oxides were hidden by the XRD pattern of  $\text{TiO}_2$  support, the oxides did not form a crystal with significant size or it did not form a crystal.

## 5.2 Catalytic reaction

This research investigated the combustion for phthalic anhydride in the presence of hexane over  $V_2O_5$  catalyst impregnated with transition metal oxides (Cu, Fe, Mo and Zn) and magnesium oxide in a nonisothermal nonadiabatic fixed bed reactor.

Phthalic anhydride comprises of an anhydride functional group and a benzene ring. It was a product in the oxidation of o-xylene. In this research, the combustion reaction was studied in an excess oxygen atmosphere. The combustion reaction was as follows:



Hexane is a member of the alkane or paraffin series of hydrocarbon. Hexane is used in low temperature thermometer, polymerization reaction, plant diluents, alcohol denaturant and solvents for vegetable oils. In this research, the combustion reaction was studied in an excess oxygen atmosphere. The combustion reaction of hexane was as follows:



In previous works, it was found that magnesium oxide could promote the adsorption of phthalic anhydride leading to better combustion of phthalic anhydride [Tongsang (2001) and Umpo (2001)]. The subsequent study found that the ratio of transition metal oxide per magnesium oxide should be at an appropriate ratio to keep a balance between the adsorption of the phthalic anhydride and the catalytic activity of the transition metal oxides [Nuampituk (2002) and Nugoolchit (2002)]. The catalytic property of  $V_2O_5 / TiO_2$  catalysts promoted with transition metals (Cu, Fe, Zn, and Mo) and MgO on the combustion of phthalic anhydride was more active than unpromoted catalyst [Charoenruay (2003)]. The addition of hexane had possibility to improve phthalic anhydride combustion but this technique has yet been prevent that it can use for the real process. This is because the previous work used a small height of

packed bed and large amount of external heat to initiate the combustion reaction [Punjasamud (2003)]. In the present work, the bed height was increased and the external heat supplied was reduced.

Figures 5.2-5.9 show catalytic activity of the catalysts for the combustion of a gas mixture containing phthalic anhydride and hexane.

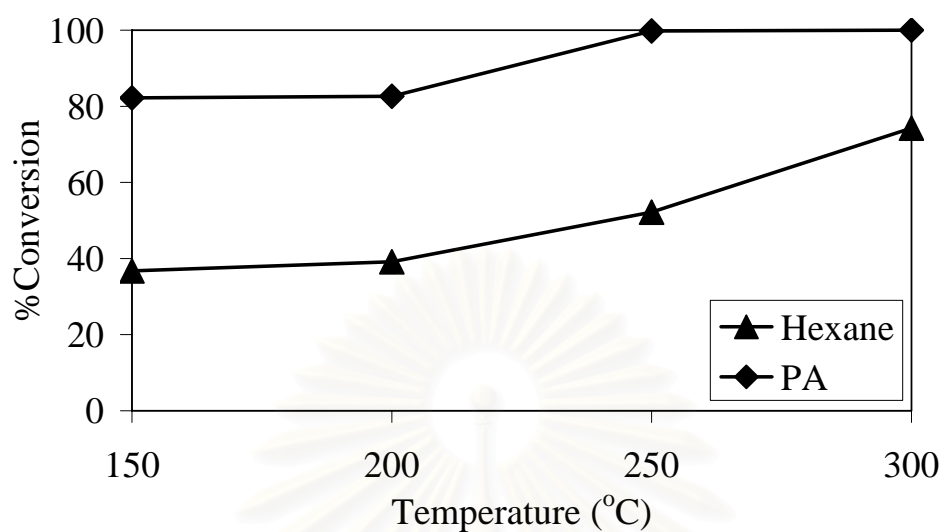
#### - **Copper oxide catalyst**

Figure 5.2 illustrates the catalytic activity of  $8\text{Cu}7\text{V}1\text{Mg}/\text{TiO}_2$  for phthalic anhydride combustion with high concentration of hexane (1.34 vol%) co-feeding. The result showed that the conversion of phthalic anhydride raised from 82% at  $150^\circ\text{C}$  and steadily increased until the temperature reached  $250^\circ\text{C}$ , where the conversion of phthalic anhydride was 100%. On the other hand, hexane conversion slightly increased from 37% to 74% at temperature range of 150 to  $300^\circ\text{C}$ .

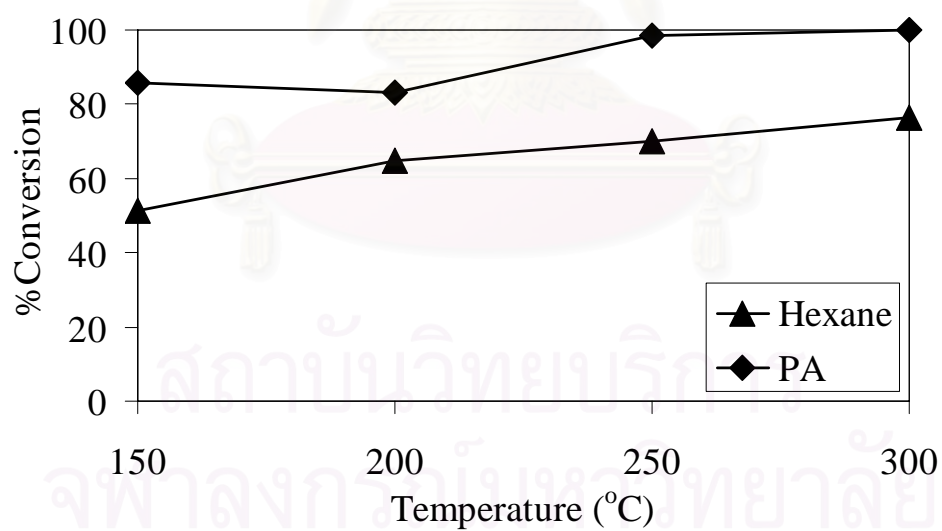
Figure 5.3 illustrates the catalytic activity of  $8\text{Cu}7\text{V}1\text{Mg}/\text{TiO}_2$  for phthalic anhydride combustion with low concentration of hexane (0.56 vol%) co-feeding. The result showed that the conversion of phthalic anhydride started up from 85% at  $150^\circ\text{C}$  and steadily increased until the temperature reached  $300^\circ\text{C}$ , which the conversion of phthalic anhydride was 100%. On the other hand, hexane conversion slightly increased from 51% to 76% at temperature range of 150 to  $300^\circ\text{C}$ .

It should be noted here that when the concentration of hexane was decreased, the conversion of phthalic anhydride was not affected. This may be because the combustion of phthalic anhydride and hexane occurred on different active sites.





**Figure 5.2** The catalytic activity of copper oxide catalyst for the combustion of phthalic anhydride and high concentration of hexane (1.34 vol%).

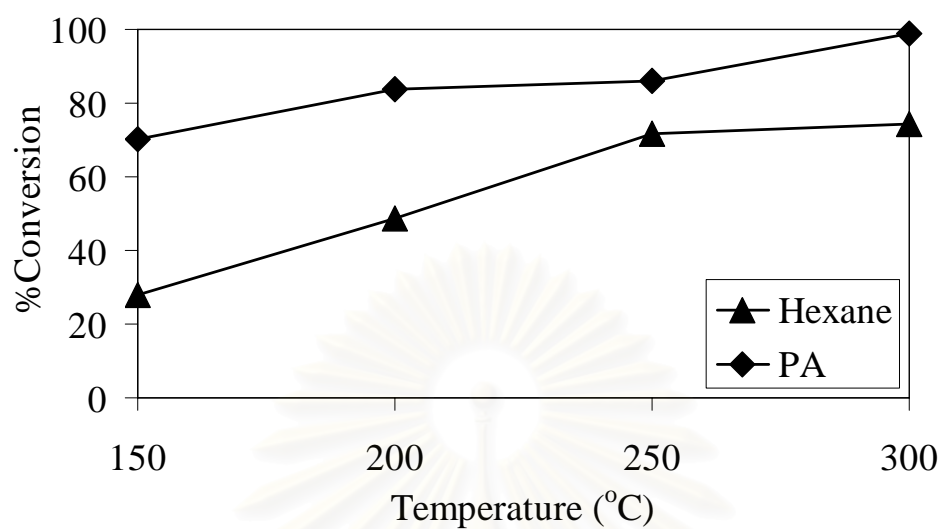


**Figure 5.3** The catalytic activity of copper oxide catalyst for the combustion of phthalic anhydride and low concentration of hexane (0.56 vol%).

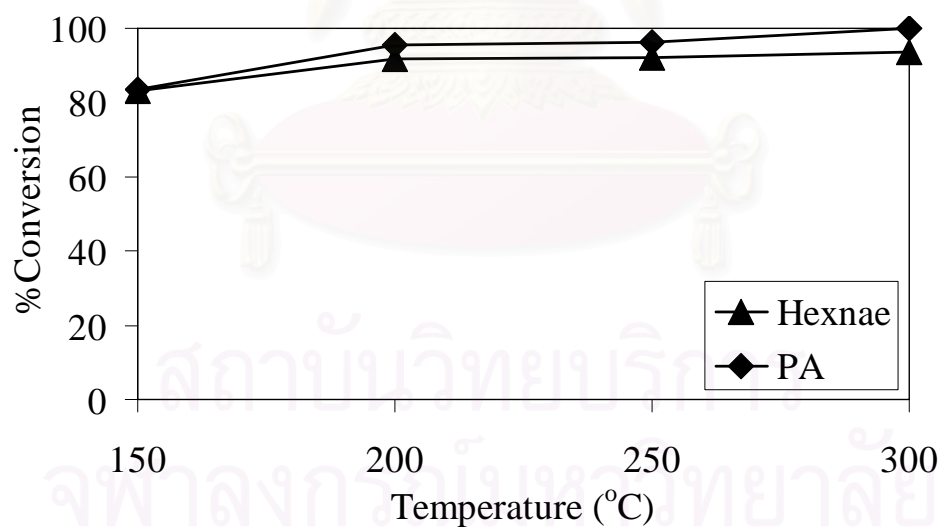
### - Iron oxide catalyst

Figure 5.4 illustrates the catalytic activity of 8Fe7V1Mg/TiO<sub>2</sub> for phthalic anhydride combustion with high concentration of hexane (1.34vol%). Figure 5.5 illustrates the catalytic activity of 8Fe7V1Mg/TiO<sub>2</sub> for phthalic anhydride combustion with low concentration of hexane (0.56vol%). The result showed that for the combustion of phthalic anhydride at high concentration of hexane, the conversion of phthalic anhydride can increased from 70% at 150°C and steadily increased to 99% at a temperature about 300°C. At the same time the conversion of hexane slightly increased from 28% to 74% in the reaction temperature range of 150 to 300°C. On the other hand, at low concentration of hexane, phthalic anhydride conversion slightly increased from 83% to 100% while hexane conversion increased from 83% to 94% at temperature range of 150 to 300°C.

The behaviour of the iron oxide catalyst was different from that of the copper oxide catalyst. For the iron oxide catalyst, the decreased in hexane concentration in the feed resulted in the increase of both phthalic anhydride and hexane conversion. It would probably due to the added height concentration of hexane in the reaction affect of competitive adsorption of the reactant.



