บทบาทของโลหะอัลคาไลและตัวส่งเสริมร่วมต่อการลดโค้กบนไซต์ที่ว่องไวของตัวเร่งปฏิกิริยา $Pt/\gamma\text{-}Al_2O_3$

นายปัจจาคม ช่วงชัยสุขเกษม

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ROLE OF ALKALI METAL AND CO-PROMOTER ON COKE REDUCTION ON AN ACTIVE SITE OF THE Pt/Υ-Al_2O_3 CATALYST

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ปัจจาคม ช่วงชัยสุขเกษม : บทบาทของโลหะอัลคาไลและตัวส่งเสริมร่วมต่อการลดโค้กบนไซท์ที่ว่องไวของตัวเร่งปฏิกิริยา Pt/γ-Al_2O_3(ROLE OF ALKALI METAL AND CO-PROMOTER ON COKE REDUCTION ON AN ACTIVE SITE OF THE Pt/γ-Al_2O_3 CATALYST) อาจารย์ที่ปรึกษา : ศ. ดร. ปิยะสาร ประเสริฐธรรม, อาจารย์ที่ปรึกษาร่วม : ผศ.ดร.สุทธิชัย อัสสะบำรุงรัตน์, 72 หน้า, ISBN 974-333-956-6

การเกาะของโค้กบนตำแหน่งที่ว่องไวของโลหะมีผลทำให้ลดกิจกรรมของตัวเร่งปฏิกิริยาลง ซึ่งการวิจัยเกี่ยวกับการเกิดสปินโอเวอร์ของไฮโดรเจน (spillover hydrogen) เป็นหัวข้อที่ได้รับการศึกษาวิจัยกันอย่างกว้างขวาง(18) เนื่องจากสปินโอเวอร์เป็นที่ทราบกันดีว่ามีผลกระทบต่อการเปลี่ยนแปลงของตัวเร่งปฏิกริยา ซึ่งถูกนำไปดัดแปลงในการทำปฏิกิริยา ในงานวิจัยนี้จึงได้ทำการศึกษาผลของสปินโอเวอร์ที่มีต่อการลดโค้กบนตำแหน่งที่ว่องไวของตัวเร่งปฏิกิริยายาดังนี้: Pt/Al_2O_3, Pt-Sn/Al_2O_3, Pt-K/Al_2O_3,และ Pt-Sn-K/Al_2O_3 จากการวิเคราะห์ผลด้วยเทคนิค H_2-TPD แสดงให้เห็นความสามารถในการเกิดสปินโอเวอร์ของไฮโดรเจนของตัวเร่งปฏิกิริยาจากมากไปน้อยตามลำดับดังนี้ Pt-Sn-K/Al_2O_3, Pt-Sn/Al_2O_3 , Pt-K/Al_2O_3 และ Pt/Al_2O_3 ซึ่งแสดงว่าดีบุกและโปแตสเซียมมีผลต่อการดูดซับไฮโดรเจนและการเกิดสปินโอเวอร์ของไฮโดรเจนบนตัวเร่งปฏิกิริยา Pt/Al_2O_3 นอกจากนั้นผลของ TPR ยังสนับสนุนว่าการเติมดีบุกและโปแตสเซียมจะช่วยเพิ่มปริมาณการดูดซับไฮโดรเจนบนตัวเร่งปฏิกิริยาอีกด้วยจากปฏิกิริยาดีไฮโดรจีเนชันของ นอร์มัลเฮกเซน ซึ่งใช้ในการบ่งชี้ชนิดของไฮโดรเจนสปินโอเวอร์ (แบบผันกลับได้และแบบผันกลับไม่ได้) พบว่าไฮโดรเจนสปินโอเวอร์บนตัวเร่งปฏิกิริยาลดลงตามลำดับดังนี้ Pt-Sn-K/Al_2O_3, Pt-Sn/Al_2O_3 , Pt-K/Al_2O_3 ,และ Pt/Al_2O_3 ดังนั้นจึงสามารถสรุปได้ว่าการเติมดีบุกร่วมกับโปแตสเซียมจะช่วยส่งเสริมให้เกิดไฮโดรเจนสปินโอเวอร์แบบผันกลับได้บนตัวเร่งปฏิกริยามากกว่าการเติมดีบุกหรือโปแตสเซียมเพียงอย่างเดียว อย่างไรก็ตามในการศึกษานี้ยังแสดงให้เห็นว่าไฮโดรเจนสปินโอเวอร์แบบผันกลับได้ช่วยลดโค้กบนตำแหน่งว่องไวบนตัวเร่งปฏิกริยา

ภาควิชา....วิศวกรรมเคมี.......... ลายมือชื่อนิสิต.ปัจจาคม ช่วงชัยสุขเกษม.........

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4070339421: MAJOR CHEMICAL ENGINEERING
KEY WORD : LOW TEMPERATURE COKE, PROMOTER, CO-PROMOTER, HYDROGEN SPILLOVER

PUDJAKOM CHOUNGCHAISUKASAM : ROLE OF ALKALI METAL AND CO-PROMOTER ON COKE REDUCTION ON AN ACTIVE SITE OF THE $Pt/\gamma\text{-}Al_2O_3$ CATALYST. THESIS ADVISOR : PROF.PIYASAN PRASERTHDAM, Dr.Ing., THESIS CO-ADVISOR : ASS. PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D. 72 pp. ISBN 974-333-956-6

Deposition of coke on metal active sites decreases the activity of catalysts. Extensive researches on the spillover phenomena been the subject of numerous reviews (18). Spillover is known to affect have catalyst performance, which may lead to modifications in the reactivity. This work investigates the effect of spillover hydrogen on coke reduction on metal active sites of bifunctional catalysts Pt/Al_2O_3, $Pt\text{-}Sn/Al_2O_3$, $Pt\text{-}K/Al_2O_3$ and $Pt\text{-}Sn\text{-}K/Al_2O_3$. TPD of hydrogen was used to display the hydrogen spillover ability of catalysts which was formed to follow the sequence : $Pt\text{-}Sn\text{-}K/Al_2O_3 > Pt\text{-}Sn/Al_2O_3$, $Pt\text{-}K/Al_2O_3 > Pt/Al_2O_3$. It is shown that Sn and K affected the adsorption of hydrogen and the hydrogen spillover on the Pt/Al_2O_3 catalyst. In addition, TPR profiles supported that the doping of Sn and K increased the quantity of adsorbed hydrogen on the catalyst, and increased the spillover hydrogen. Dehydrogenation of n-hexane was reacted to identify the type of hydrogen spillover(reversible and irreversible hydrogen spillover). It was found that the reversible spillover hydrogen on the catalysts followed the sequence: $Pt\text{-}Sn\text{-}K/Al_2O_3 > Pt\text{-}Sn/Al_2O_3$, $Pt\text{-}K/Al_2O_3 > Pt/Al_2O_3$. Thus, the promotion of Sn incorporated with K contributed reversible spillover hydrogen on the Pt/Al_2O_3 catalyst more than the promotion of only Sn or K. However, this study displayed that reversible spillover hydrogen helped reduce coke on the metal active sites.

ภาควิชา....วิศวกรรมเคมี.......... ลายมือชื่อนิสิต..

สาขาวิชา...วิศวกรรมเคมี.......... ลายมือชื่ออาจารย์ที่ปรึกษา..............................

ปีการศึกษา.....2542.................. ลายมือชื่ออาจารย์ที่ปรึกษาร่วม........................

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CONTENTS

PAGE

LIST OF TABLES

LIST OF FIGURES

CHAPTERS

PAGE

APPENDICES

LIST OF TABLE

TABLE PAGE

LIST OF FIGURE

FIGURE PAGE

CHAPTER 1

INTRODUCTION

Catalysts have been used in many industries since the beginning of nineteen century. Their purposes were to accelerate reaction rates and to improve selectivity. Hence the reaction can take place at lower temperature or in a reactor with smaller size. However, the catalysts may lose their catalytic activity due to various phenomena such as poisoning and fouling. One major problem in petrochemical industries is arisen from catalyst deactivation due to coke formation. The loss of catalyst activity makes it necessary either to shut down the unit to regenerate the catalyst or to adapt different technologies such as moving bed reactor which continuously swings out catalysts from the reactor train for regeneration and alternatively returns regenerated catalysts black to the reactor zone.

Coke depositing on the catalyst surface is a common deactivation mode in hydrocarbon conversion processes. It is a mixture of mono- and polycyclic aromatic rings connected by aliphatic and alicyclic fragments. Mechanisms of coke formation are complex with multi-step reaction sequences and greatly differ among defferent catalyst-reactant systems. Dehydrogenation, isomerization, cyclization and aromatization are reactions generally involved. Coke formation is related to acid-base properties of the catalyst-reactant system. It has been indicated by several investigators that strong acids rather than weak acids, Lewis acids rather than Bronsted acids favor coke formation (44). There have been a number of researches focusing on the reduction of coke formation on the catalyst. One approach is to add one or more metals on the catalyst. For example, for platinum based catalyst, which is the catalyst, used in their study, some alkali metals were added on the catalysts. It was generally found that tin reduced size of Pt by forming an alloy that decreased formation of coke on Pt (2). Tin formed as alloys with platinum can be detected by considering the amount of metal active sites. The decrease in the amount of metal active sites indicates that tin forms alloys with platinum (2,19,42). Zhusheng Xu et.al.

showed that the amount of carbonaceous materials migrating from the metal to the support was larger for the Pt-Sn catalyst than for the Pt catalyst.

An alkali metal is usually a second metal added to bimetallic catalysts to reduce acidity of the catalysts, and, therefore, to reduce coke on acidic the support. Roles of potassium (K) on the catalysts from the literature reviews are organized as follows:

1. Enhance a stronger Ru-H interaction on Ru/Al_2O_3catalyst (14)
2. Provide electron transfer from K onto Rh(111) (10)
3. Lower coke depositing on catalysts due to increased rate of coke gasification on 12 CaO-7Al_2O_3 (31)

Roles of sodium (Na) on the catalysts from the literature reviews are organized as follows:

1. Decrease surface area of catalysts and enhance basicity on alumina support (16)
2. Significantly enhance the catalytic decomposition of NO over cobalt oxide under hydrogen rich atmospheres and temperature below 500 K (36)
3. Promote activity in selective hydrogenation of acetylene of Pt catalyst under hydrogen rich atmospheres and temperature below 500 K. (37)

In addition, lithium (Li) modifies TPR profile and induces an important drop in the metal dispersion. This drop in the platinum dispersion is due to simultaneous reduction of residual nitrate ions with platinum precursor (7).

Definition of spillover at the First Conference on Spillover (44) was proposed as follows: Spillover involves the transport of an active species sorbed or formed on a first phase onto another phase that does not under the same condition sorb or form the species. The result may be the reaction of this species on the second phase with other sorbing gases and /or reaction with, and /or activation of the second phase. Spillover effects have been observed for several small species such as hydrogen (4,12,15,21,22,23,24,25,26,27,34), carbon monoxide, isocyanate functional group and organic species (44). Recently, Praserthdam et al. (28) found that promotion of Sn and K supported hydrogen spillover on the Pt/Al_2O_3 catalyst. Hydrogen spillover can reduce the amount of coke depositing on the catalyst (5,28). This result may cause the increased rate of coke gasification. Hydrogen spillover from metal to support (4,12,15,21,22,23,24,25,26,27,34) can be divided into two types: irreversible spillover hydrogen and reversible spillover hydrogen (32). Weigi Lu et al. (32) proposed that irreversible spillover hydrogen is favorable to aromatization reaction and reversible spillover hydrogen to the catalyst life. These effects may reduce the amount of coke on the catalyst.

Several techniques have been used to study the hydrogen spillover, e.g., Hydrogen-Temperature-Programmed Desorption (H_2-TPD) (27,32), Temperature-Programmed Reduction (TPR) (32), Fourier Transform Infrared Spectroscopy (FTIR) (22,23,24), Nuclear Magnetic Resonance (NMR) (30), Electron Spin Resonance (ESR) (21,30), X-rays Photoelectron Spectra (XPS) (26), Hydrogenation Benzene (27), etc. Among these techniques, ESR and NMR may also explain the difficulties encountered in attempts to observe the spillover species. Only the paramagnetic H atom can be expected to be observable by ESR spectroscopy. When dynamic equilibrium between H radicals and H^* ions is shifted towards the ionic species, the concentration of the H atom may be too low. There is another important problem which may cause the difficulties in detecting the paramagnetic H^* species. Due to the fast electron exchange between adsorbate and solid, the individual lifetime of the H atom is significantly shorter than for stable H atoms. Therefore, the dynamic equilibrium can result in a marked broadening of the ESR lines or even in their disappearance. Consequently, the rapid exchange between the two spillover hydrogen species is probably the cause of the difficulty in observing paramagnetic H^* species even when test reaction provided unambiguous evidence for the presence of hydrogen spillover.

From the above mentioned, promotion of alkali metal and tin modified, in many ways, catalyst performance including hydrogen spillover process, which helps reduce coke deposition on the metal active sites of the catalysts. However, there are little effort to study role of alkali metal and tin on kinds of hydrogen spillover, which can reduce coke deposition on metal active sites of Pt/ γ-Al2O3 catalyst. This study attempts to identify types of hydrogen spillover, which has effect on coke reduction on the metal active sites of Pt/γ-Al_2O_3 catalysts.

Objective of the study

To study the influence of alkali metal and co-promoter on the amount of coke on active sites of $Pt/\gamma-Al_2O_3$ catalysts.

CHAPTER 2

THEORY

This chapter is aimed to provide background information on catalytic dehydrogenation of propane, catalyst deactivation, coking on metal-based catalyst, effect of operating conditions on coking deactivation, regeneration of coked catalysts, nature of spillover hydrogen, and method for investigation hydrogen spillover phenomena. Details are summarized in the following sections.

2.1 Catalytic dehydrogenation of propane

Catalytic dehydrogenation process was developed for converting normal and iso-parafins to olefins. The catalytic dehydrogenation of light alkenes has a great importance because it represents an alternative for obtaining alkane for polymerization and other organic syntheses from low cost saturated hydrocarbon feed stocks.

Platinum supported on alumina catalyst and its series has been used for propane dehydrogenation. The catalysts provide high selectivity and conversion; however, coking can easily deactivate them.
Propane dehydrogenation is illustrated by the simple reaction:

$$C_3H_8 \longrightarrow C_3H_6 + H_2 \qquad \Delta H^{\circ}_{298} = 124\ \text{KJ/mol}$$

This reaction is highly endothermic and favorable at high temperature (>700°C) and low pressure (<100 kPa absolute).

2.2 Catalyst Deactivation

Catalyst deactivation is referred to loss of catalyst activity or selectivity. Causes of deactivation may be categorized into four groups.

2.2.1 Poisoning

A catalyst poisoning is the reduction of catalyst activity by an impurity that presents in the feed stream. The impurity absorbs on active sites and inhibits the reactant to access active sites.

2.2.2 Fouling

The term fouling is generally used to describe a physical blockage such as deposition of dust, fine power or carbonaceous substance (coke). In the latter case, activity can usually be restored by removal of the coke by burning.

2.2.3 Sintering

This phenomenon is an irreversible deactivation process leading to a reduction of active surface.

2.2.4 Loss of active species

Active compounds can be lost from catalyst by many manners such reaction with other compounds to form a new compound with less activity.

