รายงานการวิจัย

เรื่อง การผลิตสารอะโรเมติกส์จากนอร์มัลอัลเคนโดยใช้ตัวเร่งปฏิกิริยาชนิดแพลททินัมบนซีโอไลต์แอลที่ได้ปรับปรุงคุณภาพให้ดีขึ้น

(n-ALKANE AROMATIZATION OVER MODIFIED Pt SUPPORTED KL ZEOLITES)

โดย

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ABSTRACT

From previous studies, Sn-promoted Pt/KL prepared by vapor-phase co-impregnation exhibited high stability and selectivity to C8-aromatics for n-octane aromatization. Although the Pt/KL has many benefits, one of the serious drawbacks is its sensitivity to sulfur poisoning. Based on previous investigations, the addition of rare earth elements (RE; e.g. Tm, Ce, and Dy) into Pt/KL could improve sulfur tolerance of the catalysts. In this work, the sulfur resistance of PtSn/KL and RE-promoted PtSn/KL has been studied. PtSnRE/KL catalysts with Pt:Sn:RE ratio of 1:1:0.15 were prepared by sequential RE, then co-PtSn impregnation. The catalysts were characterized by TPR, TPO, H_2 chemisorption, and TEM. The reaction was carried out at 500°C and atmospheric pressure. The results showed that the activity and selectivity obtained with sulfur-containing feed was lower than those obtained with clean feed. In the presence of sulfur, PtSnRE/KL demonstrated higher conversion than Pt/KL and PtSn/KL, while the selectivity was not significantly improved. TPR profiles show the rupture of Pt-Sn alloy after exposing to sulfur. Even though TEM image showed higher distributed metal clusters on PtSn/KL and PtSnRE/KL, they exhibited much lower H_2 chemisorption which could be because Sn partially covered the platinum surface or modified electronic property resulted in low H_2 adsorption.

บทคัดย่อ

จากการศึกษาที่ผ่านมาพบว่าการเติมโลหะดีบุกลงบนตัวเร่งปฏิกิริยาแพลททินัมบนซีโอไลต์แอล (PtSn/KL) ซึ่งเตรียมสารตัวอย่างโดยวิธีการระเหิดสารประกอบแพลททินัมและดีบุกเข้าไปยังโพรงซีโอไลต์พร้อมกันมีความเสถียรและความเลือกเฉพาะกับผลิตภัณฑ์อะโรมาติกซ์ที่มีอะตอมคาร์บอน 8 อะตอมสูงสำหรับปฏิกิริยาอะโรมาไทเซชันของนอร์มัลออกเทน ถึงแม้ว่าตัวเร่งปฏิกิริยา Pt/KL จะมีข้อดีมากมาย แต่หนึ่งในข้อเสียที่สำคัญคือความว่องไวต่อการเป็นพิษของซัลเฟอร์ จากการศึกษาก่อนหน้าพบว่าการเติมธาตุหายาก (Rare earth: RE) เช่น ทูเลียม ซีเรียม และดิพโพเซียมลงบน Pt/KL น่าจะเพิ่มความทนทานต่อการเป็นพิษของซัลเฟอร์ของตัวเร่งปฏิกิริยาได้ ดังนั้นในงานวิจัยนี้จึงศึกษาความต้านทานต่อซัลเฟอร์ของตัวเร่งปฏิกิริยา PtSn/KL แบบที่มีและไม่มีการเติมธาตุหายากลงบนตัวเร่งปฏิกิริยานี้ (PtSnRE/KL) ตัวเร่งปฏิกิริยา PtSnRE/KL ที่มีสัดส่วนสารเคมี Pt:Sn:RE เท่ากับ 1:1:0.15 ถูกเตรียมโดยวิธีการระเหิดสารประกอบธาตุหายากบนซีโอไลต์ KL ก่อน และตามด้วยการระเหิดสารผสมแพลททินัมและดีบุกเข้าไปพร้อมกัน ตัวเร่งปฏิกิริยาถูกวิเคราะห์หาคุณสมบัติด้วยเทคนิคต่างๆ ได้แก่ ความสามารถในการดูดซับแก๊สไฮโดรเจน TPR TPO และ TEM การทดสอบตัวเร่งปฏิกิริยาสำหรับการเร่งปฏิกิริยาอะโรมาไทเซชันของนอร์มอลออกเทนทำที่อุณหภูมิ 500 องศาเซลเซียส และที่ความดันบรรยากาศ ผลการทดลองพบว่าความสามารถในการเกิดปฏิกิริยาและความเลือกเฉพาะกับผลิตภัณฑ์ที่ได้จากสารตั้งต้นที่เติมซัลเฟอร์ต่ำกว่าสารตั้งต้นที่ไม่มีซัลเฟอร์ การที่มีซัลเฟอร์ปรากฏอยู่ทำให้ปฏิกิริยา PtSnRE/KL มีการเปลี่ยนแปลงจากสารตั้งต้นไปเป็นผลิตภัณฑ์สูงกว่า Pt/KL และ PtSn/KL ในขณะที่ความเลือกเฉพาะกับผลิตภัณฑ์ไม่ได้ดีขึ้นอย่างชัดเจน รูปโครงร่างของ TPR แสดงให้เห็นถึงการแยกออกจากกันของอัลลอยด์ Pt-Sn เมื่อสารตั้งต้นมีซัลเฟอร์ เจือ ถึงแม้ว่ารูปของ TEM เปิดเผยถึงการกระจายตัวอย่างสูงของกลุ่มโลหะบน PtSn/KL และ PtSnRE/KL แต่จากการศึกษาความสามารถในการดูดซับแก๊สไฮโดรเจนพบว่าตัวเร่งปฏิกิริยาทั้งสองตัวมีการดูดซับแก๊สไฮโดรเจนที่ต่ำ ทั้งนี้อาจเนื่องมาจากการที่ดีบุกปกคลุมลงบนผิวหน้าของทแพลททินัมส่งผลให้มีการดูดซับแก๊สไฮโดรเจนต่ำลง