**Figure 5.4** The catalytic activity of iron oxide catalyst for the combustion of phthalic anhydride and high concentration of hexane (1.34 vol%).

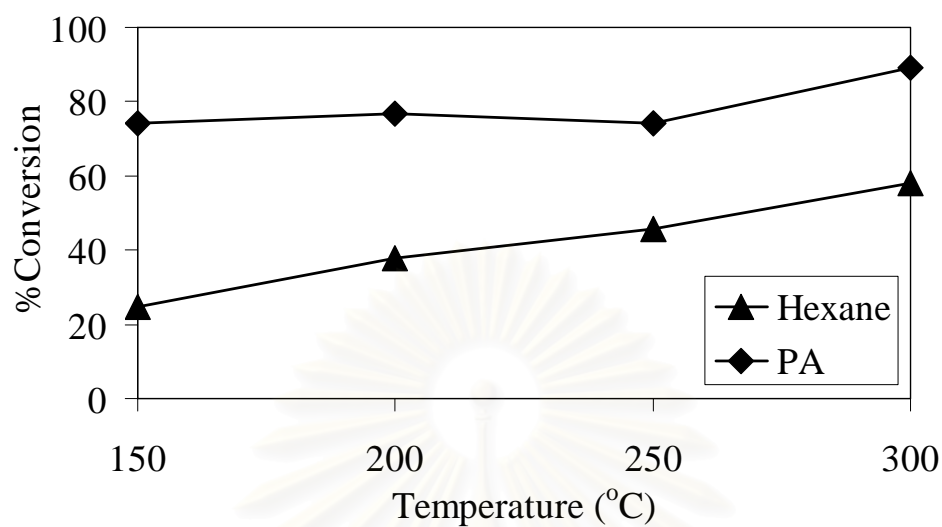


**Figure 5.5** The catalytic activity of iron oxide catalyst for the combustion of phthalic anhydride and low concentration of hexane (0.56 vol%).

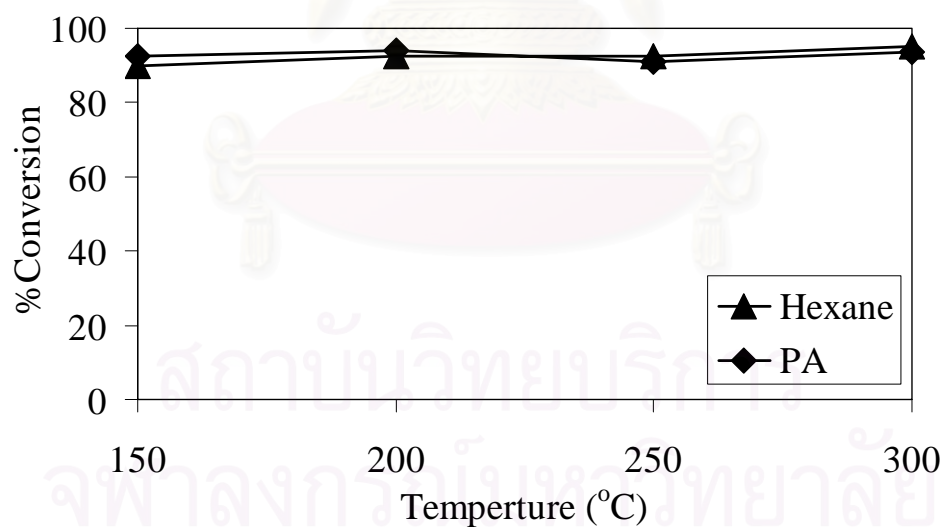
### - Molybdenum oxide catalysts

Figure 5.6 illustrates the catalytic activity of 8Mo7V1Mg/TiO<sub>2</sub> for phthalic anhydride combustion with high concentration of hexane (1.34vol%) co-feeding. The result showed that when high hexane concentration was co-fed with phthalic anhydride, the conversion of hexane slightly increased from 25% to 58% at the temperature range of 150 to 300°C and phthalic anhydride conversion started up at about 74% at 150 °C. After that the phthalic anhydride conversion steadily increased until the temperature reached 300°C, which the conversion was about 89%. Figure 5.7 illustrates the catalytic activity of 8Mo7V1Mg/TiO<sub>2</sub> for phthalic anhydride combustion in presence of low concentration of hexane. It was found that the conversion of phthalic anhydride increased from 92% to 93% at temperature range of 150 to 300°C. and hexane conversion slightly increased from 90% to 95% at temperature range of 150 to 300°C.

In the combustion of phthalic anhydride with low concentration of hexane, the increased of hexane and phthalic anhydride conversion at the same temperature compared with the combustion of hexane at high concentration was observed. It would probably be the effect of competitive adsorption of both reactants and the combustion of phthalic anhydride and hexane used the same active sites.



**Figure 5.6** The catalytic activity of molybdenum oxide catalyst for the combustion of phthalic anhydride and high concentration of hexane (1.34 vol%).



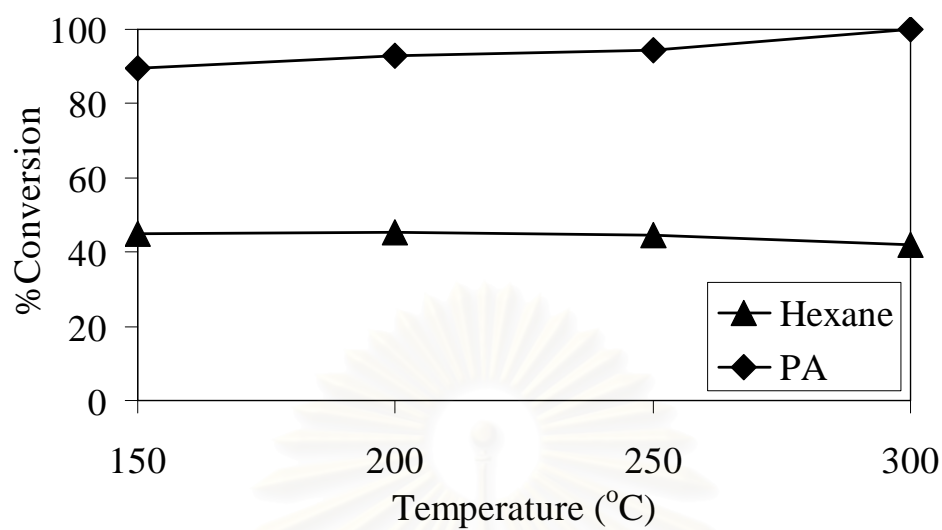
**Figure 5.7** The catalytic activity of molybdenum oxide catalyst for the combustion of phthalic anhydride and low concentration of hexane (0.56 vol%).

- **Zinc oxide catalysts**

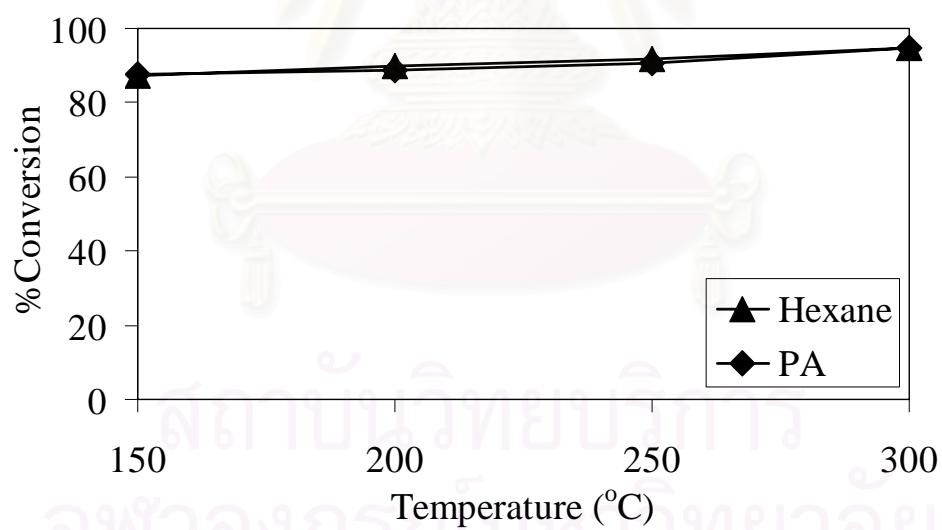
Figure 5.8 illustrates the catalytic activity of 8Zn7V1Mg/TiO<sub>2</sub> for phthalic anhydride combustion with high concentration of hexane in the feed. Figure 5.9 illustrates the catalytic activity of 8Zn7V1Mg/TiO<sub>2</sub> for phthalic anhydride combustion with low concentration of hexane. The result showed that for the combustion of phthalic anhydride and high concentration of hexane, the conversion of phthalic anhydride started up from 89% at 150°C and rapidly increased to 100% at a temperature about 300°C. The conversion of hexane increased from about 44% at 150°C to 300°C and remained around this value until the reaction temperature reached 300°C. On the other hand, at low concentration of hexane, phthalic anhydride conversion steadily increased from 88% to 95% while hexane conversion increased from 87% to 95% at temperature range of 150 to 300°C.

The result showed an increased in hexane converted when the hexane concentration in the feed was decreased. Furthermore, the added lower concentration increased in hexane conversion at the same temperature but did not affect phthalic anhydride combustion. It may be implied that the combustion of phthalic anhydride and hexane used the different of active sites.





**Figure 5.8** The catalytic activity of zinc oxide catalyst for the combustion of phthalic anhydride and high concentration of hexane.(1.34 vol%)



**Figure 5.9** The catalytic activity of zinc oxide catalyst for the combustion of phthalic anhydride and low concentration of hexane.(0.56 vol%)

### 5.3 Activity and surface acidity/basicity

The surface acidity and basicity of the catalysts can be quantitatively measured by the amount of pyridine and maleic anhydride adsorbed, respectively. The large amount of pyridine adsorbed implies the large numbers of acid sites on the catalyst surface. The large amount of maleic anhydride adsorbed implies the large numbers of basic sites. The adsorption of maleic anhydride also indicated the ability of the catalyst adsorb to the acidic reactant, i.e. phthalic anhydride. Thus, the large amount of maleic anhydride adsorption would have the large numbers of phthalic anhydride adsorption sites.

From the hypothesis in the previous works [Tongsang (2001), Umpo (2001), Nugoolchit (2002)], the acid site was the active site. The basic site (MgO) would help the adsorption of the acidic reactant, but in the same time, these basic sites would neutralize the acid site (active site). Thus, the maximum activity of the phthalic anhydride combustion needed the optimum between the adsorption of the phthalic anhydride and the catalytic activity of the transition metal oxides.

The amounts of absorbed pyridine and maleic anhydride of acidic metal oxides are shown in Table 5.3. The reported amounts were relative amounts by using the amounts adsorbed on  $\text{TiO}_2$  as reference.