2.3 Coking on metal-based catalyst

Coke or carbonaceous compound is a compound consisting of carbon and hydrogen with a ratio of H/C less than one. All reactions concerning with hydrocarbons such as dehydrogenation, reforming, catalytic cracking or oxidation reaction can cause coke depositing on catalyst Basically, coking materials can be divided into two types of coke; i) coke from reactant and ii) coke from impurities, which contaminate in feed stream. For first type of coke, coke deposition originates from cracking reaction either from reactants or from products. In addition, coking from reactants can be devided into parallel coking formation or series coking formation, which can be written as follows:

$$\left.\begin{array}{l} A \rightarrow B \\ A \rightarrow C \end{array}\right\} \quad \text{Parallel coking formation}$$

$$A \rightarrow B \rightarrow C \quad \text{series coking formation}$$

Parallel coking gives high coke deposition when reactant concentration is high. Because the reactant is the coke precursor, when coking occurs by parallel mechanism, the greatest deposition of coke would be expected near the inlet of the reactor. Conversely, high coke deposition is formed in series coking when product B has a high concentration. Since in normal operation, the product concentration increases with distance along the reaction, the coke distribution should follow a similar pattern.

The other type of coking does not involve the main reaction but coke forms on the catalyst by impurities.

$$A \longrightarrow B \qquad \text{main reaction}$$

$$I \longrightarrow C \qquad \text{side reaction}$$

It should be not that, infact, coking on the catalyst may occur by one mechanism or combination of them.

2.3.1 Coke on metal and coke on support (46)

Babia et al. proposed the meaning of coke on metal and coke on support that

coke on metal

- coke on metal was observed to be combusted by air between 396 to 642 K

coke on support

- coke on support was observed to be combusted by air between 342 to 828 K

2.3.2 Reversible and irreversible coke (46)

Biwas et al. proposed the meaning of reversible and irreversible coke that

reversible coke

- easily removed by hydrogen
- removal of reversible coke is at least 1000 times faster than removal irreversible coke
- the effect of pressure is less significant for reversible coke removal
- deposit on the metal
- the quantity does not change much with time
- the fast cleaning of reversible coke has been postulated to occur by catalytic hydrogenation
- proposed mechanism $[PM] \xrightarrow{k\ rev} C_{rev}$

  $[PM]$ = metal surface concentration of coke precursor

  C_{rev} = reversible coke

  k_{rev} = rate constant for reversible coke

irreversible coke

- more difficult to remove with hydrogen
- increase with time on stream, high temperature and low pressure
- deposit on the support
- the slower removal of irreversible coke occurs by catalytic hydrogasification
- proposed mechanism $C_{rev} \xrightarrow{k\ irr} C_{irr}$

C_{irr} = irreversible coke

k_{irr} = rate constant for irreversible coke

2.3.3 Low and high temperature coke (28)

Praserthdam et al. proposed the meaning of low and high temperature coke that

Low temperature coke

- low temperature coke was observed to be combusted by oxygen at temperature < 300°C

High temperature coke

- high temperature coke was observed to be combusted by oxygen at temperature > 300°C

2.4 Effects of operating conditions on coking deactivation

2.4.1 Effect of Pressure

Reforming reaction as well as dehydrogenation reaction is preferred to work at low pressure. At this condition coke can be easily formed. Thus, the study of coke in a laboratory usually accelerates coking by decreasing reaction pressure for obtaining high amount of coke on the catalyst. However, alternation of pressure has the effect on location and nature of coke. The increase of pressure decreases the amount of coke on the metal sites but increases the amount of coke on acidic support. Therefore, it changes the nature of coke deposited on the catalyst to be more dehydrogenated and be more graphitic or decreased H/C ratio of coke on the catalyst.

2.4.2 Effect of coke deposition on dehydrogenation reaction

Dehydrogenation of paraffins and naphthenes is a fast reaction, and under reforming condition, the corresponding thermodynamic equilibrium is quickly achieved. The results in Figure 2.1 showing the effect of coke on the dehydrogenating activity for cyclohexane of Pt/Al_2O_3 catalyst verify the fact that the majority of coke is deposited on alumina support , since the activity of the catalyst for this metal site catalyzed reaction should be nil with coke contents of less than 1 wt% if all the carbon is deposited on the platinum. Unfortunately, with such high carbon amount, there is no connection between residual activity and the carbon percentage.

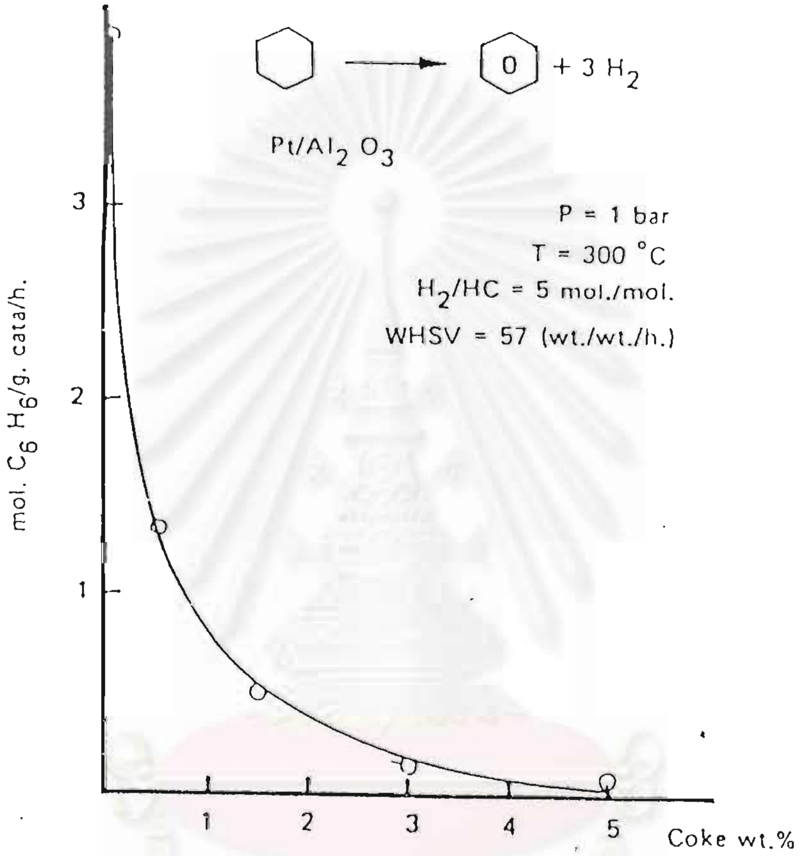


Figure 2.1 Effect of coke on dehydrogenation activity (48).

2.4.3 Effect of coke deposition on dehydroisomerization and isomerization reaction

Transformation of methylcyclopentane into benzene (Figure 2.2) shows a gradual decrease in catalyst activity with coke formed, in the case of a fresh monometallic catalyst. Coke was less toxic for this reaction compared to dehydrogenation. This is related to the fact that the rate-limiting step occurs on the acid component, while is less sensitive to coke due to its immense surface area compared to platinum.

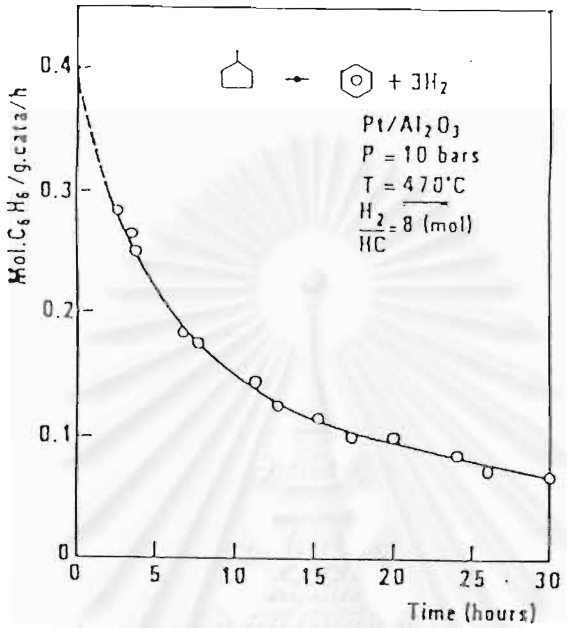


Figure 2.2 Methycyclopentane dehydrisomerization on fresh catalyst (48).

Figure 2.2 shows the quantity of coke formed and the isoheptane yield under certain experimental condition. It is noticeable that with 0.6 wt% carbon on the catalyst, the isomers' yield is multiplied by 0.3, whereas it is only halved when the carbon content goes from 0.6 up to 1.2 wt%. Since isomerization has monofunctional (Pt-catalyzed and bifunctional (rate-limiting step on alumina) mechanisms, the initial deposition of coke on the metal component would explain this behavior.

2.4.4 Effect of coke deposition on dehydrocyclization reaction

Dehydrocyclization of paraffin is the most complex and the most important of all the reforming reactions. When the evolution of dehydrocyclization activity during the first hours of operation of a fresh catalyst was examined (Figure 2.3), one can note a very high initial activity even under relatively high pressure was noticed. This activity decreases very quickly after a few hours of operation, leveling off to a “pseudoplateau” (lined-out catalyst) on which the evolution in time becomes much slower.

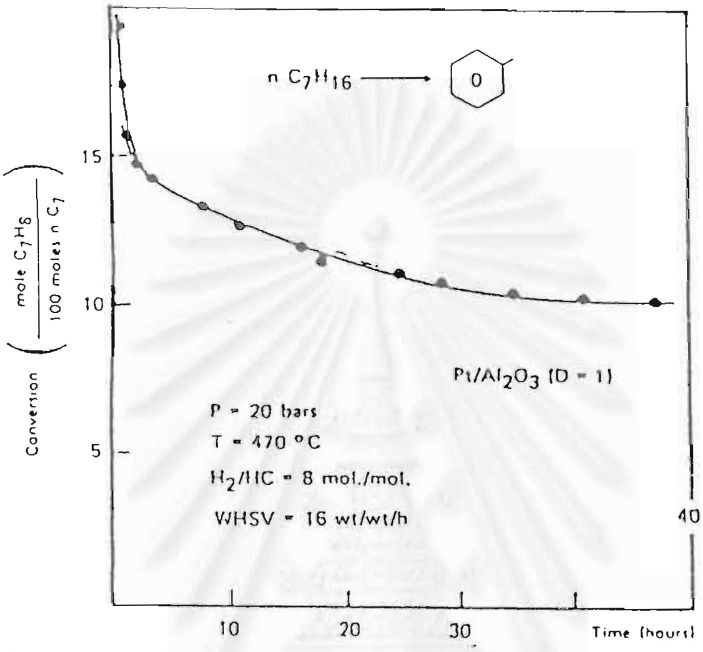


Figure 2.3 Initial activity and stabilization during n-heptane dehydrocyclization (48).

2.4.5 Effect of coke deposition on hydrogenolysis reaction

Figure 2.4 compares the toxicity of deposited coke on the metal sites of catalyst on the activities of dehydrogenation, exchange, and hydrogenolysis. A number of authors suggested that the effect of coke on Pt/Al_2O_3 was similar to alloying of sulfur adsorption. There was a sharp decrease in hydrogenolysis activity compared to the other reaction. The basic cause in the number of suitable ensembles for this reaction due to site blocking by coke, especially on the more active high coordination number face atom crystallites.

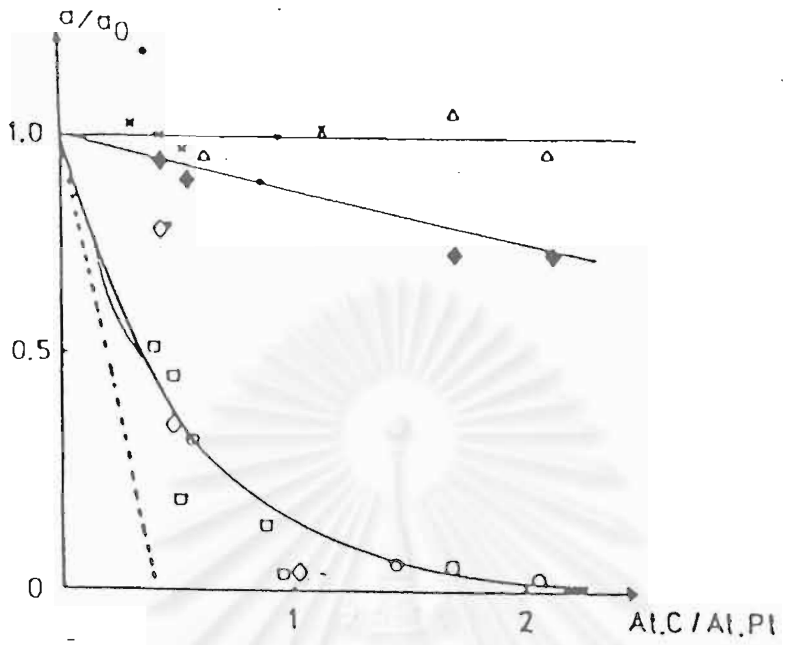


Figure 2.4 The evolution of the relative activity of 1 g of catalyst as function of the number of metal site carbon atoms deposited per platinum atom (48).

(a) Benzene exchange: Pt/Al_2O_3 0.1%(A), ; Pt/Al_2O_3, 1%(C),

(b) Cyclopentane hydrogenolysis: Pt/Al_2O_3, 13%(D), ; Pt/Al_2O_3, 1%

(c) Pt/Al_2O_3 (A), (C) Benzene hydrogenation: Pt/Al_2O_3, 0.1%(A), Pt/Al_2O_3, 1%(C).

2.4.6 Effect of temperature

Contrastly, effect of temperature reverses the effect of pressure. At the low temperature coke coverage increases due to the increase of accessible metallic atoms. On the other hand, the increase of temperature leads to a decrease in coke deposits on the catalyst. However, the change of coking temperature does not alter the nature and location of coke on Pt/Al_2O_3 catalyst.

2.4.7 Effect of H_2/HC ratio

In industrial process of dehydrogenation, hydrogen is added to feed stream to decrease coking on the catalyst. Hydrogen acts through a hydrogenolytic or by an inhibiting effect on the formation of highly dehydrogenated polymers.

To study coke formation on catalysts, the change of H_2/HC ratio in feed stream was investigated using H_2/HC of 0 and 1. The value higher than 1 was not considered due to the fact that this type of reaction produces hydrogen as a product. According to Le Chatelier's law, introducing too much hydrogen would reduce an attainable equilibrium conversion.

2.4.8 Composition, location, and nature of coke on catalyst

In temperature program oxidation, to burn coked catalyst, two peaks are generally found at temperature around 300 °C and the other around 450 °C. The first peak was defined as coke on metal sites and the second peak as coke on acidic support. Both cokes have formula CHx. But coke on metal is less dehydrogenated than coke deposited on the support. It means that coke on metal has more hydrogen in molecules than coke on support.

Extraction of coke with solvent and analysis of extractable compound shows that coke is polyaromatic compounds which possibly consist of branched chain like metal on ethyl groups. Analysis of unextractable coke by x-ray diffraction shows that the carbon deposits consisted of pseudo-graphitic carbons. Most of coke on support is graphitic, but coke on metal consists of ordered arrangement of polyaromatic compounds. However, coke sometimes forms to be filamentous carbon by means of metal carbides as an intermediate.

2.4.9 Effect of promoter on coke formation

It is well known that some additives, which are called promoter, can increase the activity, selectivity or stability of catalyst. Most of the promoters are metals that are added simultaneously with the precursor to deposit on the surface of catalyst. Generally, the promoters can be classified into two types: (i) textural promoter and (ii) structural promoter.

1. Textural promoter is an inert substance which inhibits the sintering of microcrytals of the active catalyst by being present in the form of very fine particles. These fine particles separate the true catalyst particles from contact with one another so they do not coalesce, thus preventing or minimizing loss of active catalyst area during service.
2. Structural promoter causes a chemical effect by changing the chemical composition of the catalyst. In many cases the effect of the structural promoter is clear but its mechanism of the action is not. In the other cases it is not clear whether the effect of the promoter is primarily a physical or chemical effect. Some possible mechanisms are:
    - 2.1 There may be a dual-function action. The promoter may catalyze the formation of an intermediate. Thus the addition of a chloride to a platinum/alumina catalyst may enhanced its activity and be term "promotion", although the true mechanism is more clearly seen as an example of dual functionality.
    - 2.2 The promoter may produce lattice defects or interstitial substitution.
    - 2.3 The promoter may change the electronic structural of a catalyst, e.g. the case of addition or removal of electron from a metal, and hence the strength of chemisorption.