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CHAPTER I
INTRODUCTION

One of the most important reactions in the refinery to obtain high value-added products from naphtha feedstock is the aromatization of paraffins to aromatics. In 1980, Bernard found the exceptionally high activity of platinum supported on alkaline LTL zeolite (Pt/KL) for the aromatization of *n*-hexane that is very efficient for the direct dehydrocyclization of *n*-hexane into benzene (Bernard, 1980). However, the unique behavior observed for *n*-hexane in terms of selectivity and catalyst life was not presented for *n*-octane (Huang *et al*., 1992). The selectivity for *n*-octane aromatization was still low and quickly dropped after a few hours on stream due to coke plugging in the pore of KL zeolite (Jongpatiwut *et al*., 2003). The expected products of this reaction are ethylbenzene (EB) and *o*-xylene (OX) from a direct six-membered ring closure; nevertheless, the product distribution showed benzene and toluene as major aromatic products with small quantities of EB and OX. To increase the desired products, the modification of the Pt catalyst with a second metal like Re, Ir, W, and in particular with Sn as a promoter in the zeolite provided better catalytic activity, stability, and higher product selectivity for aromatization of *n*-alkanes (Rangel *et al*., 2000; Hoang *et al*., 2007). In addition, it was observed that the bimetallic PtSn/KL catalyst prepared by vapor-phase co-impregnation for *n*-octane aromatization showed that the added tin improved the stability and selectivity to C8-aromatics products, including a decreasing the secondary hydrogenolysis reaction which occurred inside the pore of KL zeolite leading to conversion of benzene and toluene (Trakarnroek *et al*., 2006).

Although Pt/KL catalyst has many benefits hereinbefore, one of the important drawbacks is its sensitivity to sulfur poisoning. It is considerably more susceptible to sulfur than the conventional reforming catalysts such as Pt/Al_2O_3 and PtRe/Al_2O_3 (Meriaudeau *et al*., 1997). Several authors have found that the high sensitivity of Pt on the non-acidic support catalyst to poisoning by very low levels of sulfur is attributed to the loss of active platinum surface by adsorption of sulfur and the growth of the platinum clusters leading to catalyst deactivation (Vaarkamp *et al*., 1992; Lee *et al*., 1998). Moreover, as the metal size grows; larger ensembles and also coke formation are formed, favoring hydrogenolysis over dehydrocyclization and effecting to the reaction selectivity resulting in lower product selectivity (Vaarkamp *et al.*, 1992; Kao *et al.*, 1993; Paal *et al.*, 1996). As a result, one possible approach to increase sulfur tolerance could be the addition of rare earth elements as promoters. They may act as anchoring sites for Pt particles, thus preventing their growth. They may also act as sulfur getters, thus protecting Pt, albeit temporarily, from sulfur poisoning (Jacobs *et al.*, 1999). For example, in the case of *n*-hexane aromatization, heavy rare earth (e.g. Tm, Gd, Yb, Dy) elements added to Pt/KL catalyst have effect to electronic donation to Pt particles and blocking the accumulation of active Pt particles, and thus can remarkably increase the ability of resistant sulfur poisoning and the aromatic selectivity of *n*-hexane conversion on the Pt/KL catalyst. In the presence of sulfur, the Ce-promoted Pt/KL catalyst showed a higher tolerance to metal agglomeration and a lower rate of coke formation than the unpromoted Pt/KL for *n*-hexane aromatization (Jongpatiwut *et al.*, 2001). Furthermore, addition of Tm onto the KL catalyst results in an increase of the number of active site, that is, an increase of the dispersion of the active Pt particles, which results in a much slower loss of the catalytic activity of the PtTm/KL catalyst (Fang *et al.*, 1996).