**Table 5.3** The relative amounts of pyridine and maleic anhydride adsorption and the amounts of absorbed pyridine and maleic anhydride of acidic metal oxides

Catalyst	Pyridine adsorption		Maleic anhydride adsorption	
	Relative	( $\mu\text{mole}/\text{m}^2$ )	Relative	( $\mu\text{mole}/\text{m}^2$ )
TiO <sub>2</sub>	1.00	0.87	1.00	0.65
7V/TiO <sub>2</sub>	2.00	1.75	5.15	3.22
8Cu7V1MgO/ TiO <sub>2</sub>	0.99	0.86	9.16	5.73
8Fe7V1MgO/ TiO <sub>2</sub>	0.86	0.75	5.22	3.26
8Mo7V1MgO/ TiO <sub>2</sub>	1.27	1.11	4.94	3.09
8Zn7V1MgO/ TiO <sub>2</sub>	1.33	1.16	5.10	3.19

The research found that V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was not so active for the combustion of phthalic anhydride, possibly because V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst had the small numbers of the adsorption sites (basic sites) and V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst did not have the active site or it had the small numbers of the active sites for the combustion of phthalic anhydride. Although titania sites were active for phthalic anhydride combustion, when vanadium oxide was added into the TiO<sub>2</sub> support, the TiO<sub>2</sub> support may be covered by a complete monolayer of the surface vanadia species (>2% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>) with the strong interaction between vanadia and the TiO<sub>2</sub> surface. The surface vanadia species were active for the oxidation of o-xylene to phthalic anhydride but not for the combustion of phthalic anhydride [Wachs *et al.* (1985)].

When loading both transition metal oxide and magnesium oxide into the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst, it was found that metal-V-Mg-O/TiO<sub>2</sub> catalysts give the phthalic anhydride combustion higher than V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst, indicating that the transition metals were able to catalyze the reaction. Because the addition of the transition metal oxides to V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst would increase the active sites on the surface of catalyst. Moreover, the increment of the maleic anhydride adsorption indicated that the addition of magnesium oxide would increase the numbers of the basic sites on surface of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst and increased the adsorption of phthalic anhydride, thus, provided more opportunity to react with metal, resulting in higher activity [Charoenruay (2003)].

## 5.4 Conclusions

In the real process, the best catalysts for the combustion must be capable to completely remove phthalic anhydride from the effluent gas. From the result, the effect of changing in hexane concentration did not affect phthalic anhydride conversion of phthalic anhydride on Cu and Zn promoted catalysts. It may be implied that the combustion of phthalic anhydride and hexane used the different active sites. Fe and Mo promoted catalysts showed different results, the lower concentration of hexane leading to better combustion of phthalic anhydride. It would probably be the effect of competitive adsorption of both reactants and the combustion of phthalic anhydride and hexane used the same active sites.

Moreover, if considered the prices of chemicals used in this experiment for preparing all catalysts. It was found that the prices of chemicals for preparing Fe and Mo catalysts are higher than the prices of chemicals for preparing Cu and Zn catalysts (see Table 5.4). Therefore, the choice of the prices of chemicals used in this experiment is important. The optimal composition and test the reaction in a long time did not consider in this research. It is interesting to study the optimal composition and test the reaction in a long time on the combustion of phthalic anhydride in presence of hexane in the feed over  $V_2O_5/TiO_2$  catalysts promoted with transition metal (Cu, Fe, Mo and Zn) in the future.

**Table 5.4** Prices of chemicals used in this experiment to prepare 10 gram of 8wt% metal-MgO- $V_2O_5/TiO_2$  catalysts

Chemical	Weight (g)	Prices (Bath/gram)
$CuN_2O_6 \cdot 3H_2O$	3.31	2.32
$FeN_3O_9 \cdot 9H_2O$	6.48	19.51
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1.60	12.84
$ZnN_2O_6 \cdot 6H_2O$	4.00	1.54

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATION

#### 6.1 Conclusions

The conclusions of the present research are the following:

1. The use of nonisothermal nonadiabatic reactor and the addition of hexane to the PA+air gas can decrease the amount of external heat needed to guarantee the complete removal of PA from the effluent gas.
2. On Cu and Zn promoted  $V_2O_5/TiO_2$  catalysts, phthalic anhydride and hexane used different active sites. Thus, changing in hexane concentration did not affect phthalic anhydride conversion.
3. On Fe and Mo promoted  $V_2O_5/TiO_2$  catalysts, phthalic anhydride and hexane used the same active sites for the combustion reaction. Hence, changing in hexane concentration had effect on the combustion rate of phthalic anhydride i.e. high hexane concentration inhibited phthalic anhydride combustion.

#### 6.2 Recommendation for future studies

From the previous conclusions, the following recommendation for future studies can be proposed.

1. It is interesting to study the optimal composition and test the reaction in a long time on the combustion of phthalic anhydride in presence of hexane in the feed.

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**APPENDICES**

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## APPENDIX A

### CALCULATION OF CATALYST PREPARATION

**Preparation of 8Cu-7V-1Mg-O/TiO<sub>2</sub> catalysts by the Wet Impregnation Method is shown as follow:**

Reagent:	- Cupric nitrate trihydrate (CuN <sub>2</sub> O <sub>6</sub> ·3H <sub>2</sub> O) Molecular weight = 241.60 g.
	- Magnesium nitrate [Mg(NO <sub>3</sub> ) <sub>2</sub> ] Molecular weight = 256.41 g.
	- Ammonium metavanadate (NH <sub>4</sub> (VO <sub>3</sub> )) Molecular weight = 116.98 g
Support	- Titania [TiO <sub>2</sub> ]

#### **Calculation for the preparation of the 8Cu-7V<sub>2</sub>O<sub>5</sub>-1Mg-O/TiO<sub>2</sub> catalyst.**

The 8Cu-7V<sub>2</sub>O<sub>5</sub>-1Mg-O/ TiO<sub>2</sub> aqueous solution used in catalyst preparation consists of V<sub>2</sub>O<sub>5</sub> 7wt% and TiO<sub>2</sub> 93wt%. The amount of copper and magnesium in 8Cu-7V<sub>2</sub>O<sub>5</sub>-1Mg-O/ TiO<sub>2</sub> catalyst is calculated as follows:

Preparation : 7V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> 5 g

If the weight of catalyst was 100 g, 7V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> would compose of V<sub>2</sub>O<sub>5</sub> 7 g and TiO<sub>2</sub> 93 g. Therefore, in this system,

$$\begin{aligned} \text{the amount of V}_2\text{O}_5 &= 7/100 \times 5 \\ &= 0.35 \text{ g} \end{aligned}$$

Vanadia (V<sub>2</sub>O<sub>5</sub>) 0.35 g was prepared from NH<sub>4</sub>(VO<sub>3</sub>) and molecular weight of V<sub>2</sub>O<sub>5</sub> = 181.88 , then

$$\begin{aligned} \text{the amount of content NH}_4(\text{VO}_3) \text{ used} &= (116.98/181.88) \times 0.35 \\ &= 0.4502 \text{ g} \end{aligned}$$

Thus

$$\begin{aligned} \text{The amount of TiO}_2 &= 5 - 0.35 \\ &= 4.65 \text{ g} \end{aligned}$$

basis :  $7\text{V}_2\text{O}_5/\text{TiO}_2$  5 g

Then, the Cu: (support +  $\text{V}_2\text{O}_5$ ) weight ratio = 8:92

$$\begin{aligned} \text{The amount of Cu} &= 8/92 \times 5 \\ &= 0.4348 \text{ g} \end{aligned}$$

Copper (Cu) 0.4348 g was impregnated from  $(\text{CuN}_2\text{O}_6 \cdot 3\text{H}_2\text{O})$  solution and molecular weight of Cu = 63.546 g

$$\begin{aligned} \text{the amount of } (\text{CuN}_2\text{O}_6 \cdot 3\text{H}_2\text{O}) \text{ used} &= (0.4348 \times 241.60) / (63.546) \\ &= 1.6531 \text{ g} \end{aligned}$$

and the Mg: ( $7\text{V}_2\text{O}_5 / \text{TiO}_2 + \text{Cu}$ ) weight ratio = 1:100

$$\begin{aligned} \text{The amount of Mg} &= (5 + 0.4348) \times 1/100 \\ &= 0.0543 \text{ g} \end{aligned}$$

Magnesium 0.0543 g was impregnated from  $\text{Mg}(\text{NO}_3)_2$  solution 99% and molecular weight of Mg = 24.305 g

$$\begin{aligned} \text{Thus, the amount of } \text{Mg}(\text{NO}_3)_2 \text{ used} &= (0.0543 \times 256.41 \times 100) / (24.305 \times 99) \\ &= 0.5791 \text{ g} \end{aligned}$$

The calculation for the preparation of other catalysts as follow  $8\text{Fe}-7\text{V}_2\text{O}_5-1\text{Mg}-\text{O} / \text{TiO}_2$ ,  $8\text{Mo}-7\text{V}_2\text{O}_5-1\text{Mg}-\text{O} / \text{TiO}_2$  and  $8\text{Zn}-7\text{V}_2\text{O}_5-1\text{Mg}-\text{O} / \text{TiO}_2$  catalysts were the same as the preparation of  $8\text{Cu}-7\text{V}_2\text{O}_5-1\text{Mg}-\text{O} / \text{TiO}_2$  catalysts.



## APPENDIX B

### CALCULATION OF DIFFUSIONAL LIMITATION EFFECT

#### B.1 External diffusion limitation

The phthalic anhydride and hexane combustion reactions are considered to be irreversible first order reactions occurred on the surface of interior pore surface of catalyst particles in a fixed bed reactor.

In the experiment, 0.06% phthalic anhydride, 0.56% hexane and 21% O<sub>2</sub> was used as reactant in the system. Because percentage of phthalic anhydride and hexane was rather small compared to the air, their contribution on the physical of the gas mixture can be neglected. Molecular weight of nitrogen and oxygen are 28.02 and 31.98, respectively, the average molecular weight of the gas mixture was calculated as follows:

$$\begin{aligned}M_{AB} &= 0.79 \times 28.02 + 0.21 \times 31.98 \\ &= 28.85 \text{ g/mol}\end{aligned}$$

#### Calculation of reactant gas density

Consider the phthalic anhydride combustion is operated at low pressure and high temperature. The gas is assumed to obey the ideal gas law. The gas density at various temperature, therefore, can be calculated from the following equation:

$$\rho = PM / RT$$

where  $\rho$  = gas density  
M = molecular weight  
R = gas constant

T = absolute temperature

P = pressure

We obtained :  $\rho = 0.614 \text{ kg/m}^3$  at 300 °C

### Calculation of the gas mixture viscosity

The simplified methods for determining the viscosity of low pressure binary gas mixture are described elsewhere (Reid, 1988). The method of Wilke is chosen to estimate the gas mixture viscosity.