2.4.10 Effect of the catalyst dispersion

Crystallite sites are very active in alkane hydrogenolysis, probably due to the lower self-poisoning of these crystallites. Multiple metal-carbon bond formation is necessary for carbon formation on metal crystallites and there is more likely on large crystallites where there is an abundance of high coordination number atoms and the increased possibility of larger ensembles. The lower effect of metal support interactions with larger crystallites would make its surface more attractive for multiple metal-carbon bond formation also.

2.4.11 Effect of chloride content in the catalyst

Chloride has an important effect of both the initial dispersion of the platinum and the maintenance of its dispersion. It also modifies the acidity of the catalyst which controls the relative rates of isomerization and hydrocracking. Industrial catalysts work with a chloride content which is deliberately maintained in a range 0.8-1.1 wt% as although some chloride is needed, and excess leads to excessive hydrocracking and coking activity. The amount of coke on a reforming catalyst is minimum when the catalyst's chloride content is in the range 0.7-0.9 wt%. With this chloride content, the deactivation rate is also a minimum and this has been attributed to a maximum in hydrogen spillover on the surface of the alumina, thus hydrogenating unsaturated substances which may subsequently have pursued alkylation and polymerization reactions to coke.

2.5 Regeneration of coked catalyst

Since catalysts are expensive, the catalysts used in dehydrogenation or reforming processes should be regenerated. Many researchers have studied regeneration phenomenon.

Coke composition has effect on coke burning characteristics. Coke on metallic function containing high ratio of H/C of Pt-Re-S/γ-Al_2O_3 was found to be burned at lower temperature with a rapid treatment and then continued on the acidic sites. At high regeneration temperature the burning is nonselective and all species are simultaneously burned. Infrared spectroscopy showed that there are C=O and C-OH occurred during coke burning. From that result, Carlos et al. proposed the following coke burning mechanism:

$$\text{Coke} + O_2 \longrightarrow \text{oxidized coke} \longrightarrow CO_2 + H_2O$$

There are also other methods, which can be used to regenerate coke catalyst such as using hydrogen or steam as a substance for regeneration. Regeneration by hydrogen obtains only methane as a gaseous product. At low temperature the functional groups are hydropyrolyzed whereas at high temperature uncatalyzed gasification of the remaining coke takes place. Coke on platinum catalyst could be divided into two types by the ability of coke removal by hydrogen as reversible coke and irreversible coke.

2.6 Nature of spillover hydrogen

Surface mobility of reactants and intermediates is a well-known phenomenon in heterogeneous catalysis. The corresponding mobile species are formed at surface sites, which are distinct from sites where the reaction takes place. Very often, they may show a special type of activity and this can open new reaction pathways for the catalytic process. In some cases activation of species and reaction sites of the catalyst system are separated (even sometimes on separate phases) and active species formed on one surface site (e.g. on transition metal clusters in the case of hydrogen) can diffuse to another surface site (e.g. to an acidic center in zeolite catalysis) without the loss of their activity. This effect was called spillover and defined at the First Conference on Spillover (44) as follows: Spillover involves the transport of an active species sorbed or formed on a first phase onto another phase that does not under the same condition sorb or form the species. The result may be the reaction of this species on the second phase with other sorbing gases and / or reaction with, and / or activation of the second phase. Spillover effects have been observed for several small species such as hydrogen. (and its isotopes), oxygen, nitrogen, carbon monoxide, isocyanate functional group and organic species.

The spillover (or more precisely back-spillover) phenomenon was found for the first time by Kuriacose in the late 1950's who studied the hydrogen desorption from GeH_4 contacted with platinum. He found that the formation of hydrogen was enhanced four fold by the presence of platinum due to facilitated recombination of atomic hydrogen at the platinum wire. This experimental result could only be explained by the diffusion of atomic hydrogen to the wire, i.e. back-spillover, where it recombined to molecular hydrogen, which could be desorbed more easily. The first direct evidence for spillover originates form Khoobiar who observed the formation of the hydrogen bronze H_xWO_3 from WO_3 at room temperature after the application of hydrogen in the presence of a platinum-containing catalyst.

Though spillover, especially that of hydrogen, has been continually studied in the last three decades, several questions in connection with the spillover phenomenon remained unanswered until now. Especially, the nature of the activated species and the way they interact with the support remained unsolved problems. For a large part, this is the consequence of failing to observe these species by spectroscopic methods in a direct manner.

Ulf Roland et al. (44) classified kinds of hydrogen spillover as follows:

2.6.1 Indications of the atomic nature of spillover species

The occurrence of hydrogen spillover has been demonstrated in the presence of several supported metals, e.g. Ni, Ru, Rh, Pd, Pt, which are known to adsorb hydrogen dissociatively. In particular, this has been shown for platinum by using infrared spectroscopy. Only two bands were observed for the adsorption of a hydrogen/deuterium mixture on platinum corresponding to the Pt-H and Pt-D bonds whereas three bands corresponding to H_2, HD and D_2 bound to Pt would be expected for molecular adsorption. This result was confirmed by NMR spectroscopy also indicating the presence of atomic hydrogen species. Of course, the fact that hydrogen and deuterium formed in catalysts containing metals, which adsorb hydrogen dissociatively, are atomic species. This does not allow to extend this conclusion to the H^* and D^* species which have spillover onto the support. Nevertheless, the necessity of dissociation on the metal strongly suggests that this be also atomic spillover species.

A further indication for atomic spillover species is the fact that they are able to enter metal oxide frameworks, e.g. WO_3 and MoO_3, to form hydrogen bronzes. This process takes place already at room temperature when a spillover source, i.e. an activating metal, is present. The color change associated with the low temperature formation of bronzes can be used as a test for the presence of atomic hydrogen, because the bronze-forming reaction with molecular H_2 occurs only above ca. 670 K. Several spectroscopic methods (IR, EPR, NMR spectroscopy) have been applied to show that in such bronzes atomic hydrogen is present on interstitial sites.

It was found that some effects which are related to hydrogen spillover in metal-containing catalysts do also take place after a treatment with hydrogen atoms formed externally in the gas phase. In the latter case atomic hydrogen can be produced either by a microwave discharge or by a hot filament. The formation of hydrogen bronzes from metal oxides such as WO_3, MoO_3 and V_2O_5 was observed at low temperature (e.g. room temperature) via hydrogen spillover as well as under the action of hydrogen atoms formed in the gas phase. The same similarity was found for the reduction of metal cation in metal oxide as detected by ESR spectroscopy.

Comparing the interaction of hydrogen with Al_2O_3, Pt/ Al_2O_3 and Ni/ Al_2O_3 by means of temperature programmed desorption (TPD), characteristic desorption peak at 480 °C corresponding to spillover hydrogen was present in the metal-containing samples. This peak was absent after hydrogen adsorption on pure Al_2O_3. The TPD peak at 480 °C was also observed for metal-free Al_2O_3 after a treatment with H atoms. This experimental result indicates that the species which was desorbed at 480 °C could be formed either by hydrogen spillover or by the adsorption of H atoms.

The formation of catalytically active sites on initially inactive oxide surfaces by a treatment with spillover hydrogen was demonstrated by using an experimental setup that allowed to separate the spillover to be activated (e.g. SiO_2). An activation procedure including hydrogen spillover from Pt/ Al_2O_3 to SiO_2 was necessary to initiate the hydrogenation of ethane on SiO_2. It was shown that the spillover hydrogen itself was not active for this catalytic reaction. Its role consisted only in the formation of new catalytic sites on the SiO_2 surface. The same activation of a solid surface leading to the creation of catalytic sites was achieved by a treatment with hydrogen atoms produced in the gas phase by a microwave discharge. The activation energy of the catalytic sites formed on SiO_2 was found to be the same for both activation procedures.

Comparison between the isotopic distributions of various hydrocarbons after reactions either with deuterium on metal-containing heterogeneous catalysts or, in the presence of a solid surface, with D atoms procedure by a microwave discharge in the gas phase showed that a striking similarity for both reaction pathways.

The large number of effects corresponding to hydrogen spillover as well as to externally produced H atoms has often been interpreted by postulating H atoms as spillover hydrogen (H*) species. As it will be shown that this straightforward conclusion is not completely true. Though after hydrogen spillover and after the application of H atoms the same effects are observed, the interaction of the H atoms with the surface can change their physical nature, especially their charge. Consequently, it can only be concluded that the dissociative adsorption on a metal and the external formation of H atoms in the gas phase are two ways to form an active atomic species and to let it come in contact with a surface. This species as existing on the surface is defined as H* or spillover hydrogen. Therefore, the physical nature of the activated spillover species has to be considered by taking into account their interaction with the support.

A further clue for atomic H* species was provided by electrical conductivity measurement studying the influence of hydrogen on the resistance of metal/semiconductor junctions of chemical sensors. Lundstrom et al. found a decrease of the interface barrier by 0.5 eV at the junction between Pd and SiO_2 in hydrogen atmosphere. This effect leading to a significant increase of the electrical conductivity was due to the ionization of atomic hydrogen. When Al was used instead of Pd hydrogen could not be dissociated and the conductivity effect of the hydrogen atmosphere was negligible. The same influence of hydrogen was observed for other hydrogen-activating metal/insulator or metal/semiconductor systems such as Ni/ SiO_2, Pd/GaAs and Pt/Si.

2.6.1.1 Indications for H_3 species

In contrast to the above studies favoring atomic spillover hydrogen species. The presence of H_3 species on the basis of kinetic results on the demethoxylation of methoxylated SiO_2 in the presence of an admixed Pt/Al_2O_3 catalyst. According to reaction mechanism hydrogen would be dissociated on platinum and the resulting H atom reacted with molecular hydrogen to form an H_3 species. Taking into account theoretical considerations an H_3^+ ion was suggested.

2.6.1.2 Indications for ion pairs

In addition to atomic and H_3 species there is the possibility that ion pairs (H^+-H^-) would be the spillover hydrogen. This model has been taken up to interpret experimental results on the bifunctionally catalyzed conversion of hydrocarbons. Particularly, in the case of the hydroisomerization of n-heptane on a platinum-containing ZSM-5 zeolite the proton was assumed to initiate the hydride abstraction from the paraffin whereas the hydride ion should stabilize the carbenium ion on the catalyst surface. Investigations on a Pt/SO^{2-}_4 $-ZrO_2$ catalyst showed that the application of hydrogen in the presence of platinum led to the transformation of Lewis acidic sites to Brφnsted acidic sites. The results were interpreted by heterolytic dissociation of molecular hydrogen on platinum leading to the formation of spillover H^+ and H^- species on the surface.

2.6.1.3 Indications for H atoms

Different spectroscopic techniques (e.g. NMR, ESR, IR spectroscopy) have been used in attempts to detect the spillover species in a direct manner, with the hope that this would also allow to answer the question of the physical nature of the H* species.

An indication for the presence of H atoms was found by studying hydrogen spillover in a two-component Pt/Al_2O_3-SiO_2 catalyst by means of NMR spectroscopy. Further NMR studies on the adsorption of hydrogen at supported metal clusters have shown that in addition to the NMR-detectable amount of hydrogen on the metal other hydrogen species should be present at the surface of the support which could not be directly observed by NMR spectroscopy. Comparing the hydrogen species observed by NMR spectroscopy with the amount determined by gravimetric and volumetric adsorption measurements could provide additional evidence for a spillover of hydrogen onto the support. A spectroscopically non-observable amount of hydrogen is formed on the silica support of a Rh/SiO_2 catalyst as found by NMR spectroscopy. The longitudinal NMR relaxation time T_1 of hydroxyl protons can be significantly shortened by the presence of paramagnetic species. Since such an effect was observed for hydrogen spillover it was concluded that the spillover species should be paramagnetic H atoms.

However, the attempt to investigate directly the paramagnetic H atoms supposed to correspond to the spillover species by ESR spectroscopy has not been successful unit now. Even in catalytic systems was hydrogen spillover evidently occurred, H atoms could not be observed. But, on the other hand, reactions of spillover species with organic radicals could be monitored by ESR and IR spectroscopy repeatedly. Particularly, the reaction of spillover hydrogen produced by Pt or Pd supported on or admixed to a Y zeolite with two organic radicals (anthracene and perylene ions) by means of ESR spectroscopy. The disappearance of the radicals was correlated with the reaction of what to be H* radical species (i.e. H atoms). The ESR technique was also used to detect the dissociation of hydrogen on a Pd/Al_2O_3 catalyst at room temperature. Atomic hydrogen reacted with the spin trap N-benzylidene-tert-butylamine-N-oxide (PBN) producing paramagnetic species up to a level detectable by ESR spectroscopy. However, there was no direct ESR spectroscopic evidence for H atoms. Taking into account these results, it seems very likely that the spillover hydrogen species is a radical but the activated hydrogen should not be considered as a stable H atom like, e.g. atomic hydrogen on an interstitial site in CaF_2 or KCl at low temperature. Similar experiments were observed by infrared spectroscopy the reaction of spilt-over hydrogen with different reducible compounds, e.g. the 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical. In contrast to most of the other studies on hydrogen spillover. It was proposed that the reactive hydrogen was diffusing in the gas phase (e.g. as uncharged H atoms). This conclusion was questioned because of thermodynamic reasons.

2.6.1.4 Indications for H^+ ions

In contrast to the above results indicating the occurrence of paramagnetic H* species, most likely H atoms, a large number of studies led to the conclusion that H^+ ions should be present in the spillover process. The influence of cocatalysts with different proton affinities on the formation of hydrogen bronze from WO_3 in the presence of Pt black or a Pt/SiO_2 catalyst. A strong correlation between the reaction rate and the proton affinities of the cocatalysts with high proton affinities and concluded that the spillover species were H^+ ions. However, the conclusion that the electrons removed from the H atoms would remain on platinum is very unlikely, because H/Pt ratios of up to 35 were observed during a study of bronze formation via hydrogen spillover. The accelerating effect of water, which has also been observed before, was interpreted by postulating the diffusion of the spillover hydrogen as solvated proton.

The deuteration of surface hydroxyl groups can be considered as a model reaction for the investigation of hydrogen and deuterium spillover, because this can be easily monitored by IR spectroscopy. It has been frequently shown that the deuteration is markedly enhanced by the presence of platinum or another hydrogen-activating metal supported on Al_2O_3, SiO_2 and zeolites. Two different reactions of spillover H* on alumina in the presence of a Pt/ Al_2O_3 spillover source: the hydrogenation of unsaturated carboxylic acids and the H-D exchange of surface hydroxyl groups. On reaction of the activated hydrogen with preadsorbed unsaturated organic compounds occurred in spite of the fact that hydrogen spillover took place as indicated by the H-D exchange reaction. It is concluded that hydrogen spillover does not necessarily lead to the formation of active hydrogen species, which are able to hydrogenate unsaturated hydrocarbons. Obviously, the spillover hydrogen cannot be considered as a universally active species. Its activity is determined by the specific reaction and possibly by the (ionic or radical) nature of the H* species on the catalyst surface. In the case of the H-D exchange on zeolites a correlation between the acidity of the OH and OD groups and the reactivity of the activated hydrogen and deuterium as experimentally found could be an indication for an ionic nature of the spillover H* species.