This research aims to study 1) the sulfur tolerance of PtSn/KL for *n*-octane aromatization reaction 2) the improvement of sulfur tolerance of PtSn/KL after adding rare earth elements (Tm and Ce). The catalysts were prepared by vapor-phase impregnation method in which all metals were loaded on the KL zeolite by co-impregnation and sequential impregnation methods. All the fresh (reduced) samples were tested at 500°C under atmospheric pressure and characterized by a combination of techniques including hydrogen chemisorption. Transmission electron microscopy (TEM) analysis was also performed on the fresh catalyst to estimate the metal dispersion. Furthermore, temperature programmed reduction (TPR) was used to test the metal interaction. While temperature programmed oxidation (TPO) was employed to analyze the amount of coke deposits on the spent catalysts during reaction.

CHAPTER II

LITERATURE REVIEW

2.1 Catalytic Reforming

Catalytic reforming of hydrocarbons is an important industrial process for producing aromatics and increasing the octane number of hydrocarbons in the gasoline boiling range. The catalytic reforming process consists of a number of reactions which takes place on bifunctional catalysts for converting the hydrocarbons contained in naphtha fractions to monocyclic aromatics.

These are major reforming reactions of naphtha as shown below in figure 2.1. In fact, four reactions of (a) – (d) are used to beneficially obtain an increase in

(e) Hydrocracking and hydrogenolysis (f) Coke formation

bon-carbon scissions), which result in low molecular weight paraffins and coke formation that will eventually deactivate the catalyst.

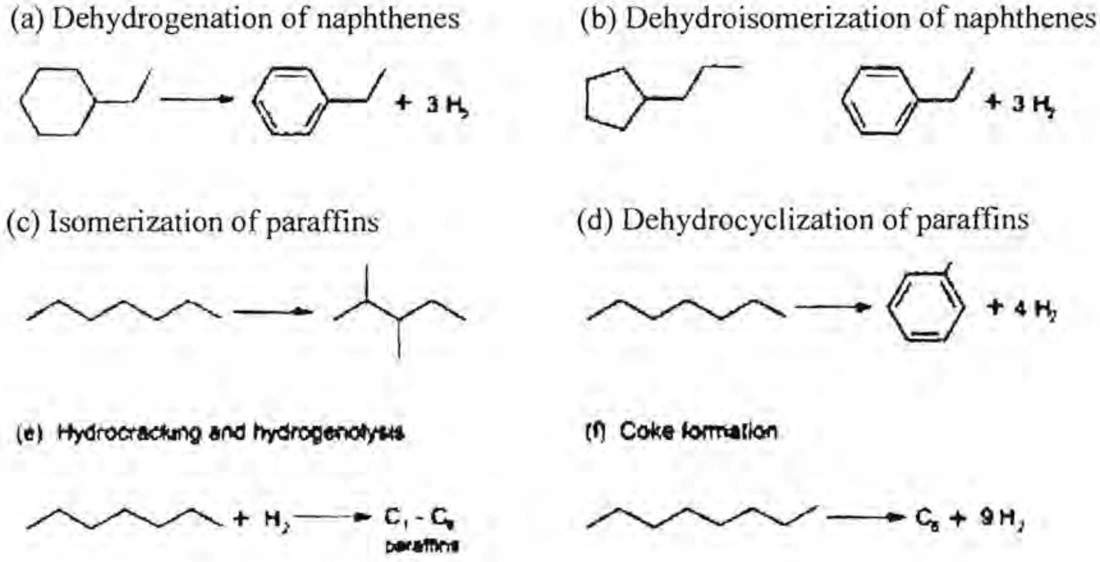

(a) Dehydrogenation of naphthenes
(b) Dehydroisomerization of naphthenes
(c) Isomerization of paraffins
(d) Dehydrocyclization of paraffins

Figure 2.1 Major reactions in catalytic reforming of naphtha

There are two ways in which catalytic reforming may be used. One option is to process the heavy fractions of straight run naphtha in order to increase their octane rating by 40-50 units. The other way is to process a narrow fraction of gasoline such as C_6-C_8 or C_7-C_8. From the obtained reformate (called in this case BTX) is then separated the aromatic hydrocarbons (mainly benzene, toluene and xylenes), for the petrochemical industry. This second process is also called aromatization which is important process in order to increase the production of those hydrocarbons that present a higher interest for the petrochemical industry. Both processing option are performed in the same units, working under similar operating conditions. The presentation that follows will be referring to both options at the same time (Raseev *et al.*, 2003).