For a binary system of species 1 and species 2,

$$\mu_m = \frac{y_1 \mu_1}{y_1 + y_2 \Phi_{12}} + \frac{y_2 \mu_2}{y_2 + y_1 \Phi_{21}}$$

where  $\mu_m$  = viscosity of the mixture

$\mu_1, \mu_2$  = pure component viscosity

$y_1, y_2$  = mole fractions

$$\phi_{12} = \frac{\left[ 1 + \left( \frac{\mu_1}{\mu_2} \right)^{1/2} \left( \frac{M_1}{M_2} \right)^{1/4} \right]^2}{\left[ 8 \left( 1 + \frac{M_1}{M_2} \right) \right]^{1/2}}$$

$$\phi_{21} = \phi_{12} \left( \frac{\mu_2}{\mu_1} \right) \left( \frac{M_1}{M_2} \right)$$

$M_1, M_2$  = molecular weight

Let 1 refer to nitrogen and 2 to oxygen

$$M_1 = 28.02 \text{ and } M_2 = 31.98$$

From Perry (1973) the viscosity of nitrogen at 300°C are 0.0282 cP. The viscosity of oxygen at 300°C are 0.0329 cP.

$$\phi_{12} = 0.928$$

$$\phi_{21} = 0.948$$

$$\mu_m = 2.98 \times 10^{-5} \text{ kg/m-s}$$

### Calculation of diffusion coefficients

Diffusion coefficients for binary gas system at low pressure calculated by empirical correlation are proposed by Reid (1988). Wilke and Lee method is chosen to estimate the value of  $D_{AB}$  due to the general and reliable method. The empirical correlation is

$$D_{AB} = \frac{\left(3.03 - \frac{0.98}{M_{AB}^{1/2}}\right) (10^{-3}) T^{3/2}}{PM_{AB}^{1/2} \sigma_{AB}^2 \Omega_D}$$

where  $D_{AB}$  = binary diffusion coefficient,  $\text{cm}^2/\text{s}$

T = temperature, K

$M_A, M_B$  = molecular weights of A and B, g/mol

$$M_{AB} = 2 \left[ \left( \frac{1}{M_A} \right) + \left( \frac{1}{M_B} \right) \right]^{-1}$$

P = pressure, bar

$\sigma$  = characteristic length, Å

$\Omega_D$  = diffusion collision integral, dimensionless

The characteristic Lennard-Jones energy and Length,  $\epsilon$  and  $\sigma$ , of nitrogen and oxygen are as follows: (Reid, 1988)

For  $\text{O}_2$ :  $\sigma = 3.467 \text{ \AA}$ ,  $\epsilon/k = 106.7$

For  $N_2$  :  $\sigma = 3.798 \text{ \AA}$ ,  $\varepsilon/k = 71.4$

The sample rules are usually employed.

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = \frac{3.798 + 3.467}{2} = 3.63$$

$$\varepsilon_{AB}/k = \left( \frac{\varepsilon_A \varepsilon_B}{k^2} \right)^{1/2} = (71.4 \times 106.7)^{1/2} = 87.28$$

$\Omega_D$  is tabulated as a function of  $kT/\varepsilon$  for the Lennard-Jones potential. The accurate relation is

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$

where  $T^* = \frac{kT}{\varepsilon_{AB}}$ ,  $A = 1.06036$ ,  $B = 0.15610$ ,  $C = 0.19300$ ,  $D = 0.47635$ ,  $E = 1.03587$ ,  $F = 1.52996$ ,  $G = 1.76474$ ,  $H = 3.89411$

Then  $T^* = 6.565$

$$\Omega_D = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)}$$

$$\Omega_D = 0.799$$

With equation of  $D_{AB}$ ,

$$D(N_2-O_2) = 0.679 \text{ m}^2/\text{s}$$

Reactant gas mixture was supplied at 150 ml/min to the tubular microreactor used in the phthalic anhydride oxidation system at 30°C

air flow rate through reactor = 150 ml/min at 30°C

The density of air ,  $\rho = 1.161 \text{ kg/m}^3$

Mass flow rate =  $2.918 \times 10^{-6} \text{ kg/s}$

Diameter of stainless steel tube reactor = 8 mm

Cross-sectional area of tube reactor =  $\frac{\pi(8 \times 10^{-3})^2}{4} = 5.03 \times 10^{-5} \text{ m}^2$

Mass Velocity ,  $G = 0.058 \text{ kg/m}^2\text{-s}$

Catalyst size = 40-60 mesh = 0.178-0.126 mm

Average catalyst size =  $(0.126+0.178)/2 = 0.152 \text{ mm}$

Find Reynolds number,  $Re_p$ , which is well known as follows:

$$Re_p = \frac{d_p G}{\mu}$$

We obtained

$$Re_p = 0.296$$

Average transport coefficient between the bulk stream and particles surface could be correlated in terms of dimensionless groups, which characterize the flow conditions. For mass transfer the Sherwood number,  $k_m \rho / G$ , is an empirical function of the Reynolds number,  $d_p G / \mu$ , and the Schmit number,  $\mu / \rho D$ . The j-factors are defined as the following functions of the Schmidt number and Sherwood numbers:

$$j_D = \frac{k_m \rho}{G} \left( \frac{a_m}{a_t} \right) (\mu / \rho D)^{2/3}$$

The ratio  $(a_m/a_t)$  allows for the possibility that the effective mass-transfer area  $a_m$ , may be less than the total external area,  $a_t$ , of the particles. For Reynolds number greater than 10, the following relationship between  $j_D$  and the Reynolds number well represents available data.

$$j_D = \frac{0.458}{\varepsilon_B} \left( \frac{d_p G}{\mu} \right)^{-0.407}$$

where  $G$  = mass velocity(superficial) based upon cross-sectional area of empty reactor

$$(G = u\rho)$$

$d_p$  = diameter of catalyst particle for spheres

$\mu$  = viscosity of fluid

$\rho$  = density of fluid

$\varepsilon_B$  = void fraction of the interparticle space (void fraction of the bed)

$D$  = molecular diffusivity of component being transferred

Assume  $\varepsilon_B = 0.5$

$$j_D = 1.503$$

A variation of the fixed bed reactor is an assembly of screens or gauze of catalytic solid over which the reacting fluid flows. Data on mass transfer from single screens has been reported by Gay and Maughan. Their correlation is of the form

$$j_D = (\varepsilon k_m \rho / G) (\mu / \rho D)^{2/3}$$

Where  $\varepsilon$  is the porosity of the single screen.

Hence,  $k_m = (j_D G / \rho) (\mu / \rho D)^{-2/3}$

$$k_m = (j_D G / \rho) Sc^{-2/3}$$

$$k_m = \left( \frac{1.503G}{\varepsilon_B \rho} \right) Re^{-0.407} Sc^{-2/3}$$

Find Schmidt number,  $Sc$  :  $Sc = \frac{\mu}{\rho D}$

$$Sc = 7.148 \times 10^{-5}$$



Find  $k_m$  :  $k_m = 82.48 \text{ m/s}$

### Properties of catalyst

Density = 0.375 g/ml catalyst

Diameter of 40-60 mesh catalyst particle = 0.152 mm

$$\text{Weight per catalyst particle} = \frac{\pi(0.152 \times 10^{-1})^3 \times 0.375}{6} = 6.895 \times 10^{-7} \text{ g/particle}$$

$$\text{External surface area per particle} = \pi(0.152 \times 10^{-3})^2 = 7.26 \times 10^{-8} \text{ m}^2/\text{particle}$$

$$a_m = (7.26 \times 10^{-8}) / (6.895 \times 10^{-7}) = 1.052 \text{ m}^2/\text{gram catalyst}$$

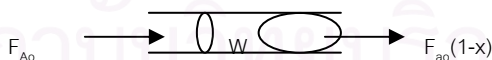
Volumetric flow rate of gaseous feed stream = 150 ml/min

Molar flow rate of gaseous feed stream =  $1.01 \times 10^{-4} \text{ mol/s}$

Hexane molar feed rate =  $0.0056 \times 1.01 \times 10^{-4} = 5.656 \times 10^{-7} \text{ mol/s}$

Hexane conversion (experimental data): 74.23% at 300°C

The estimated rate of phthalic anhydride oxidation reaction is based on the ideal plug flow reactor which there is no mixing in the direction of flow and complete mixing perpendicular to the direction of flow (i.e., in the radial direction). The rate of reaction will vary with reaction length. Plug flow reactors are normally operated at steady state so that properties at any position are constant with respect to time. The mass balance around plug flow reactor becomes



$$\begin{aligned} & \{\text{rate of } i \text{ into volume element}\} - \{\text{rate of } i \text{ out of volume element}\} \\ & + \{\text{rate of production of } i \text{ within the volume element}\} \\ & = \{\text{rate of accumulation of } i \text{ within the volume element}\} \end{aligned}$$

$$F_{A_0} = F_{A_0}(1-x) + (r_W W)$$

$$(r_W W) = F_{A_0} - F_{A_0}(1-x) = F_{A_0} x = F_{A_0} x$$

$$r_w = \frac{F_{A_0X}}{W} = 0.699 \times 10^{-6} \text{ mol/s-gram catalyst}$$

At steady state the external transport rate may be written in terms of the diffusion rate from the bulk gas to the surface. The expression is:

$$\begin{aligned} R_{\text{obs}} &= k_m a_m (C_b - C_s) \\ &= \frac{\text{phthalic anhydride converted (mole)}}{(\text{time})(\text{gram of catalyst})} \end{aligned}$$

where  $C_b$  and  $C_s$  are the concentrations in the bulk gas and at the surface, respectively.

$$(C_b - C_s) = \frac{r_{\text{obs}}}{k_m a_m} = 0.806 \times 10^{-8} \text{ mol/m}^3$$

Consider the difference of the bulk and surface concentration is small. It means that the external mass transport has no effect on the phthalic anhydride oxidation reaction rate.

## B.2 Internal diffusion limitation

Next, consider the internal diffusion limitation of the phthalic anhydride reaction. An effectiveness factor,  $\eta$ , was defined in order to express the rate of reaction for the whole catalyst pellet,  $r_p$ , in terms of the temperature and concentrations existing at the outer surface as follows:

$$\eta = \frac{\text{actual rate of whole pellet}}{\text{rate evaluated at outer surface conditions}} = \frac{r_p}{r_s}$$

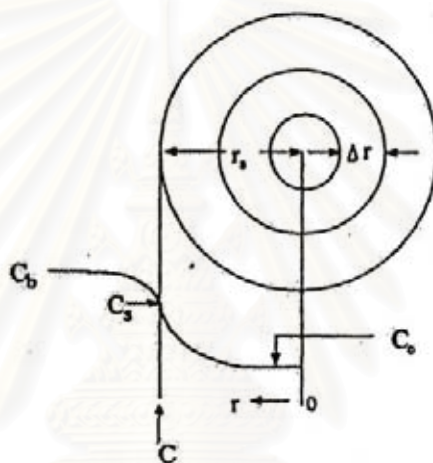
The equation for the local rate (per unit mass of catalyst) may be expected functionally as  $r = f(C, T)$ .

Where  $C$  represents, symbolically, the concentrations of all the involved components

Then, 
$$r_p = \eta r_s = \eta f(C_s, T_s)$$

Suppose that the phthalic anhydride oxidation is an irreversible reaction  $A \rightarrow B$  and first order reaction, so that for isothermal conditions  $r = f(C_A) = k_1 C_A$ . Then  $r_p = \eta k_1 (C_A)_s$ .