Out results on the influence of a homogeneous magnetic field on the H-D exchange in two-component Pt/NaY-HNaY zeolite samples led to the conclusion that the spillover hydrogen species should be electrically charged, most likely diffusing H^+ ions influenced. This conclusion rests on the experimental finding that the exchange rate was decreased by a magnetic field directed perpendicularly to the main direction of diffusion (from Pt/NaY to HnaY) and was not influenced by a magnetic field parallel to this direction. This is what theoretical considerations predict when considering the diffusion constant of charged particles in a homogeneous magnetic field.

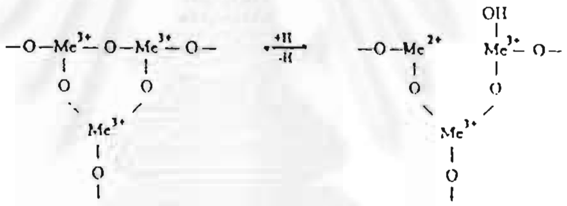
The assumption that the spillover hydrogen species are H^+ ions is strongly supported by the results of electrochemical and electrical conductivity measurements on several catalysts. A mechanism for spillover that was adapted from the description of an electrode-liquid electrolyte system. The observed long-rang spillover by the following reaction steps: dissociation of molecular hydrogen into H^+ ions and metal conduction band electrons, subsequent transfer of electrons through the metal/support interface and electronic and protonic conductance on the catalyst surface. Electrical conductivity changes due to the interaction of hydrogen with noble-metal-containing metal oxides exhibiting semiconductor properties were observed for different oxides such as TiO_2, SnO_2 and ZnO. The increase of the n-type conductivity at low temperature, i.e. under condition where no additional oxygen vacancies were formed by reduction, was interpreted by an electron transfer from hydrogen species to the metal oxide and the adsorption of the H* species as protons. Alternatively, changes of the work function of the metal clusters and effects at the metal/support interface have been discussed to explain the cooperative conductivity effect between the metal, the semiconducting support and hydrogen. In recent studies on the influence of hydrogen spillover on Pt-containing TiO_2 a special geometry for two-component samples in order to exclude such influences of the metal/semiconductor interface were adopted. By measuring the conductivity changes after exposure to hydrogen in the platinum-free TiO_2 component of two-component Pt/ TiO_2- TiO_2 samples (pellets, thick-film and powder samples) it could be demonstrate that the increase of the n-type conductivity was due to an electron transfer from the H* species to titania. The diffusion of the spillover species occurred on the surface over a distance of some millimeters and gas phase diffusion could be excluded. As already discussed for other effects related to hydrogen spillover the conductivity of metal oxide could also be increased by a treatment with H atoms externally produced in the gas phase. An influence of hydrogen on the conductivity was observed even for an insulator like Al_2O_3. The dissociative adsorption of hydrogen on η- Al_2O_3 at 600 °C led to an increase of the n-type conductivity whereas the adsorption of oxygen caused a switch from n- to p-type conductivity for oxygen pressure above ca. 100 Pa. In a way similar to the case of semiconductors, a protonization of the atomic hydrogen on the surface was proposed.

An electronic interaction due to an electron transfer from the spillover hydrogen to the surface region of metal oxides was also found by means of optical spectroscopy. The transparency of Cu/ZnO and Ru/ZnO catalysts in the infrared region was markedly reduced by a H_2 and D_2 atmosphere. This loss corresponded to a broad absorption band in the spectra region around 1500 cm^- (independently, whether the sample was exposed to H_2 or exposed to D_2) and it was interpreted by the photoionization of oxygen vacancies producing two electronic donor states in the band gap of ZnO. Specifically, the photoionization process involved the single ionized vacancies whose concentration was enhanced by a charge transfer from the adsorbed H* species. Similar results were obtained by means of FT-NIR Raman spectroscopy study with Pt-containing TiO_2. The presence of H* species on the surface of TiO_2 was shown to result in a charge transfer to a diminution of the photoionization process which produces a broad fluorescence band in the FT-NIR Raman spectrum.

2.7 Methods for investigating hydrogen spillover phenomena.

2.7.1 Hydrogen-Temperature-Programmed Desorption (H_2-TPD) (27,32)

Hydrogen Temperature Programmed Desorption (H_2-TPD) is used to determine the quantity of chemisorbed hydrogen. High temperature H_2 desorption (usually interpreted as spillover hydrogen) occurring under TPD conditions is the reoxidation of reduced surface sites by -OH groups (on alumina) (17). The -OH groups on alumina was formed at high temperature reduction condition the alumina surface (impurities on it) is reduced by spillover hydrogen, forming - OH groups, as shown by the following:



Thus, this hydrogen accumulation on the catalyst surface proceeds via a reversible redox reaction. The spillover hydrogen consists of - OH groups and reduced cations (or metal atoms). In the absence of H_2 ,- OH groups can oxidize the reduced centers, releasing hydrogen.

2.7.2 Temperature-Programmed Reduction (TPR) (32)

The quantitative determination of the reduced oxygen on the catalysts by Temperature-programmed reduction (TPR) technique is related to quantity of reducing hydrogen. If quantity of oxygen is high, the adsorbed hydrogen ability of catalyst is high too.

TPR can be used to investigate hydrogen spillover phenomena by comparing the amount of hydrogen consumption for reducing the catalysts. If the amount of hydrogen used is high hydrogen spillover phenomena may be significant.

2.7.3 Electron Spin Resonance (ESR) (21,30,44)

The interpretation of the ESR signals lead to the understanding of the process taking place after loading the catalysts samples with hydrogen and cooling down to 77 K.

Immediately after gas treatment negatively charged platinum clusters (Pt^{-}_{n}) are formed in connection with the adsorption of hydrogen from the gas phase. A partial electron transfer takes place from the atomic hydrogen formed by dissociation to the Pt cluster providing the adsorption sites.

Subsequently, atomic hydrogen species are able to migrate over the metal-support interface and to spill over onto the support where they form a reservoir of adsorbed hydrogen (H^{*}).

2.7.4 Fourier Transform Infrared Spectroscopy (FTIR) (22,23,24)

In the case of Pt/SiO_2-H-ZSM-5, the phenomenon that spillover hydrogen hydrogenated adsorbed pyridine on ZSM-5 acidic sites can be explained as that the gas phase hydrogen is first dissociated on metal sites, presumably atomic or charged, and then spilled over to ZSM-5 as in the case of Pt/H-ZSM-5, or move to SiO_2, support, then cross the interface between Pt/SiO_2 and H-ZSM-5 and finally move to zeolite acidic sites through surface migration as in the case of Pt-hybride. Here pyridine molecules bonded on ZSM-5 acid sites acted as an acceptor for spillover hydrogen, the pyridine become piperidine.

In the experiment, the samples were adsorbed by pyridine and then, detected the amount of pyridine by used FT-IR spectrometer. After that, doped hydrogen on the samplesin order to change the pyridine to piperidine and detected the amount of piperidine. If it could detect the amount of piperidine, it had shown that occurred spillover hydrogen on the catalyst.

CHAPTER 3

LITERATURE REVIEWS

The decreases of activity and selectivity of catalysts because of their deactivation is the main problem in petrochemical industry. Many researchers found that doping of promoter can slow the deactivation of catalysts. Thus, the literature reviews on role of alkali metal and tin on Pt/Al_2O_3 catalyst and hydrogen spillover are provided in this chapter

3.1Role of tin and alkali metal on Pt/Al_2O_3 catalyst

Effects of promoters on the catalyst performance have been studied by many researchers. Various results were found for example, doping of alkali metals on Pd/SiO_2 solids leads to very small variation of the initial heats of carbon monoxide and hydrogen adsorption (8). Potassium enhancing Fischer-Tropsch synthesis activity is dependent on the space velocity and synthesis gas conversion level (35). Potassium also promotes the catalytic performance of $CuFe_2O_4$ for the simultaneous removal of NO_x and diesel soot particulate (38). Consequently, alkali metals increases charge density over Pt/L-zeolites (11) similar to Ru metal that has a higher electron density when added to alkali metal (14). These results were confirmed by T.V.W.Janssens et al.(10) who indicated that potassium gave electron onto Rh(111). The higher electrons enhance hydrogen spillover on the catalyst surface, thus reducing the amount of coke deposits (28). In addition, the incorporation of potassium to the 12 CaO-$7Al_2O_3$ lowers the coke depositing on the catalysts due to the increased rate of coke gasification (31). In addition, the promoter K is found to help in decreasing the coking rate of nickel catalyst (51). Cortright R.D., and Dumesic J.A. (50) found that K increases the saturation extent of hydrogen adsorption and decreases the extent of carbon monoxide adsorption on Pt/SiO_2 and $Pt/Sn/SiO_2$. Sodium enhances the catalytic decomposition of NO over cobalt oxide (36). In some cases promotion of sodium helps to hydrogen rich atmospheres at temperature below 500°K (37).

Various authors have studied roles of tin and alkali metals on Pt/Al_2O_3 catalysts. Fabio B.Passos and Martin Schmal (7) indicated that lithium modifies the metal dispersion in the Pt/Al_2O_3 catalysts. Cristina et al. (49) studied stability and regeneration of supported PtSn catalysts doped with potassium for propane dehydrogenation. They observed that potassium added to the Pt/Al_2O_3 blocks acidic sites of the support. It also substantially decreases the deactivation of the catalyst, diminishing the amounts of carbon depositing not only on the support but also on the metal. The coke deposited on Pt displays a lower degree of polymerization. These effects are probably caused by electronic modification of the metallic phase due to the addition of potassium. These results are confirmed by Praserthdam et al. (28) who found that Sn and Sn-alkai metal promoted catalysts show higher excess mobile electrons than unpromoted ones. The excess mobile electrons enhance hydrogen spillover on the catalyst surface, thus reducing the amount of coke deposits.

Generally, tin reduces size of Pt by forming an alloy, which decreases coke formation on Pt (2,19). Verbeek and Sachtler (2) found that the amount of adsorbate (CO) molecules decreased with an enrichment of the alloy surface with tin. In addition, Sn on the Pt/ Al_2O_3 catalysts helps the carbon depositing on the active platinum to migrate onto alumina support surface (33) and as a result, reduces the ability of coke to multibond to the surface (40).

3.2 Hydrogen spillover

3.2.1 Hydrogen adsorption and desorption on the catalysts

Gervasini and Flego (6) studied hydrogen adsorption and desorption on alumina supported platinum-multicomponent catalysts. They observed that platinum was the only active element able to chemisorb hydrogen. In fact, neither the γ-Al_2O_3 support nor the Sn/ γ-Al_2O_3 samples displayed any capability of hydrogen sorption. Adsorption hydrogen can be classified into two kinds of reversible and irreversible adsorption hydrogen. Reversible adsorption hydrogen can be removed from the surface of catalyst by evacuating and purging at the adsorption temperature while irreversible adsorption hydrogen can be desorbed only by raising the temperature (1). Chemisorption of hydrogen at approximately 175°C was shown to be due to reversibly chemisorbed hydrogen. Small hydrogen desorption at about 250°C was speculated to be due to interfacial hydrogen,i.e., a layer of chemisorbed hydrogen between platinum particles and the support, and a large, irreversible hydrogen desorption at 450°C were derived from species always from the platinum cluters,i.e., hydrogen species located on the support (18). Oleg Alexeev et al. (43) observed that hydrogen species desorbed at about 580 °C, originating from water (hydroxyl) species as a result of Pt-catalyzed decomposition. The maximum desorption was observed between 450 and 840 °C.

3.2.2Effect of spillover hydrogen on the catalysts

Definition of spillover at the First Conference on Spillover (44) is as follows: Spillover involves the transport of an active species sorbed or formed on a first phase onto another phase that does not under the same condition sorb or form the species. The result may be the reaction of this species on the second phase with other sorbing gases and /or reaction with, and /or activation of the second phase. Spillover effects have been observed for several small species such as hydrogen (4,12,15,21,22,23,24,25,26,27,34), carbon monoxide, isocyanate functional group and organic species (44).

Marecot et al. (4) studied regeneration of bifunctional catalysts deactivated by coke deposition by hydrogen treatment. They proposed that cracking of coke was due to hydrogen spilling over from metals to alumina. This result agrees with Stanislas Jean Teichner (5) who observed that the spillover of various adsorbed species created a cleaning effect on the poisoning substances such as coke. Consequently, hydrogen spillover on catalytic process may be described as (24) spillover species that (I) keep catalyst clean, (II) create or regenerate selective site through a remote control mechanism, and (III) accelerate, catalytic reaction and inhibit catalyst deactivation. In addition, the spillover effect may promote the catalytic activity and selectivity (5).

The group VIII metal was found as providing the 'portholes' or centers of spillover from the donor D to the acceptor. A support (26) corresponded to the role of platinum is to continuously supply spillover hydrogen to the acidic centers (15,41). Hoang and Lieske (12) studied the effect of hydrogen treatment on ZrO_2 and Pt/ ZrO_2 catalysts. They proposed that platinum promoted the hydrogen uptake by a hydrogen spillover onto the support.

CHAPTER 4

EXPERIMENT

This chapter describes the procedures of catalyst preparation, Temperature-Programmed Reduction (TPR), measurement of coke deposition on metal active site by CO adsorption, dehydrogenation n-hexane, Temperature-Programmed Desorption (TPD) and benzene hydrogenation.

4.1 Catalysts Preparation

Alumina support (obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan) was grounded to the required mesh size of 60/80 and, washed with distilled water 3-4 times to remove the very fine particles and other impurities. Then it was dried at 110 °C overnight. Subsequently, the support was calcined in air at 300 °C for 3 hours.

4.1.1 Preparation of platinum catalysts

-Preparation of impregnation solution

The impregnating solution for two grams of support was prepared by calculating the amount of the chloroplatinic acid (manufactured by Wako Pure Chemical Industries Co., Ltd., Japan.) stock solution (1 gram of chloroplatinic acid in de-ionized water 25 ml.) to the required metal loading. Hydrochloric acid, 5wt% of alumina support, was then added to the solution. De-ionized water was finally added until 2 ml of the solution was obtained.

-Preparation of platinum catalyst

Two grams of alumina support was impregnated with the impregnation solution for 6 hours to obtain good distribution of metal complex. After that the impregnated support was dried at 110 °C in air overnight and the dried material was calcined in air (100 ml/min.) at 500 °C for 3 hours with heating rate of 10 °C/min.

4.1.2 Preparation of platinum-tin catalysts

-Preparation of impregnation solution

The same method used for preparing platinum impregnation solution was employed but stannous chloride dihydrate ($SnCl_2.2H_2O$ manufactured by Fluka Chemie AG, Swizerland) was added to the impregnation solution before impregnating with the support. This method is called "Co- impregnation method".

-Preparation of platinum-tin catalyst

The preparation method was similar to the preparation method of platinum catalyst.

4.1.3 Preparation of platinum-potassium catalysts

-Preparation of impregnation solution

1. Prepare platinum impregnation solution by using the same method as the preparation of platinum solution
2. Prepare potassium solution by mixing potassium nitrate (KNO_3 manufactured by E.Merck, Federal Republic of Germany) at desired amount with water to make 2 ml solution.

-Preparation of platinum-potassium catalyst

The preparation of Pt-K catalyst the same method for preparing Pt catalyst. After calcination of Pt catalyst, the calcined sample was re-impregnated by potassium solution. The re-impregnation sample was calcined again under the same condition.

4.1.4 Preparation of platinum-tin-potassium catalysts

-Preparation of impregnation solution

1. Prepare platinum-tin impregnation solution by using the same method as the preparation of platinum-tin solution
2. Prepare potassium solution by mixing potassium nitrate (KNO_3 manufactured by E.Merck, Federal Republic of Germany) at desired amount with water to make 2 ml solution.

-Preparation of platinum-tin-potassium catalyst

The preparation of Pt-Sn-K catalyst used co-impregnation method, the same method as preparing Pt-Sn catalyst, then followed by re-impregnation. After calcination of co-impregnated Pt-Sn catalyst, the calcine sample was re-impregnated by potassium solution. The re-impregnation sample was calcined again with the same condition.