For a spherical pellet, a mass balance over the spherical-shell volume of thickness  $\Delta r$ . At steady state the rate of diffusion into the element less the rate of diffusion out will equal the rate of disappearance of reactant within the element. This rate will be  $\rho_p k_1 C_A$  per unit volume, where  $\rho_p$  is the density of the pellet. Hence, the balance may be written, omitting subscript A on C,



**Figure B1.** Reactant (A) concentration vs. position for first-order reaction on a spherical catalyst pellet.

$$\left( -4\pi r^2 D_e \frac{dC}{dr} \right)_r - \left( -4\pi r^2 D_e \frac{dC}{dr} \right)_{r+\Delta r} = -4\pi r^2 \Delta r_p k_1 C$$

Take the limit as  $\Delta r \rightarrow 0$  and assume that the effective diffusivity is independent of the concentration of reactant, this difference equation becomes

$$\frac{d^2 C}{dr^2} + 2 \frac{dC}{dr} - \frac{k_1 \rho_p C}{D_e} = 0$$

At the center of the pellet symmetry requires

$$\frac{dC}{dr} = 0 \text{ at } r = 0$$

and at outer surface

$$C = C_s \text{ at } r = r_s$$

Solve linear differential equation by conventional methods to yield

$$\frac{C}{C_s} = \frac{r_s \sinh\left(3\phi_s \frac{r}{r_s}\right)}{r \sinh 3\phi_s}$$

where  $\phi_s$  is Thiele modulus for a spherical pellet defined by  $\phi_s = \frac{r_s}{3} \sqrt{\frac{k_1 \rho_p}{D_e}}$

Both  $D_e$  and  $k_1$  are necessary to use  $r_p = \eta k_1 (C_A)_s$ .  $D_e$  could be obtained from the reduced pore volume equation in case of no tortuosity factor.

$$D_e = (\varepsilon_s)^2 D_{AB}$$

$$D_e = (0.5)^2 (0.679) = 0.170$$

Substitute radius of catalyst pellet,  $r_s = 7.6 \times 10^{-5}$  m with  $\phi_s$  equation

$$\phi_s = 1.191 \times 10^{-6} \sqrt{k} \text{ (dimensionless)}$$

Find  $k$  (at 300°C) from the mass balance equation around plug-flow reactor.

$$r_w = \frac{F_{A0} dx}{dW}$$

where  $r_w = kC_A$

Thus, 
$$kC_A = \frac{F_{A0} dx}{dW}$$

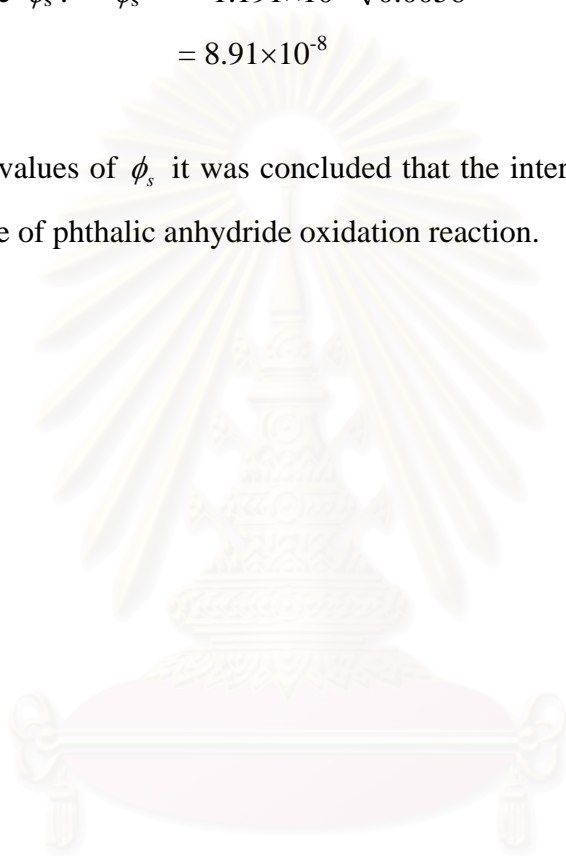
$$kC_{A_0}(1-x) = \frac{F_{A_0} dx}{dW}$$

$$W = \frac{F_{A_0}}{kC_{A_0}} \int_0^{0.742} \frac{1}{1-x} dx$$

$$k = 0.0056 \text{ m}^3/\text{s}\cdot\text{kg catalyst}$$

$$\begin{aligned} \text{Calculate } \phi_s : \quad \phi_s &= 1.191 \times 10^{-6} \sqrt{0.0056} \\ &= 8.91 \times 10^{-8} \end{aligned}$$

For such small values of  $\phi_s$  it was concluded that the internal mass transport has no effect on the rate of phthalic anhydride oxidation reaction.



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## APPENDIX C

### CALCULATION OF SPECIFIC SURFACE AREA

From Brunauer-Emmett-Teller (BET) equation [Anderson and co-worker (1985)]

$$\frac{p}{n(1-p)} = \frac{1}{n_m C} + \frac{(C-1)p}{n_m C} \quad (C1)$$

- Where,  $p$  = Relative partial pressure of adsorbed gas,  $P/P_0$   
 $P_0$  = Saturated vapor pressure of adsorbed gas in the condensed state at the experimental temperature, atm  
 $P$  = Equilibrium vapor pressure of adsorbed gas, atm  
 $n$  = Gas adsorbed at pressure  $P$ , ml. at the NTP/g of sample  
 $n_m$  = Gas adsorbed at monolayer, ml. at the NTP/g of sample  
 $C$  =  $\text{Exp} [(H_C - H_1)/RT]$   
 $H_C$  = Heat of condensation of adsorbed gas on all other layers  
 $H_1$  = Heat of adsorption into the first layer

For the single point method, the graph must pass through the origin. Therefore, the value of  $C$  must be assumed to be infinity.

$C \rightarrow \infty$ , then equation C1 is reduced to

$$\frac{p}{n(1-p)} = \frac{p}{n_m}$$
$$n_m = n(1-p) \quad (C2)$$

The surface area,  $S$ , of the catalyst is given by

$$S = S_b \times n_m \quad (C3)$$

From the gas law

$$\frac{P_b V}{T_b} = \frac{P_t V}{T_t} \quad (C4)$$

- Where,  $P_b$  = Pressure at  $0^\circ\text{C}$   
 $P_t$  = Pressure at  $t^\circ\text{C}$   
 $T_b$  = Temperature at  $0^\circ\text{C} = 273.15 \text{ K}$



$T_t$  = Temperature at  $t^\circ\text{C}$  =  $273.15 + t$  K

$V$  = Constant volume

Then,  $P_b = (273.15 / T_t) \times P_t = 1$  atm

Partial pressure

$$P = \frac{[\text{Flow of (He + N}_2\text{)} - \text{Flow of He}]}{\text{Flow of (He + N}_2\text{)}} \quad (\text{C5})$$

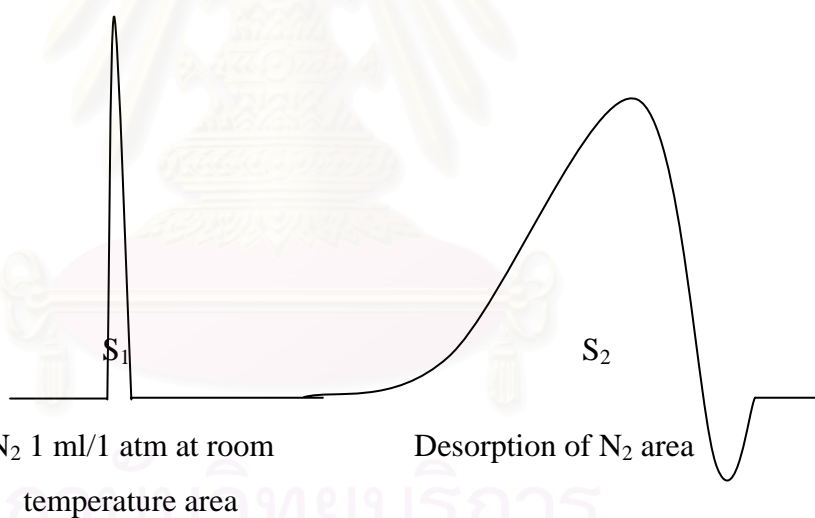
$$= 0.3 \text{ atm}$$

For nitrogen gas, the saturated vapor pressure equals to

$$P_0 = 1.1 \text{ atm}$$

then,  $p = P/P_0 = 0.3/1.1 = 0.2727$

To measure the volume of nitrogen adsorbed,  $n$



$$n = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \text{ ml/g of catalyst} \quad (\text{C6})$$

Where,  $S_1$  =  $\text{N}_2$  1 ml/1 atm at room temperature area

$S_2$  = Desorption of  $\text{N}_2$  area

$W$  = Sample weight, g

$T$  = Room temperature, K

Therefore,

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times (1-p)$$

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7272 \quad (C2.1)$$

Whereas, the surface area of nitrogen gas from literature equal to

$$S_b = 4.373 \text{ m}^2/\text{ml of nitrogen gas}$$

Then,

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7272 \times 4.343$$

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 3.1582 \text{ m}^2/\text{g} \quad (C7)$$

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## APPENDIX D

### CALIBRATION CURVE

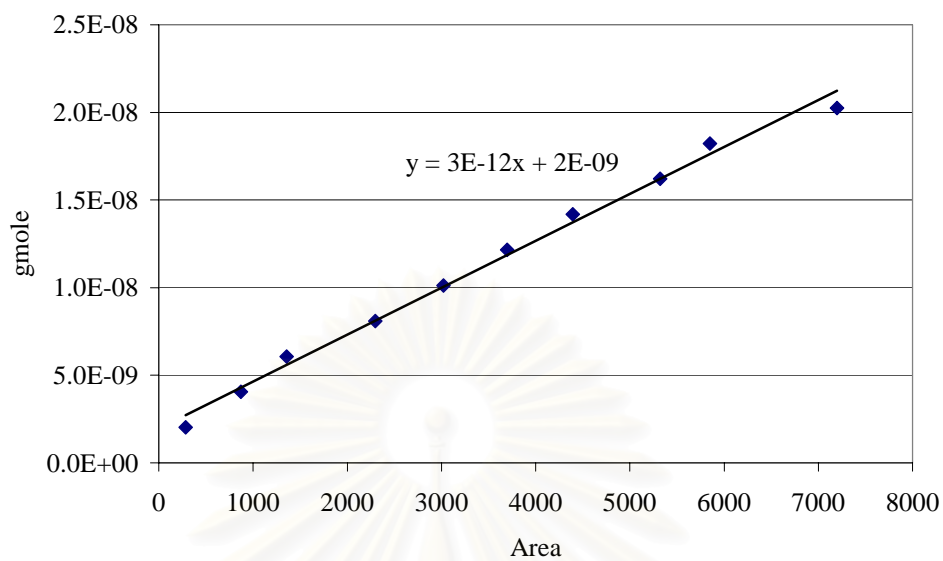
Flame ionization detector gas chromatographs Shimadzu model 9A equipped with a Chromosorb WAW column is used to analyze the concentrations of phthalic anhydride, maleic anhydride, acetic acid, ethylbenzene, toluene, hexane and benzene.

The Porapak-Q and Molecular Sieve 5-A column are used with a gas chromatograph equipped with a thermal conductivity detector, Shimadzu model 8A, to analyze the concentration of CO<sub>2</sub> and CO.

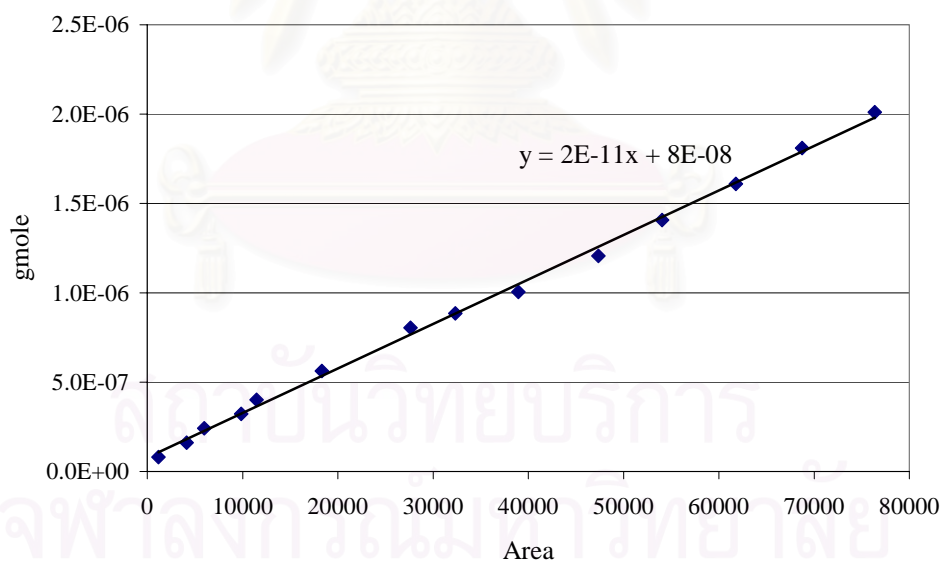
The calibration curves of phthalic anhydride, hexane and carbon dioxide are illustrated in the following figures.



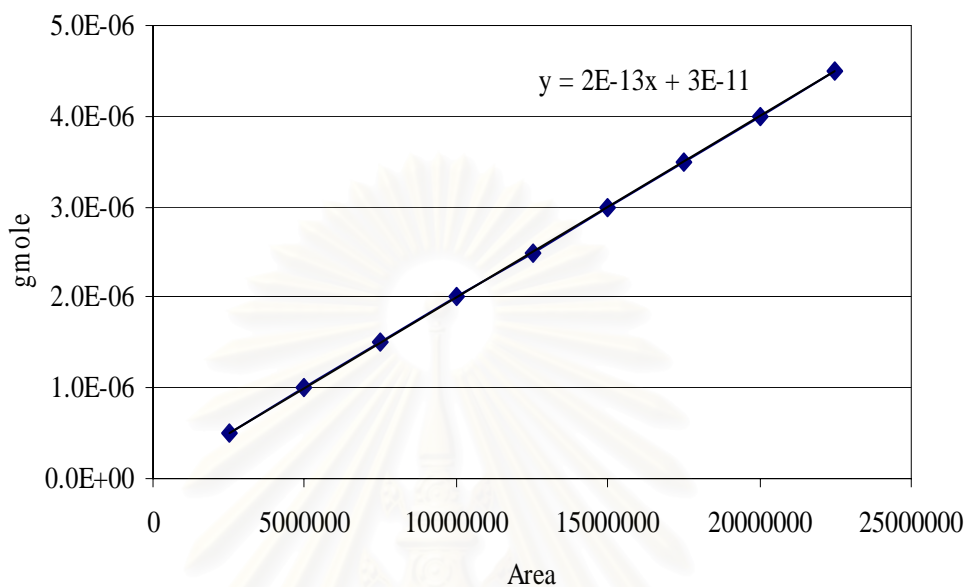
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**Figure D1** The calibration curve of phthalic anhydride



**Figure D2** The calibration curve of carbon dioxide



**Figure D2** The calibration curve of Hexane

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## APPENDIX E

### DATA OF EXPERIMENTS

**Table E1** Data of Figure 5.2

Temp (°C)	8Cu-7V-1Mg-O/ TiO <sub>2</sub>	
	PA conversion (%)	Hexane conversion (%)
150	82.19	36.80
200	82.62	39.15
250	99.74	52.17
300	100.00	74.23

**Table E2** Data of Figure 5.3

Temp (°C)	8Cu-7V-1Mg-O/ TiO <sub>2</sub>	
	PA conversion (%)	Hexane conversion (%)
150	85.75	51.22
200	83.33	64.72
250	98.68	69.93
300	100.00	76.53

**Table E3** Data of Figure 5.4

Temp (°C)	8Fe-7V-1Mg-O/ TiO <sub>2</sub>	
	PA conversion (%)	Hexane conversion (%)
150	70.18	27.92
200	83.73	48.60
250	86.12	71.67
300	98.72	74.39

**Table E4** Data of Figure 5.5

Temp (°C)	8Fe-7V-1Mg-O/ TiO <sub>2</sub>	
	PA conversion (%)	Hexane conversion (%)
150	83.35	83.17
200	95.67	91.59
250	96.31	91.98
300	100.00	93.60



**Table E5** Data of Figure 5.6

Temp (°C)	8Mo-7V-1Mg-O/ TiO <sub>2</sub>	
	PA conversion (%)	Hexane conversion (%)
150	74.32	24.75
200	76.62	37.67
250	74.10	45.66
300	89.00	57.96

**Table E6** Data of Figure 5.7

Temp (°C)	8Mo-7V-1Mg-O/ TiO <sub>2</sub>	
	PA conversion (%)	Hexane conversion (%)
150	92.41	89.78
200	94.16	92.64
250	91.01	92.39
300	93.47	95.01

**Table E7** Data of Figure 5.8

Temp (°C)	8Zn-7V-1Mg-O/ TiO <sub>2</sub>	
	PA conversion (%)	Hexane conversion (%)
150	89.45	44.97
200	93.05	45.42
250	94.35	44.50
300	100.00	42.12

**Table E8** Data of Figure 5.9

Temp (°C)	8Zn-7V-1Mg-O/ TiO <sub>2</sub>	
	PA conversion (%)	Hexane conversion (%)
150	87.66	87.35
200	88.81	89.72
250	90.65	91.94
300	94.69	94.74

**Table E9** Data of pyridine and maleic anhydride adsorption of Table 5.3

<b>Metal</b>	<b>Pyridine adsorption</b>	<b>Maleic anhydride adsorption</b>
TiO <sub>2</sub>	15077711	1447268
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	5944558	1327671
8Cu-7V-1Mg-O/ TiO <sub>2</sub>	2550686	1631007
8Fe-7V-1Mg-O/ TiO <sub>2</sub>	3463724	1950966
8Mo-7V-1Mg-O/ TiO <sub>2</sub>	4975504	2354161
8Zn-7V-1Mg-O/ TiO <sub>2</sub>	4196533	1117899



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## APPENDIX F

### MATERIAL SAFETY DATA SHEETS

#### Phthalic anhydride

#### Safety data for phthalic anhydride

##### General

Synonyms: 1,2-benzenedicarboxylic acid anhydride, phthalic acid anhydride

Molecular formula:  $C_8H_4O_3$

##### Physical data

Appearance: white crystalline solid with choking odor

Melting point: 131 °C

Boiling point: 295 °C

Vapour density: 5.1 (air = 1)

Density ( $g\ cm^{-1}$ ): 1.53

Flash point: 152 °C (closed cup)

Explosion limit: 1.7-10.5%

Water solubility: slight

##### Stability

Stable. Combustible. Incompatible with strong oxidizing agents, strong bases, moisture, nitric acid, alkalies. Dust may form an explosive mixture with air.

**Toxicology**

Corrosive - causes burns. Harmful if swallowed or inhaled. Skin or eye contact may cause severe irritation. Typical TLV/TWA 1 ppm. Typical STEL 4 ppm. Typical PEL 2 ppm.

**Personal protection**

Safety glasses, gloves, adequate ventilation.



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## Hexane

### Safety data for Hexane

#### General

Synonyms: n-hexane, normal hexane

Molecular formula:  $C_6H_{14}$

#### Physical data

Appearance: colourless liquid

Melting point:  $-95\text{ }^{\circ}\text{C}$

Boiling point:  $69\text{ }^{\circ}\text{C}$

Vapour density: 3 (air = 1)

Vapour pressure: 132 mm Hg at  $20\text{ }^{\circ}\text{C}$

Specific gravity: 0.659

Flash point:  $-10\text{ }^{\circ}\text{F}$

Explosion limits: 1.2% - 7.7%

Autoignition temperature:  $453\text{ }^{\circ}\text{F}$

#### Stability

Stable. Incompatible with oxidising agents, chlorine, fluorine, magnesium perchlorate. Highly flammable. Readily forms explosive mixtures with air. Note low flash point.

#### Toxicology

May cause impaired fertility. Harmful by inhalation, ingestion or skin absorption. Irritant. May cause CNS depression. Prolonged exposure may cause serious health damage.

**Personal protection**

Safety glasses. Effective ventilation.