4.2 Temperature-Programmed Reduction (TPR)

Apparatus

The reducible site was determined by measuring the amount of H_2, which reduced oxide species on the surface. The product of this reaction was water vapor, which was trapped by dried ice mixed with isopropanal. The thermal conductivity detector was used to measure the amount of H_2. The operating condition is summarized in Table 4.1.

Table 4.1 Operating condition of TCD gas detector for temperature programmed reduction:

Carrier gas and flow	5%H_2/Ar 50ml./min.
Temperature of detector	80 °C
Detector current	80 mA

Procedures

1. Catalyst sampled 0.1 g was placed in a sample tube. Flow rate of air through the sample was 100 ml/min. The reactor was heated up to 500°C at a rate of 10 ml/min and, held for 1 hour to ensure that the surface was covered with oxide form.
2. Flow He at 100 ml/min through the sample for 5 minutes and then cool down to room temperature under He atmosphere.
3. After calcination: switch the carrier gas H_2 to flow through the sample at 50 ml/min. Wait until the baseline became constant.
4. The TPR runs were started at 50 °C by allowing the temperature to increase to 700°C at the rate of 10°C /min.

4.3 Measurement of coke deposition on metal active site by CO adsorption

Apparatus

The procedure was divided into 3 parts: measurements of (1) metal active site of fresh catalyst,(2)spent catalyst,(3)regenerated catalyst after coked combustion at 200 °C and 300 °C . The amount of remaining active sites was measured by CO adsorption technique on the basis that one CO molecule adsorbed on one metal active site (45,46). The Thermal Conductivity Detector (GOW MAC) measured the amount of CO adsorbed on the catalyst. Table 4.2 summarized the operating condition of the detector.

Table 4.2 Operating condition of gas chromatograph (GOW MAC)

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

Procedures

1. 0.1 g. of catalyst was placed in the stainless steel tubular reactor. Helium gas was introduced into the reactor at the flow rate of 30 ml/min. The reactor was heated until the temperature reached 200 °C, then the helium gas was changed to hydrogen gas at a flow rate of 100 ml/min. The reactor was continuous by heated at the same rate until the temperature reached 500 °C. The reactor was held at this temperature for 1 hour.
2. The reactor was cooled down to the room temperature.
3. The catalyst was then ready to measure metal active sites; 40 μl of CO gas was injected to the TCD at the injection port. The CO gas injection was repeated until the sample did not adsorb CO gas.
4. The amount of metal active sites of fresh catalyst was calculated from the amount of adsorbed CO gas.
5. To measure the amount of spent metal active sites, the reactor was heated up to 170°C in helium gas for 30 mins to desorb CO gas. The reactor was heated to 200°C and then helium gas was changed to hydrogen until the temperature reaching 500°C.

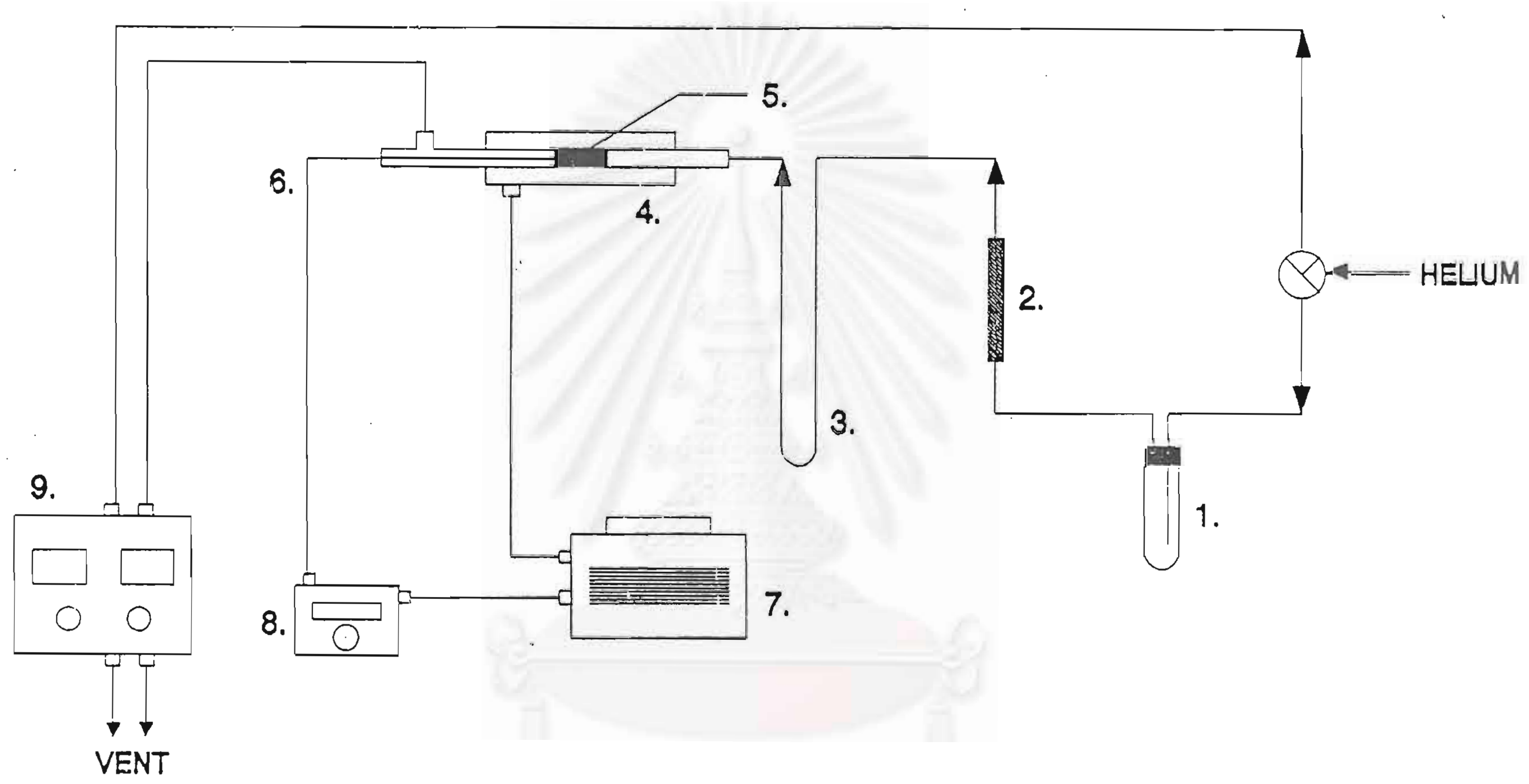
- for the case H_2/HC=O, change hydrogen to high purity argon for 5 mins and then change to the 20% propane in nitrogen.
- for the case $H_2/HC \neq 0$, adjust flow rate of hydrogen to the desired value. Then simultaneously introduce propane to the reactor with hydrogen.

6. When reaching the desired time on stream, change feed gas to helium and cool down the reactor to the room temperature. Then repeat step 3 to obtain the amount of metal active sites of spent catalyst.
7. To measure the amount of metal active sites covered by low temperature coke on the catalyst, the reactor was heated up to 170°C in helium gas for 30 mins to desorb CO gas.
    - for the case of regenerating temperature equal to 200°C, the reactor was

      heated to 200°C then change helium gas to 1 mole % of oxygen for 30 mins.
    - for the case of regenerating temperature equal to 300°C, the reactor was heated to 300°C then change helium gas to 1 mole % of oxygen for 30 mins.

Then cool down the reactor to 150°C in helium, after that, change oxygen to hydrogen at 150°C and hold at this temperature for 3 hours.

8. Switch from hydrogen gas to helium and cool down the reactor to room temperature. Then repeat step 3 to obtain the amount of metal active sites of regenerated catalyst.
9. Calculate amount of total coke, high-temperature coke and low-temperature coke covering on metal active sites.



1. H_2O trap
2. O_2 trap
3. Gas cooler
4. Heater
5. Catalyst bed
6. Thermocouple
7. Variable voltage transformer
8. Temperature controller
9. Thermal conductivity detector

Fig. 4.1 Flow diagram of CO adsorption, H_2-TPD and TPR apparatus

4.4 Dehydrogenation of n-hexane

Apparatus

Selectivity of the aromatization catalyst to dehydrogenation of n-hexane was measured in a conventional microreactor made from a quartz tube. The reaction was carried out under atmospheric pressure. Table 4.3 summarizes the operating condition of the gaschromatograph.

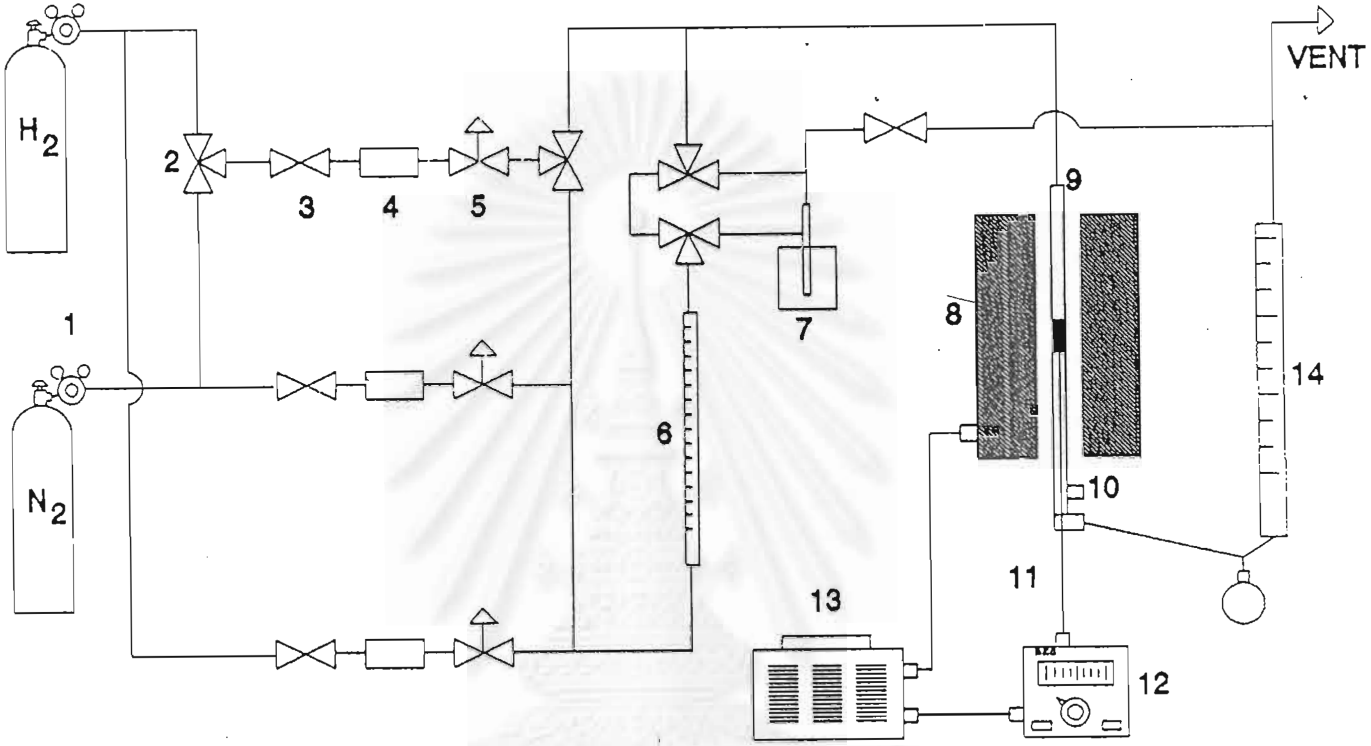
Table 4.3 Operating Conditions of Gas Chromatograph

SHIMADZU GC 14 A, FID	
Detector Type	FID*
Detector Temperature	100 °C
Column Type	Capillary Silicon OV-1, 0.25 mm.x 50m.
Column Temperature	60 °C
Carrier Gas	Nitrogen
Integrator	Chromatopac C-R6A

FID= Flame Ionization Detector

Procedures

Reduction of 100 mg of catalyst was carried out in a micro-catalytic reactor. The reduction was performed at heating rate of 10 °C/min under a hydrogen atmosphere with the flow rate of 100 ml/min and maintained at 500 °C for 1 h. The aromatization of n-hexane was carried out at 460 °C with the hydrogen flow rate of 30 ml/min.



1. Regulator
2. Tree-way valve
3. On-off valve
4. Filter
5. Needle valve
6. Flow meter
7. N-hexane
8. Furnace
9. Reactor
10. Sampling port
11. Thermocouple
12. Temperature controller
13. Variable voltage transformer
14. Bubble flow meter

Figure 4.2 Flow diagram of the n-hexane dehydrogenation system

4.5 Temperature-Programmed Desorption (TPD)

Apparatus

The amount of H_2, which asorded on the surface was determined by rise temperature with rate 10 °C/min. The thermal conductivity detector was used to measure the amount of H_2. Table 4.4 summarizes the operating condition of the detector.

Table 4.4 Operating condition of TCD gas detector for temperature programmed reduction:

Carrier gases and flows	He 30 ml/min
Temperature of detector	80 °C
Detector current	80 mA

Procedures

1. 100 mg of catalyst was packed in the reactor and reduced by hydrogen flowing over catalyst at the rate of 100 ml/min. The reactor was heated up from room temperature to 500°C and maintained at this temperature for 1 hour.
2. The reactor was cooled down from 500°C to the room temperature. Then loaded hydrogen 10 mins. The catalyst adsorbing hydrogen was subsequently purged with He at the same temperature to remove physisorbed hydrogen.
3. The H_2-TPD experiment was carried out in quartz tube from room temperature to 550 °C at rate of 10 °C/min.

4.6 Benzene Hydrogenation

Apparatus

The activity of catalyst for benzene hydrogenation was measured in a conventional microreactor made from quartz tube. The reaction was carried out under atmospheric pressure. Table 4.5 summarizes the operating condition of the detector.

Table 4.5 Operating Conditions of Gas Chromatograph

SHIMADZU GC 14 A, FID	
Detector Type	FID*
Detector Temperature	100 °C
Column Type	Capillary Silicon OV-1, 0.25 mm.x 50m.
Column Temperature	60 °C
Carrier Gas	Nitrogen
Integrator	Chromatopac C-R6A

FID= Flame Ionization Detector

Procedures

1. 100 mg of catalyst was packed in the reactor and reduced by hydrogen flowing over catalyst at the rate of 60 cm^3 per minute. The reactor was heated up from room temperature to 400°C and maintained at this temperature for 1.5 hours.
2. The reactor was cooled down from 400°C to reaction temperature of 100°C and held at this temperature for 10 minutes. The hydrogen-benzene mixture, from another line, with the same flow rate of 60 cm^3 per minute was fed into the reactor, replacing the flow of pure hydrogen. The mixture was obtained by passing hydrogen through the benzene vaporizer.
3. Gas Chromatograph was used to analyze the quantity of benzene and cyclohexane in the sample from the reactor. The conversion of the reaction was then calculated from the obtained data.