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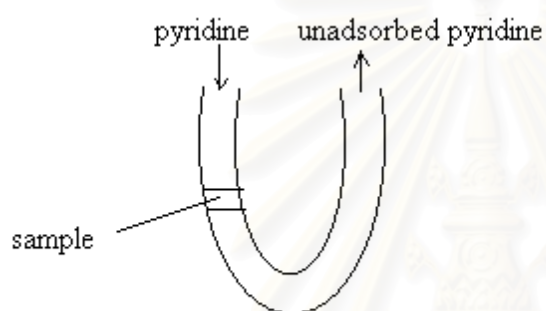


## APPENDIX G

### PROCEDURE AND CALCULATION OF PYRIDINE AND MALEIC ANHYDRIDE ADSORPTION

#### Pyridine adsorption

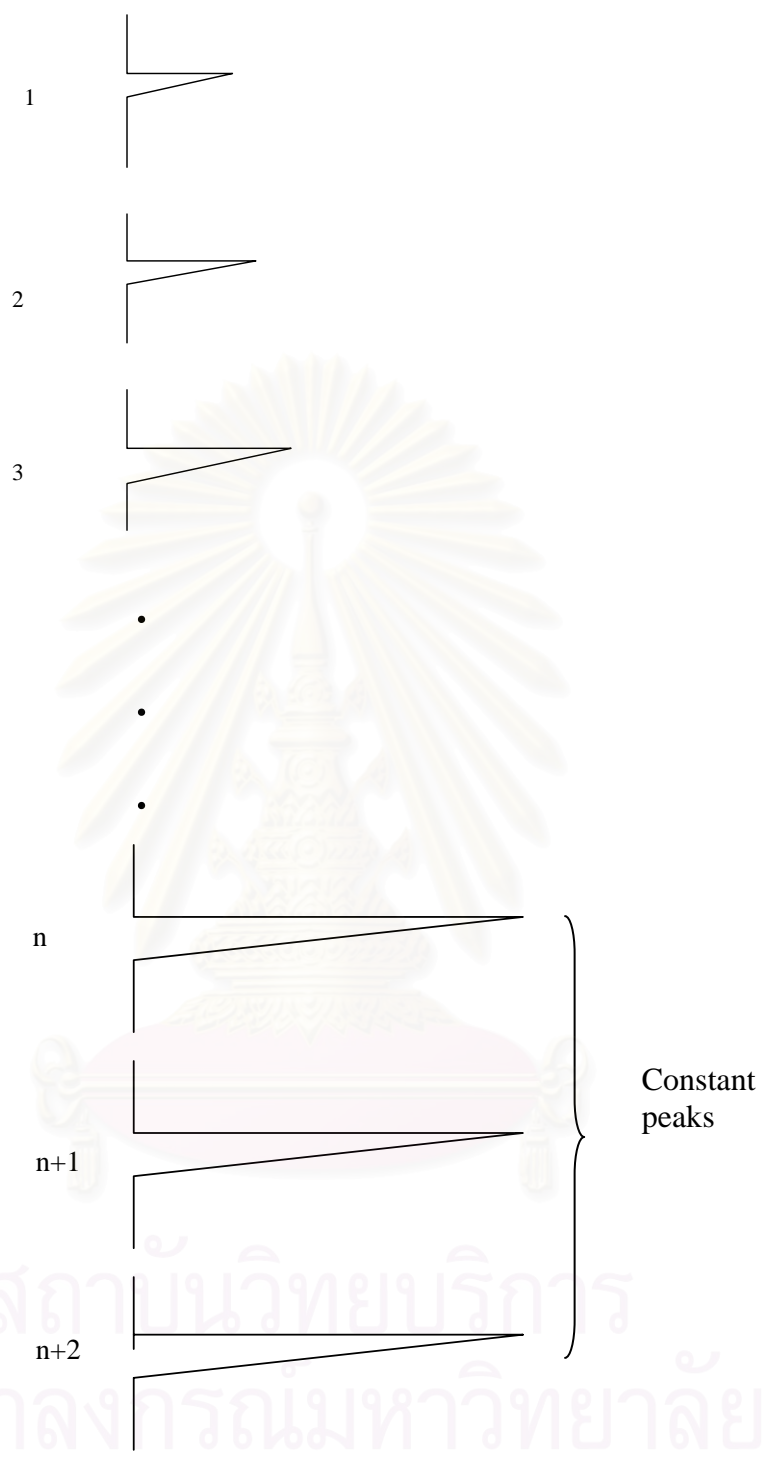
The nitrogen gas flowed through the system that consisted of a tube connected to the gas chromatograph (GC9A). The sample was placed in the tube as shown in Figure G1.



**Figure G1** The adsorption system

The pyridine was injected into the column. The sample would adsorb a part of the pyridine. The pyridine that was not adsorbed on the sample was measured by the gas chromatograph. The pyridine was injected until the peaks were constant. It meant that the sample was saturated with pyridine.

The peaks of the unadsorbed pyridine that were detected from the gas chromatograph were shown in Figure G2.



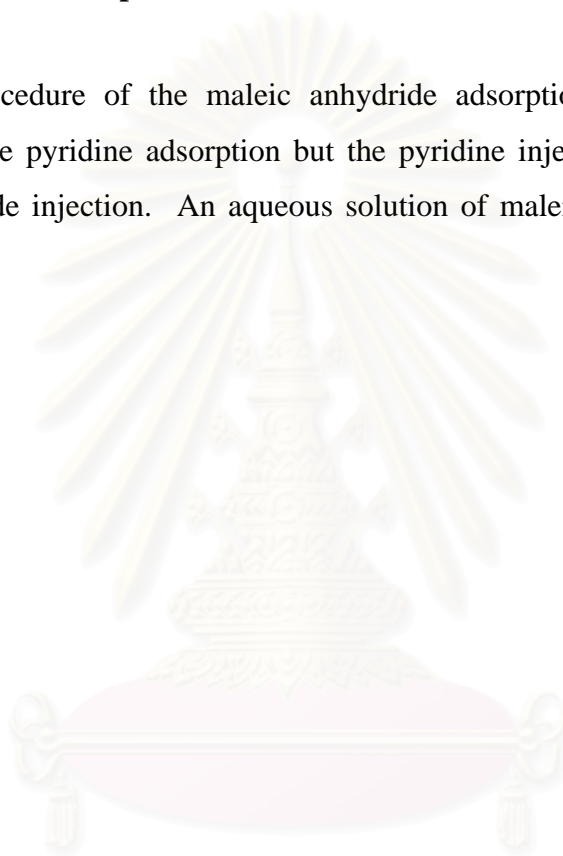
**Figure G2** The unadsorbed pyridine peaks

The overall pyridine adsorbed was calculated by subtraction the area of constant peaks with the 1<sup>st</sup> peak, 2<sup>nd</sup> peak, ..., respectively. The summation of these subtracted areas was the overall area of the pyridine adsorbed.

$$\text{Overall pyridine adsorbed} = \sum (\text{area of constant peak} - \text{area of peak}_i)$$

### **Maleic anhydride adsorption**

The procedure of the maleic anhydride adsorption was the same as the procedure of the pyridine adsorption but the pyridine injection was changed to the maleic anhydride injection. An aqueous solution of maleic anhydride (0.104 g/ml) was used.



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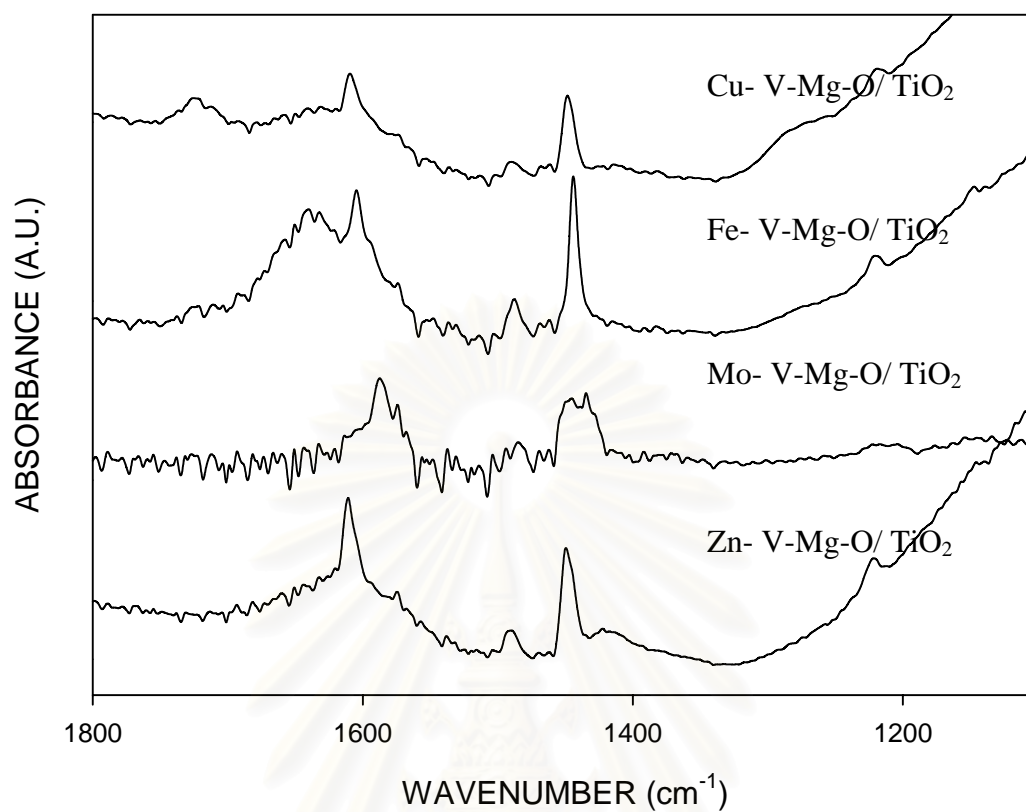
## APPENDIX H

### FT-IR

The IR spectra reported here are for catalyst data base. Figure H-1 showed the IR spectra obtained from adsorbed pyridine on the catalysts at room temperature. It is cleared from the present work and other published works that the spectrum of the adsorbed pyridine at the room temperature shows the band at  $1445\text{ cm}^{-1}$  and the band near  $1600\text{ cm}^{-1}$  due to coordinative adsorbed pyridine on Lewis acid sites. The weaker band around  $1480\text{ cm}^{-1}$  is ascribed to proton acidity [Parry (1973)], while both band at  $1540\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  representative of pyridium ions adsorbed on Brönsted acid sites which are not observe in this experiment. The IR spectra obtained from the adsorbed pyridine on the catalysts at  $100\text{ }^{\circ}\text{C}$  up to  $500\text{ }^{\circ}\text{C}$  not found any significant.