CHAPTER 5

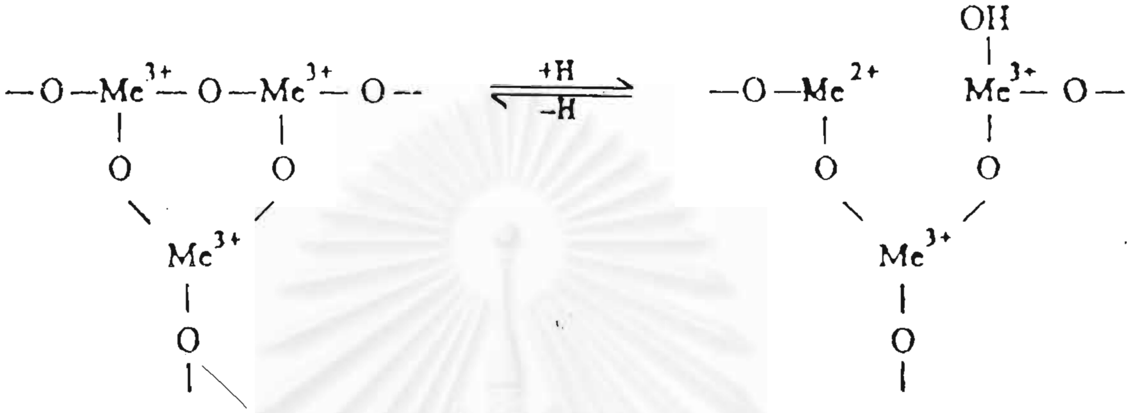
RESULTS AND DISCUSSION

In this chapter, the experimental results and discussion are divided into four sections: 5.1) Temperature-programmed desorption (TPD), 5.2) temperature-programmed reduction (TPR), 5.3) dehydrogenation of n-hexane and 5.4) effect of promoter on low temperature coke on metal active site

5.1 Temperature-Programmed Desorption (TPD)

Hydrogen Temperature Programmed Desorption (H_2-TPD) was used to determine the quantity of chemisorbed hydrogen. H_2 desorption at high teperature (usually interpreted as spillover hydrogen) occurring under TPD conditions is the reoxidation of reduced surface sites by OH groups (on alumina) (17). So, this work studies the presence of hydrogen spillover by using H_2- TPD.

Figure 5.1 shows board bands of γ-Al_2O_3, Sn-K/Al_2O_3, Pt/ Al_2O_3, Pt-K/ Al_2O_3, PtSn/ Al_2O_3, and Pt-Sn-K/ Al_2O_3 obtained from H_2-TPD. It was found that H_2 uptake of Pt-Sn-K/ Al_2O_3 was higher than those of Pt-Sn/ Al_2O_3, Pt-K/ Al_2O_3, and Pt/Al_2O_3. In addition, H_2 uptake of PtSn/ Al_2O_3 was close to that of Pt-K/ Al_2O_3 but it was higher than that of Pt/Al_2O_3. Board band at low temperature (T<450°C) represented desorbed hydrogen from Pt (18, 19, and 27) while the band at high temperature (T> 450°C) represented desorbed hydrogen from Al_2O_3 (9, 18, 19) which occurred from reoxidation of reduced parts of the support by -OH group (17, 43). The -OH groups on alumina took place at high temperature reduction condition. The alumina surface (impurities on it) was reduced by spillover hydrogen, forming - OH groups, as shown by the following reaction: (17)



It was also concluded by Badenes et al. (1997) that deuterium desorption at temperature higher than 377 °C can be assigned to desoption of spillover deuterium (because his work used different carbon as support and hydrogen can be desorbed from the bare support).

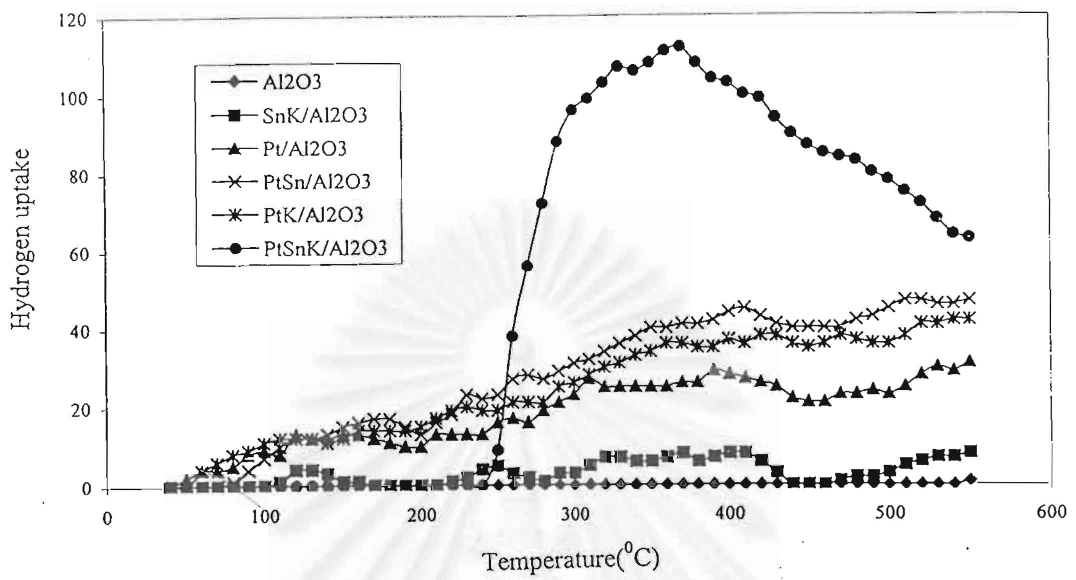


Figure 5.1 The temperature-programmed desorption (TPD) profiles of catalysts

Sn-K/Al_2O_3 shows the little H_2 uptake while γ-Al_2O_3 does not show H_2 uptake (6, 41). This result shows that only hydrogen adsorbed on Pt metal and then dissociated apart on Pt to be hydrogen species (21, 22). It agrees with the result of Yang et al. (1997) who observed that the transition metal sulfides such as NiS could dissociate gaseous hydrogen species. Thus desorbed hydrogen from Al_2O_3 of Pt/Al_2O_3, Pt-Sn/ Al_2O_3, Pt-K/Al_2O_3, and Pt-Sn-K/Al_2O_3 catalyst was hydrogen spillover from Pt to Al_2O_3 (15, 21) or hydrogen spillover from metal to support (4,12, 15, 21, 22, 23, 24, 25, 26, 27, 34)

The results also show that addition Sn and alkali metal enhances the ability of hydrogen spillover on the Pt/γ-Al_2O_3 catalyst. However, the promotion of the catalyst with both metals provides the highest improvement.

5.2 Temperature-programmed reduction (TPR)

Quantitative determination of reduced oxygen on the catalysts by Temperature-programmed reduction (TPR) technique is related to the quantity of reducing hydrogen. If the quantity of oxygen is high, the ability of hydrogen adsorption of the catalyst is high too. So that, TPR can be employed to determine the quantity of adsorbed hydrogen.

The TPR profiles of Pt, Pt-Sn, Pt-K, and Pt-Sn-K supported on Al_2O_3 are shown in Figure 5.2. It was found that Pt/Al_2O_3 catalyst gave the least H_2 uptake while H_2 uptake of Pt-Sn/ Al_2O_3 in the vicinity Pt-K/ Al_2O_3 catalyst and PtSnK/ Al_2O_3 catalyst had the best H_2 uptake. This result supported the result from H_2-TPDmeasurements (Figure 5.1)

The H_2-TPD (Figure 5.1) and TPR (Figure 5.2) supported that the addition of Sn and K contributed to the increase of hydrogen adsorption on the catalyst (6, 28) and the promotion of Sn in cooperating with K to the catalyst provided the best composition for hydrogen spillover on the catalyst.

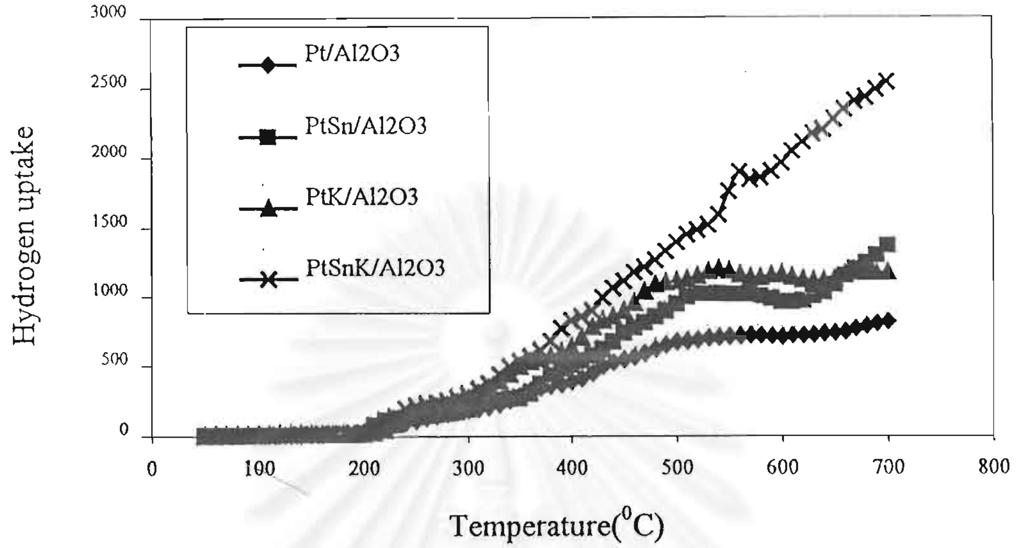


Figure5.2 The temperature-programmed reduction (TPR) of catalysts

5.3 Benzene Hydrogenation

Benzene hydrogenation could determine ability of adsorbed hydrogen because this reaction occurred on metal active site (32). High conversion of benzene reflects that the catalyst had low ability of hydrogen spillover.

From the experimental result, H_2-TPD (Figure 5.1) and TPR (Figure 5.2) were used to display the hydrogen spillover of catalysts which was found to follow the sequence: Pt-Sn-K/Al_2O_3 > Pt-Sn/Al_2O_3 >Pt-K/Al_2O_3 > Pt/Al_2O_3 which agree with Figure 5.3. Figure 5.3 showed the benzene conversion follow the sequence Pt/ Al2O3> Pt-K/Al_2O_3> Pt-Sn/Al_2O_3> Pt-Sn-K/Al_2O_3.

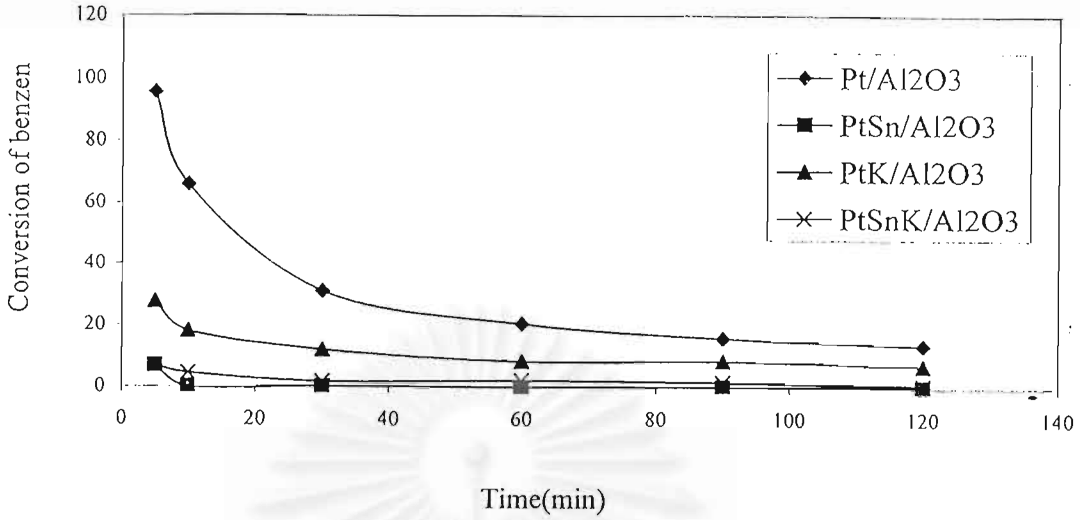


Figure5.3 conversion of benzene hydrogenation of catalysts

From the above result, it could describe that in the case Pt/Al_2O_3 catalyst, a little of hydrogen spillover from metal to support so that the many hydrogen atoms remain on metal. Reaction of dehydrogenation of benzene occurs plentiful; thus benzene conversion is high. For the case of Pt-Sn-K/ Al_2O_3, a large of hydrogen spillover from metal to support so that a little of hydrogen atom remain on support thus the benzene dehydrogenation occurs less than. The value of benzene conversion is low. It concludes that the ability of hydrogen spillover formation of catalysts follow as: Pt-Sn-K/ Al_2O_3 > Pt-Sn/ Al_2O_3 > Pt-K/ Al_2O_3 > Pt/ Al_2O_3.

5.4 Dehydrogenation of n-hexane

Weiqi Lu et al. (1997) uses the dehydrogenation of n-hexane to classify the type of hydrogen spillover on Pt/ Al_2O_3 and zeolite.

Dehydrogenation of n-hexane could be employed to classify the types of hydrogen spillover (reversible hydrogen spillover or irreversible hydrogen spillover) the quantitative determination of benzene (aromatic compound) which was the product of this reaction. Irreversible hydrogen spillover was favorable to aromatization reaction whereas reversible hydrogen spillover to the catalyst life (32).

From the experiment all results, H_2-TPD (Figure 5.1) and TPR (Figure 5.2) showed that hydrogen spills over from Pt to Al_2O_3. Chen et al. (1993) detected two types of hydrogen adsorption on Pt/ Al_2O_3 and Pt-Ga/ Al_2O_3 at 450 °C, which is the temperature of reforming reaction. They further confirmed that the results from the reversible and irreversible spillover hydrogen and the adsorption of hydrogen on Pt/ Al_2O_3 at 450 °C is a characteristic of the supported Pt catalyst because no adsorption of hydrogen on Pt black at the same temperature was detected. The irreversible spillover hydrogen was favorable to amortization reaction and reversible spillover hydrogen to the catalyst life (32). However, in order to classify the group of hydrogen spillover in this study, dehydrogenation of n-hexane was carried out.

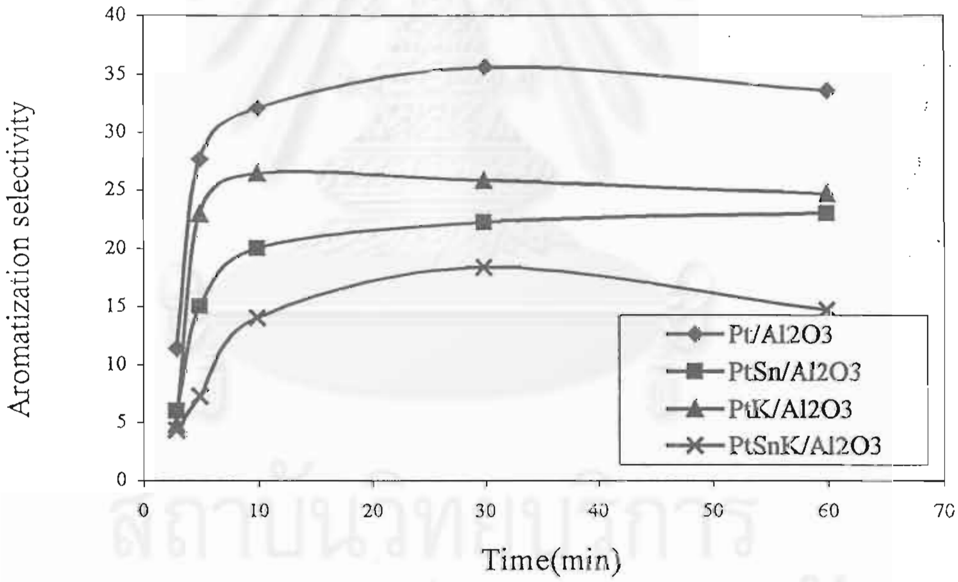


Figure5.4 Aromatization selectivity of catalysts

It can be seen in Figure 5.4 that aromatization selectivity of n-hexane on the catalysts decreased in the following: Pt/ Al_2O_3 > Pt-K/Al_2O_3 > Pt-Sn/Al_2O_3 > Pt-Sn-K/Al_2O_3. Selectivity of Pt/ Al_2O_3 is twice as high as that of Pt-Sn-K/Al_2O_3. Weiqi Lu et al. (1997) observed that the irreversible spillover hydrogen was favorable to amortization reaction and reversible spillover hydrogen to the catalyst life. From Figure 5.5-Figure 5.12 showed the catalytic deactivation rate on the catalysts. They decreased in the sequence: Pt/ Al_2O_3> Pt-K/Al_2O_3, Pt-Sn/Al_2O_3> Pt-Sn-K/Al_2O_3. From the above results, it can be concluded that the reversible spillover hydrogen on the catalysts decreased in sequence: Pt-Sn-K/Al_2O_3> Pt-K/Al_2O_3, Pt-Sn/Al_2O_3> Pt/ Al_2O_3. In the other words, addition of Sn and K contributed the ability of reversible hydrogen spillover on the catalysts. This agrees with the results from the previous two studies.

5.5 Effect of promoter on low temperature coke deposition on metal active site

Since promoters provided significant effect on active sites and behavior of catalyst deactivation by coke formation. This study investigated the influence of promoters on low temperature coke on regeneration at different temperature of Pt/Al_2O_3, Pt-K/Al_2O_3, Pt-Sn/ Al_2O_3, and Pt-Sn-K/Al_2O_3. It was found from Figure 5.5, 5.7, 5.9 and 5.11 that when temperature of regeneration was increased from 200°C to 300° C, the percentage of low temperature coke on metal active sites increased significantly. However, the characteristic of the curves was not changed. In addition, It shows that the determination of percentage of low temperature coke on metal active sites was not necessary to be carried out at 200°C but the catalysts could be regenerated at any temperature because the characteristic of curve were similar.

Figure 5.5, the change of curve with time on stream could describe the change of low temperature coke covered active sites follows: at the starting time, low temperature coke form a little and then increase to the maximum value according the shown curve. After that, the part of low temperature of coke change to be high temperature coke, the low temperature coke will decrease so that the curve drop to be a constant value.

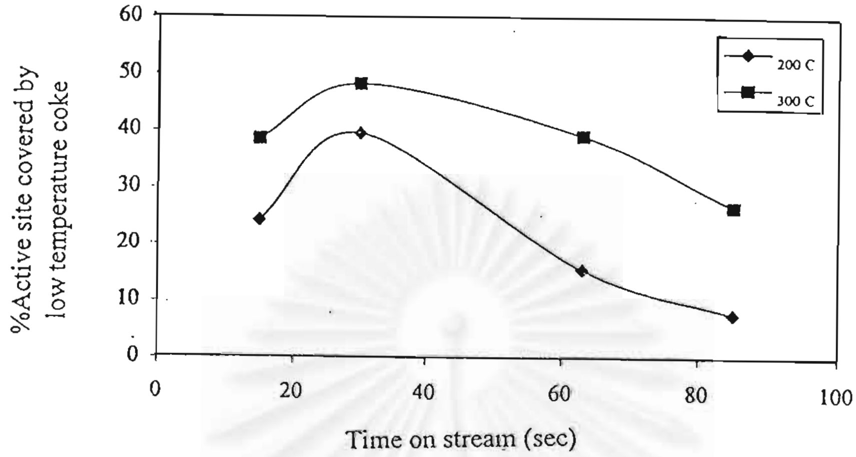


Figure 5.5 **%Active site covered by low temperature coke of Pt/Al_2O_3 at reaction temperature 500 °C, GHSV=22,525 hr^{-1},100%propane regeneration temperature 200 °C and 300 °C,H_2/HC=0**

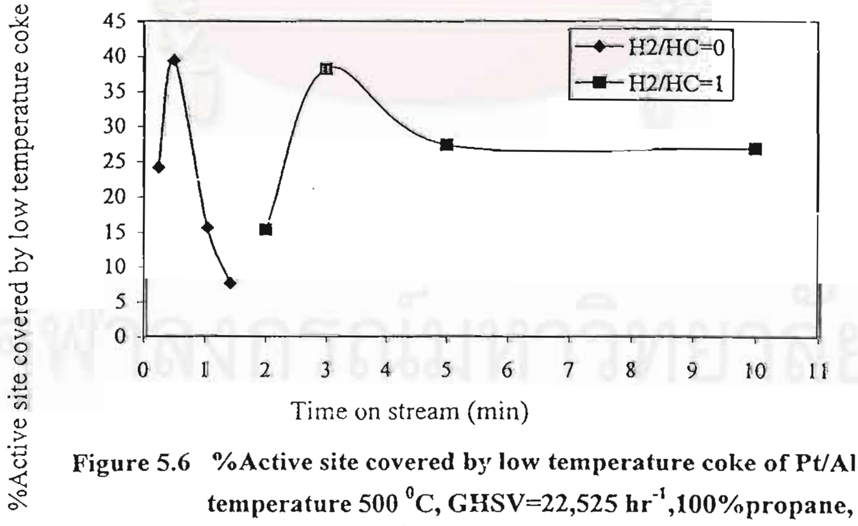


Figure 5.6 **%Active site covered by low temperature coke of Pt/Al_2O_3 at reaction temperature 500 °C, GHSV=22,525 hr^{-1},100%propane, regeneration temperature 200°C**

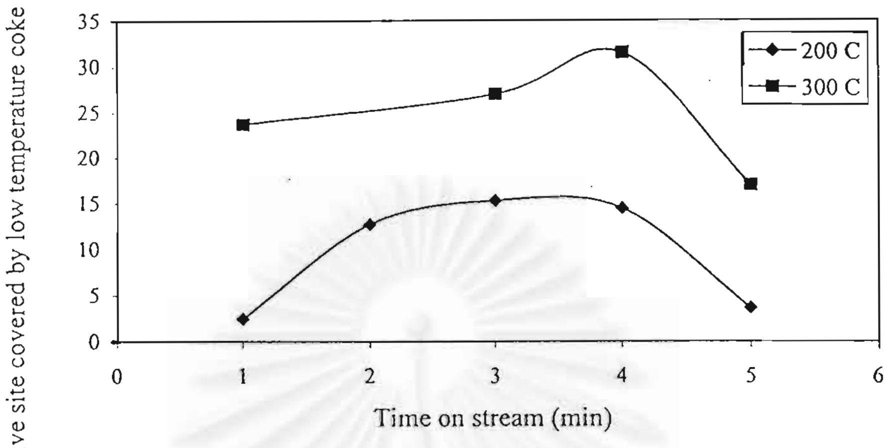


Figure 5.7 %Active site covered by low temperature coke of PtSn/Al_2O_3 at reaction temperature 500 ^{0}C, GHSV=22,525 hr^{-1},100%propane, regeneration temperature 200^{0}C and 300^{0}C,H_2/HC=0

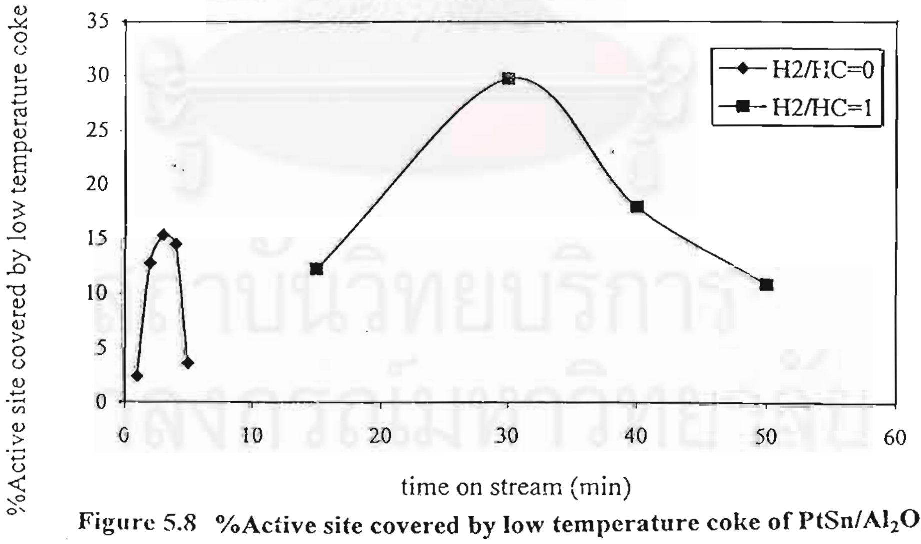


Figure 5.8 %Active site covered by low temperature coke of PtSn/Al_2O_3 at reaction temperature 500 ^{0}C, GHSV=22,525 hr^{-1},100%propane, regeneration temperature 200^{0}C

Figure 5.6, 5.8, 5.10 and 5.12 showed the percentage of active sites covered by low temperature coke at different ratio of H_2/HC of Pt/ Al_2O_3, Pt-K/Al_2O_3, Pt-Sn/Al_2O_3, and Pt-Sn-K/Al_2O_3 catalysts, respectively. It was observed that the increase of the ratio of H_2/HC from 0 to 1 increased the lifetime of the catalysts (time on stream).

According to Figure 5.5-5.12, It was shown that the lifetime of the catalysts followed the sequence: Pt-Sn-K/Al_2O_3 > Pt-K/Al_2O_3, Pt-Sn/Al_2O_3 > Pt/Al_2O_3. It postulated that the increase of catalyst lifetime was affected by hydrogen spillover. This agrees with the results of Stanislas Jean Teichner (1990) that the spillover of various adsorbed species creates a cleaning effect on the poisoning substances like coke on the catalyst. The lifetime increased when hydrogen was fed in the feed stream of Pt-Sn-K/Al_2O_3, as shown in Figure 5.12. The lifetime of Pt-Sn-K/Al_2O_3 with the H_2/HC of 1 was higher than that of Pt-Sn-K/Al_2O_3 with H_2/HC of 0. Similar results were observed for Pt-Sn/ Al_2O_3 (Figure 5.8) and Pt-K/Al_2O_3 (Figure 5.12). The lifetime increases as follows: Pt-Sn-K/Al_2O_3 > Pt-K/Al_2O_3, Pt-Sn/ Al_2O_3 > Pt/ Al_2O_3 with the similar manner for the increase of the amount of reversible hydrogen spillover.

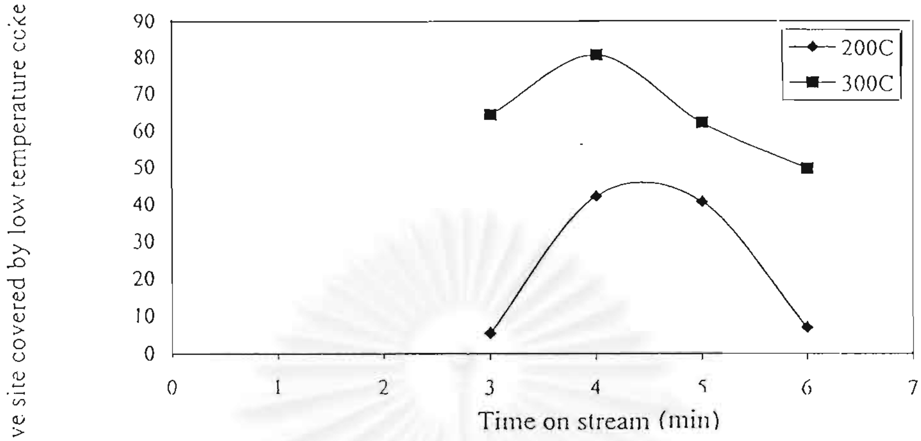


Figure 5.9 %Active site covered by low temperature coke of PtK/Al_2O_3 at reaction temperature 500 ^{0}C, GHSV=22,525 hr^{-1},100%propane, regeneration temperature 200^{0}C and 300^{0}C,H_2/HC=0

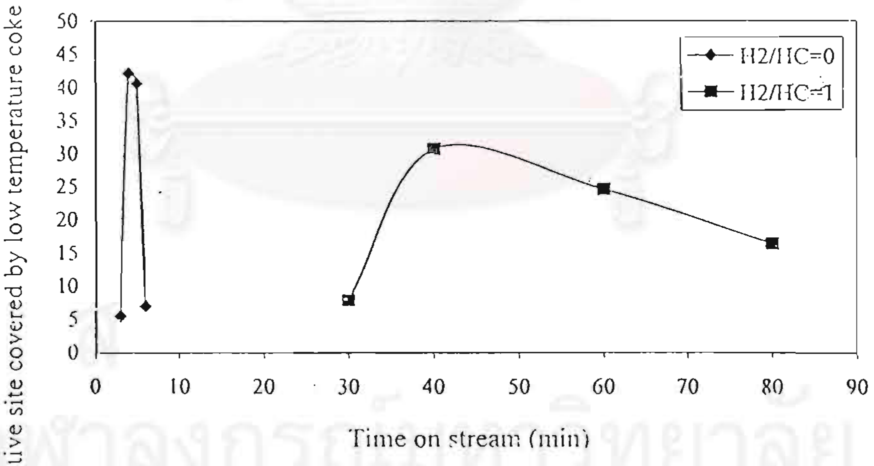


Figure 5.10 %Active site covered by low temperature coke of PtK/Al_2O_3 at reaction temperature 500 ^{0}C, GHSV=22,525 hr^{-1},100%propane, regeneration temperature 200^{0}C

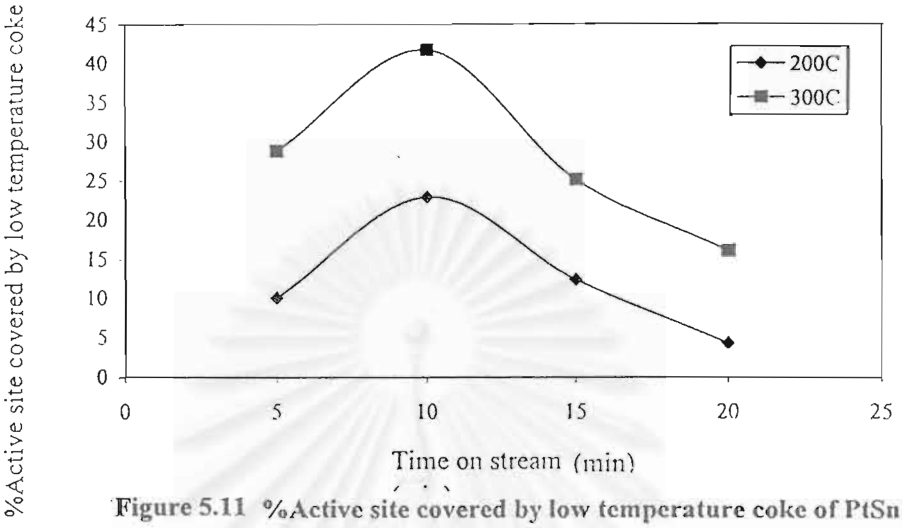


Figure 5.11 %Active site covered by low temperature coke of $PtSnK/Al_2O_3$ at reaction temperature 500 °C, GHSV=22,525 hr^{-1},100%propane, regeneration temperature 200 °C and 300 °C,$H_2/HC=0$