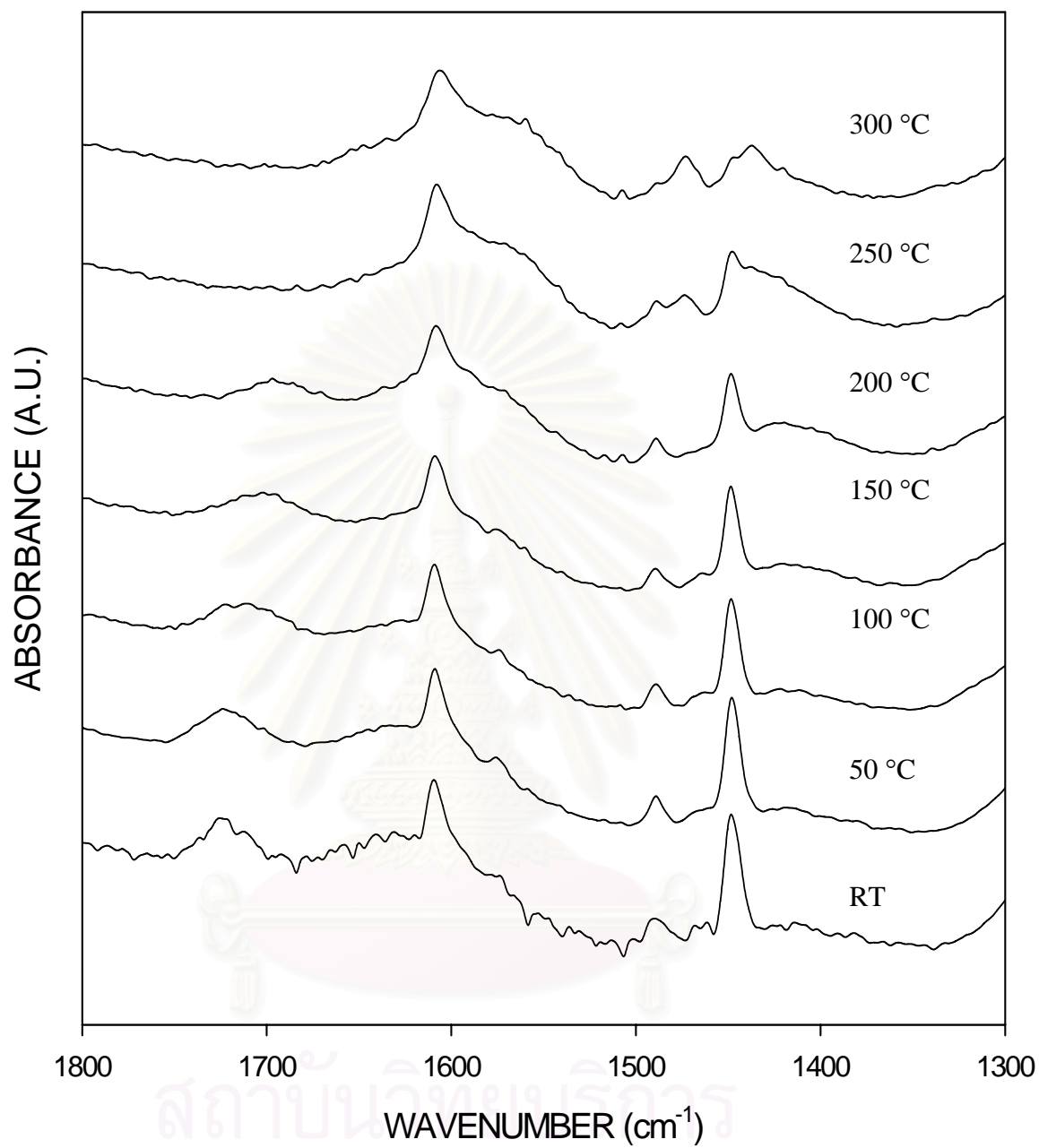
-for  $8\text{Mo}1\text{Mg}7\text{V}/\text{TiO}_2$  catalyst cannot measure FT-IR pyridine adsorption because no peak appear after dope pyridine. But pyridine adsorption measure by gas chromatograph. can detect amount of pyridine adsorption of  $8\text{Mo}1\text{Mg}7\text{V}/\text{TiO}_2$  catalyst. The different of two techniques was pressure so pyridine may not adsorb on  $8\text{Mo}1\text{Mg}7\text{V}/\text{TiO}_2$  catalyst at very low pressure (vacuum).

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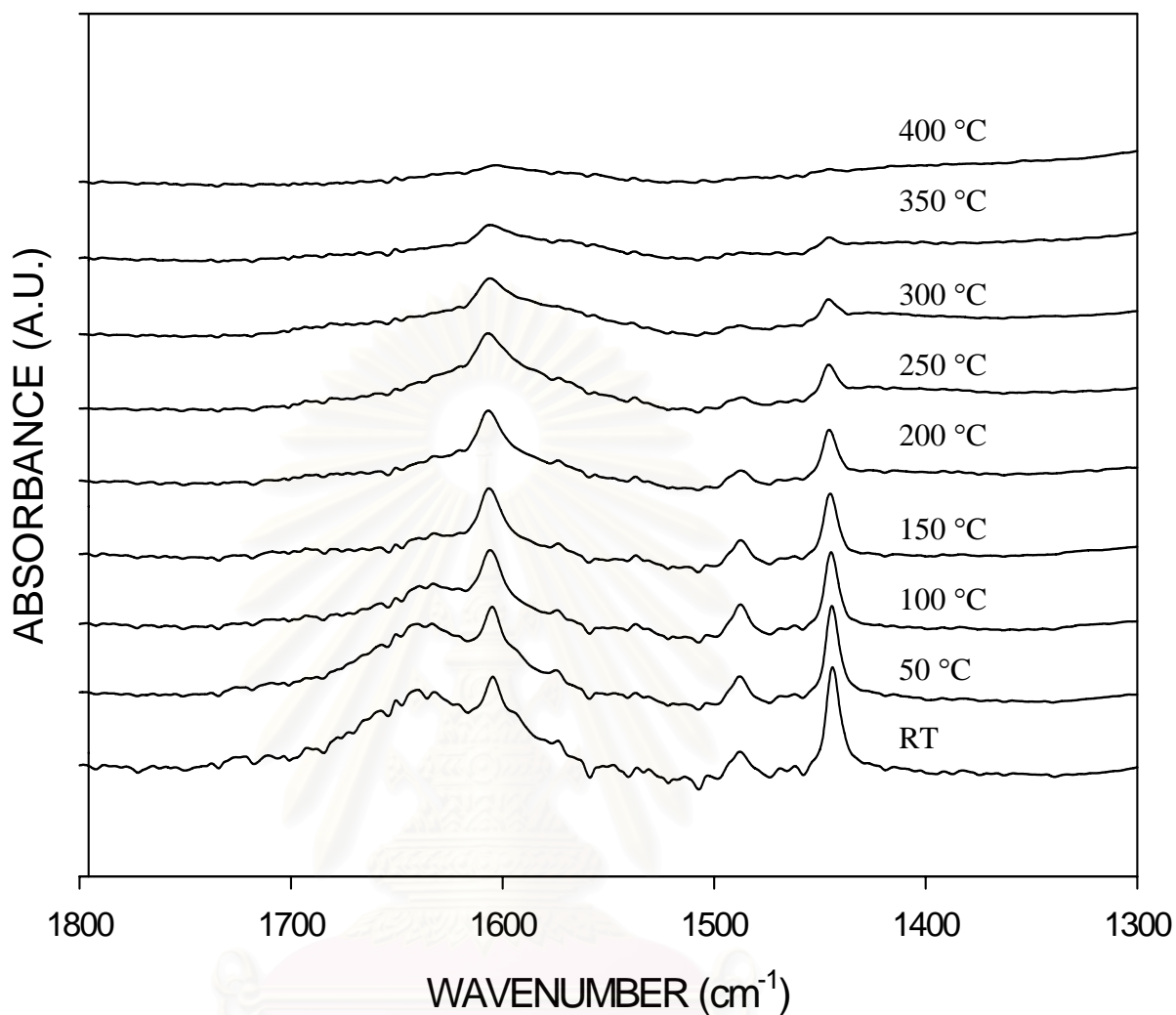
**Figure H-1** Pyridine adsorption on the catalysts at room temperature

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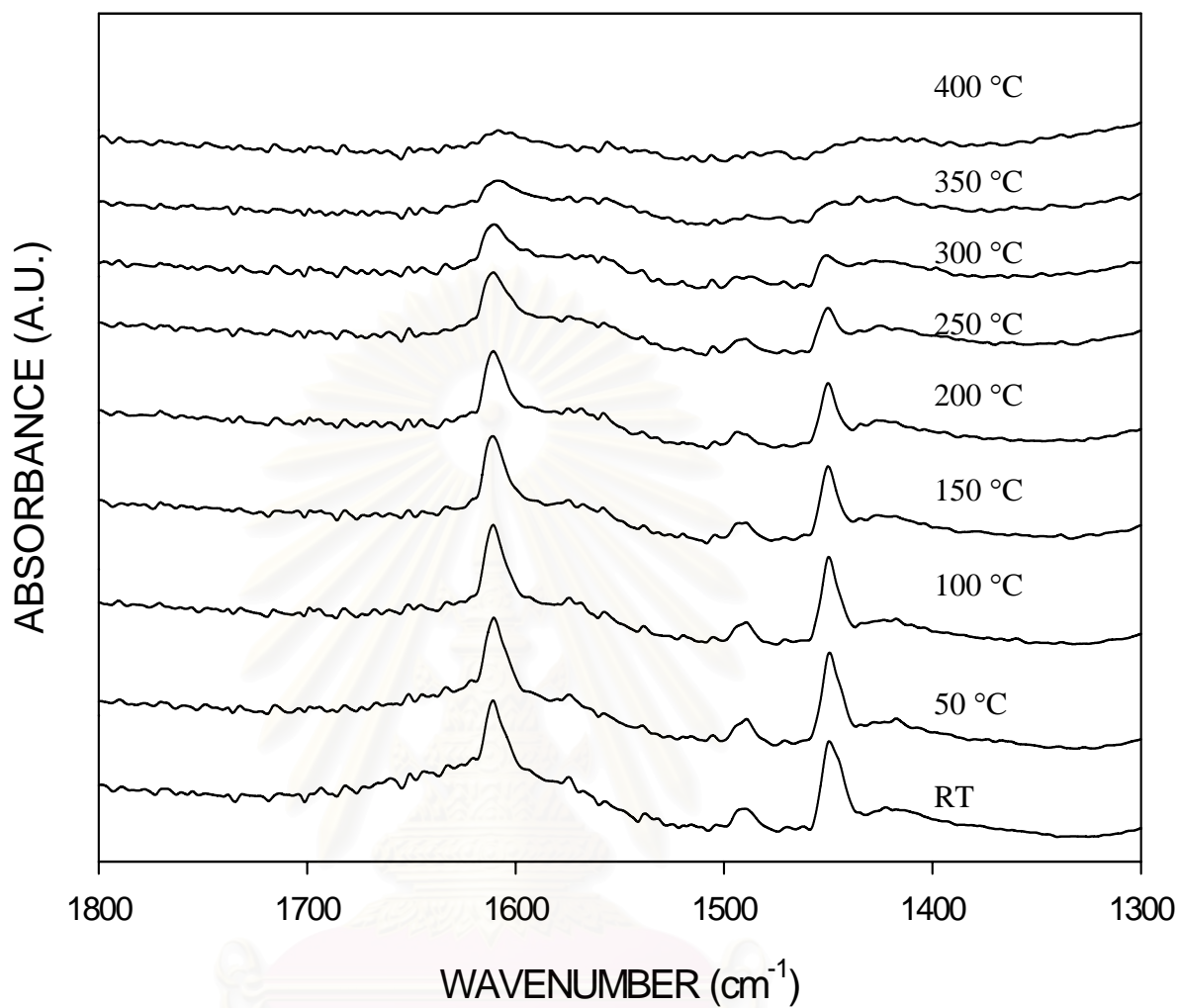
**Figure H-2** Pyridine adsorption on the 8Cu7V1Mg/TiO<sub>2</sub> catalyst





**Figure H-3** Pyridine adsorption on the 8Fe7V1Mg/TiO<sub>2</sub> catalyst

-for 8Fe1Mg7V/TiO<sub>2</sub> catalyst found the band at 1644 cm<sup>-1</sup> which disappeared after pretreatment under vacuum at 150 °C. It believed that this band can be assigned to OH deformation (adsorbed water on catalyst surface) [Hayes N.W. (1996)].



**Figure H-4** Pyridine adsorption on the 8Zn7V1Mg/TiO<sub>2</sub> catalyst

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## VITA

Miss. Amonrut Muanpug was born on April 12<sup>nd</sup>, 1981 in Uttaradit, Thailand. She received the Bachelor Degree of Chemical Thechnology from Faculty of Science, Chulalongkorn University in 2002. She continued her Master's Study at Chulalongkorn University in June, 2003.



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