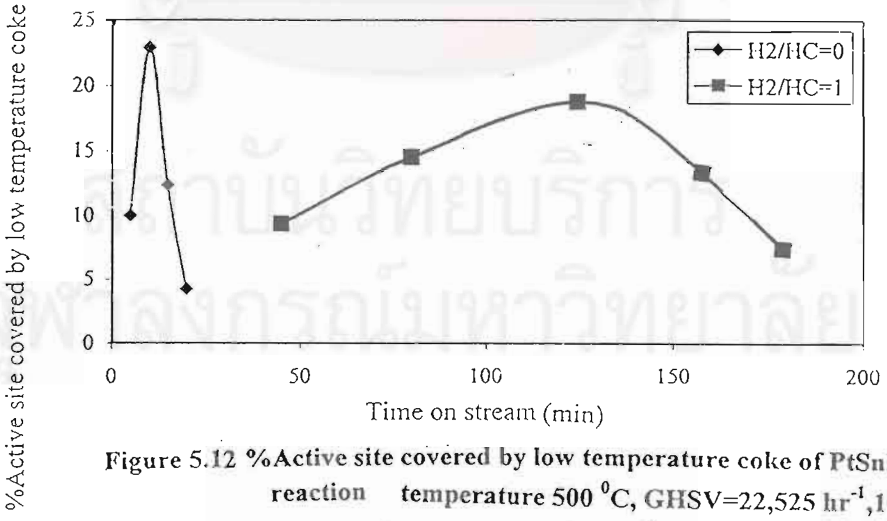


Figure 5.12 %Active site covered by low temperature coke of $PtSnK/Al_2O_3$ at reaction temperature 500 °C, GHSV=22,525 hr^{-1},100%propane, regeneration temperature 200 °C

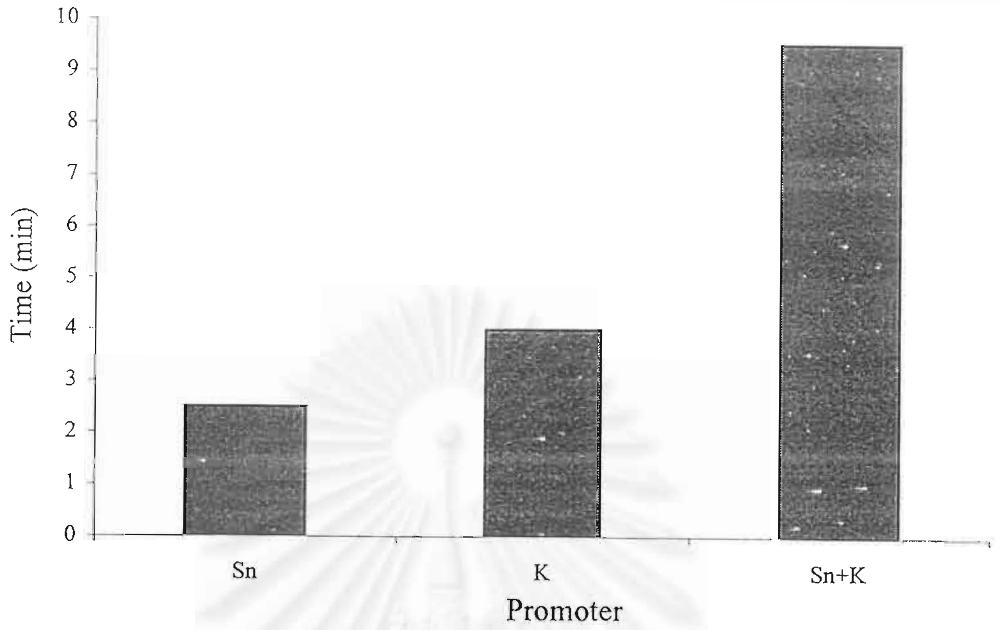


Figure 5.13 Effect of promoter on time of maximum peak of %active site covered by low temperature coke of Pt/Al$_2$O$_3$

Figure 5.13 showed the maximum peak of % active site covered by low temperature coke at ratio of H_2/HC = 0 and the regeneration temperature = 200 °C. It showed that doping of Sn, K and both of Sn and K on Pt/Al_2O_3 catalyst changed the maximum peak of % active site covered by low temperature coke to be 2.5, 4 and 9.5 mins. The maximum peak of doping of both of Sn and K was not equal to the summation of maximum peak of doping Sn and K because of syngeristic effect of Sn and K. The maximum peak at longer time showed the higher ability of catalyst to reduce coke formation on metal active site than the maximum peak of the catalyst at shorter time. It could explain that if catalyst had maximum peak at shorter time, the coke deposited faster on metal active sites to decrease the quantity of maximum peak. On the other hand, maximum peak at longer time showed that the ability of coke deposition on metal active site was slower.

From that above reason, PtSnK/Al_2O_3 catalyst is the best catalyst with the slowest coke formation.

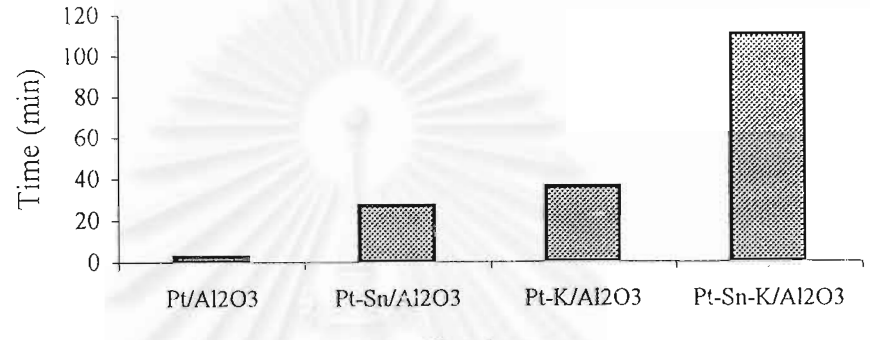


Figure 5.14 Effect of H_2/HC ratio changed from 0 to 1 on time of maximum peak of % active site covered temperature coke of the catalysts

Figure 5.14 show ΔT of maximum peak of %active site covered by low temperature coke at ratio of H_2/HC which change from 0 to 1 and the regeneration temperature = 200°C. It show that doping of H_2 in feed stream which cause Pt/Al_2O_3, Pt-Sn-K/Al_2O_3, Sn-Pt/Al_2O_3, and K-Pt/Al_2O_3 catalyst change the ΔT of maximum peak of %active site covered by low temperature coke to be 2.5, 27, 35.5, and 110, subsequently. ΔT of both of Sn and K was not equal to the summation of ΔT of doping Sn and K, which the reason was same as Figure 5.13. ΔT that was wide shown the higher ability of catalyst, which could form the higher hydrogen spillover, too. Because of hydrogen spillover contribute to decrease the low temperature coke formation on metal active site, thus it caused to slow the coke deposition on metal active site when the H_2/HC became from 0 to 1. While ΔT that was narrow gave the opposite result from the above reason, Pt-K-Sn/Al_2O_3 catalyst was the best catalyst with the higher ability hydrogen spillover.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

1. Hydrogen Temperature Programmed Desorption (H_2-TPD) was used to display the hydrogen spillover of catalysts which was found to follow the sequence: Pt-Sn-K/Al_2O_3> Pt-Sn/Al_2O_3, Pt-K/Al_2O_3 > Pt/Al_2O_3. It was concluded that Sn and K affected the adsorption and spillover of hydrogen on the Pt/Al_2O_3 catalyst. Promotion with Sn and K could enhance hydrogen spillover, especially reversible hydrogen spillover, on the catalysts at high level promotion with either Sn or K only.

2. The result from Temperature-programmed reduction (TPR) supported that the addition of Sn and increased hydrogen adsorption on the catalyst. In addition, the the promotion of Sn incorporating with K was the best composition enhancing the hydrogen spillover on the catalysts.

3. The experimental results show that the aromatization selectivity of hexane on the catalysts decreased in the sequence: Pt/ Al_2O_3 > Pt-K/Al_2O_3 > Pt-Sn/Al_2O_3 > Pt-Sn-K/Al_2O_3 and the catalytic deactivation rate on the catalysts decreased in the sequence: Pt/ Al_2O_3> Pt-K/Al_2O_3, Pt-Sn/Al_2O_3> Pt-Sn-K/Al_2O_3. Investigation results from the literature reviews that the irreversible spillover hydrogen was favorable to amortization reaction and reversible spillover hydrogen to the catalyst life was used to conclude that the reversible spillover hydrogen on the catalysts decreased in the sequence: Pt-Sn-K/Al_2O_3> Pt-K/Al_2O_3, Pt-Sn/Al_2O_3> Pt/ Al_2O_3. The increase of catalyst life was due to hydrogen spillover, especially reversible hydrogen spillover.

Recommendation

It was clearly shown that addition of Sn and K to Pt/Al_2O_3 enhances hydrogen spillover, especially, reversible hydrogen spillover. It is recommended that promotion with others metals such as Na, Li, and Cs on the Pt/Al_2O_3 catalyst should also be investigated. Even though the other alkali metals should provide the same trend, the degree of hydrogen may be different.

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APPENDICES

APPENDIX A

Sample of calculation for catalyst preparation

The sample of calculation shown below is for 0.3 wt.% Pt- 0.3 wt.% Sn-0.6 wt.% K/γ-Al_2O_3 catalyst. The hydrochloric acid is also added to the impregnating solution by 5 wt % of the alumina support. The alumina support weight used for all preparation is 2 grams.

If X grams of alumina support is used, so each 100 grams of the catalyst is composed of

	Platinum	0.3	g.
	Tin	0.3	g.
	Potassium	0.6	g.
	Hydrochloric acid	0.05*X	g.
	Alumina support	X	g.
Then	0.3+0.3+0.6+(0.05*X)+X	= 100	g.
	X	= 94.0952	g.

The platinum compound used is chloroplatinic acid ($H_2PtCl_6.6H_2O$), its molecular weight is 517.92, and the platinum content in the compound is 37.67 wt %. The stock solution of chloroplatinic acid has the concentration of 1 g in 25 ml. of water.

The tin compound used is stannous chloric dihydrate ($SnCl_2$. $2H_2O$), its molecular weight is 118.69, and the tin content in the compound is 51.02 wt %.

The potassium compound used is potassium nitrate (KNO_3), its molecular weight is 101, and potassium content is 38.61 wt%. The stock solution of potassium nitrate has the concentration 3 g. in 25 ml. of water.

Concentration of hydrochloric acid solution is 37 % volume by volume, its density is 1.19 kg/l.

The calculation procedure of the amount of each ingredient for the required composition of the 0.3 wt% Pt-0.3 wt% Sn-0.6 wt% K catalyst shows below.

For two grams of alumina support used:

1. Platinum required = (0.3x2)/94.10 g.
   = 6.37x10^{-3} g.
   Chloroplatinic acid required = 6.37x10^{-3}x100x25/37.67 ml.
   = 0.4232 ml.
2. Tin required = 2x0.3/94.0952 g.
   = 6.37x10^{-3} g.
   Stannous chloride dihydrate required = 6.37x10^{-3}x100/51.02 g.
   = 0.0125 g.
3. Potassium required = 2x0.6/94.0952 g.
   = 0.0128 g.
   Potassium nitrate required = 0.0128x100x25/(38.61x3) ml.
   = 0.2763 ml.
4. Hydrochloric and solution required = 2x0.05 g.
   = 0.1 g.

The amount of hydrochloric and by volume
= 0.1/(1.190x0.37) ml.
= 0.2271 ml.

As the pore volume of the alumina support is 1 ml/g, the total volume of impregnating solution that must be used is 2 ml by the requirement of dry impregnation method, the de-ionized water is added until the volume of impregnating solution is 2 ml as equal to the volume of the alumina pore volume.

APPENDIX B

Calculation of metal active sites

The calculation of metal active sites of the catalyst by purity CO adsorption at room temperature has the procedure as follows:

Let the weight of catalyst used = W g.

Height of CO peak after adsorption = A unit.

Height of 40 μl. standard CO peak = B unit.

Amounts of CO adsorbed on catalyst = B-A unit

Volume of CO adsorbed on catalyst = [(B-A)/B](40) μl.

Volume of gas 1 mole at 30 °C = 24.86×10^{6} μl.

Mole of CO adsorbed on catalyst = $[(B-A)/B](40/24.86 \times 10^{6})$ mole.

Molecule of CO adsorbed on catalyst= $1.61 \times 10^{-6}\,[(B-A)/B](6.02 \times 10^{23})$ molecules

Metal active sites = $\{9.68 \times 10^{17}[(B-A)/B]\}/W$ molecules of CO/g. catalyst

APPENDIX C

The amounts of covered metal active sites by coke deposition

Calculation of amount of metal active sites covered by coke deposition

A = Metal active sites of fresh catalyst.

B = Metal active sites of spent catalyst.

C = Metal active sites of regenerated catalyst at 200 °C

%Total coke covered on metal active sites (%TC) = [(A-B)/A] x100

%Height temperature coke covered on metal active sites (%HC) = [(A-C)/A] x100

%Low temperature coke covered on metal active sites (%LC) = [(C-B)/A] x100

APPENDIX D

Calibration curve of benzene and n-hexane

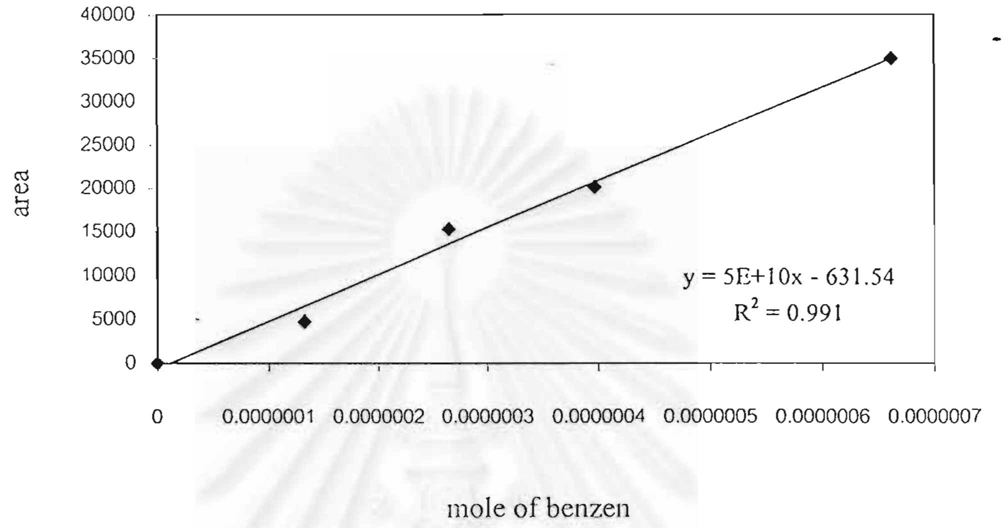
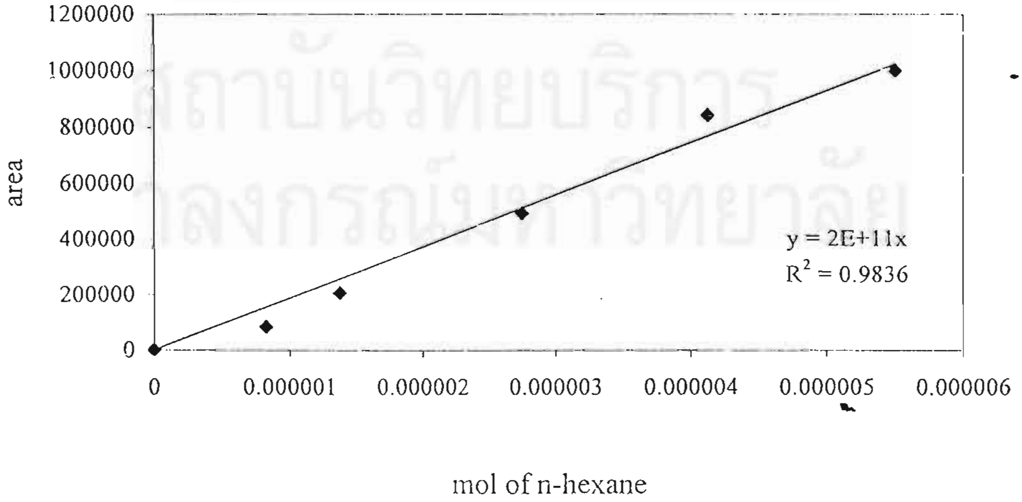


Figure D.1 caribation curve of benzen



FigureD.2 caribation curve of n-hexane

VITA

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