One of the most common-important reactions to obtain high value added products from naphtha feedstock is the aromatization of *n*-alkane which is of considerable theoretical and industrial importance. Aromatization is believed to proceed via a two-step mechanism which first includes dehydrogenation and cracking of paraffins to form an olefinic intermediate and then dehydrocyclization of the olefinic intermediate to form aromatics (Harandi *et al.*, 1991). The expected products of this reaction are ethylbenzene (EB) and *o*-xylene (OX) from a direct six-membered ring closure which are widely used in petrochemical industry as an intermediate compound for the production of plastics (Trakarnroek *et al.*, 2006).; nevertheless, the product distribution shows benzene and toluene as major aromatics products with small quantities of EB and OX. The applications of *o*-xylene and ethylbenzene are explained briefly below (Chenier, 2002).

2.1.1 *o*-Xylene

The xylenes can be used as a mixture or separated into pure isomers, depending on the application. The mixture is obtained from catalytic reforming of naphtha and separated from benzene and toluene by distillation. Pure *o*-xylene is converted into phthalic anhydride. About 53% of phthalic anhydride is an intermediate in the synthesis of plasticizers, substances that make plastics more flexible. A common plasticizer is dioctyl phthalate. Phthalic anhydride is also used to make unsaturated polyester resins (21%) and alkyd resins (15%).

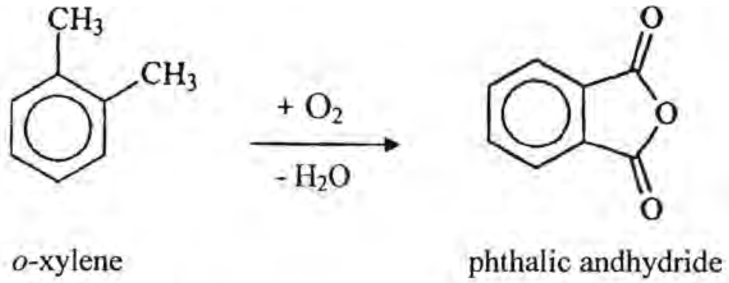


Figure 2.2 Schematic of *o*-xylene oxidation to phthalic anhydride

2.1.2 Ethylbenzene

Ethylbenzene is an organic chemical compound which is an aromatic hydrocarbon. Its major usage is in the petrochemical industry as an intermediate compound for the production of styrene, which in turn is used for making polystyrene, a commonly used plastic material. Although often present in small amounts in crude oil, ethylbenzene is produced in bulk quantities by combining the petrochemicals benzene and ethylene in an acidically-catalyzed chemical reaction. Catalytic dehydrogenation of the ethylbenzene then gives hydrogen gas and styrene, which is vinylbenzene.

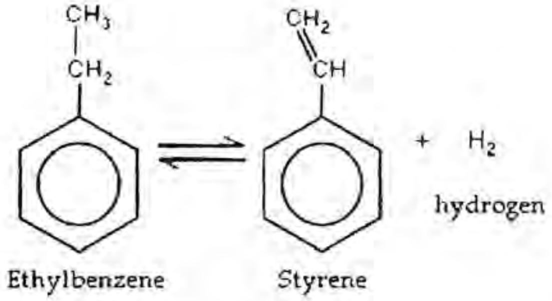


Figure 2.3 Schematic of ethylbenzene dehydrogenation to styrene

2.2 Catalysts for Aromatization of *n*-Alkane

The effectiveness of reforming catalysts comprising a non-acidic L-zeolite and a platinum-group metal for dehydrocyclization of paraffins is well known in the art. In 1980, Bernard found the exceptionally high activity of Platinum supported on alkaline LTL zeolite (Pt/KL) for the aromatization of *n*-hexane that is very efficient for the direct dehydrocyclization of *n*-hexane into benzene (Bernard, 1980). Since properties of Pt-KL catalysts are responsible for their high aromatization efficiency as following (Davis, 1993; Meriaudeau *et al.*, 1997):

- The nonacid character of Pt-KL, which suppresses every possible cracking reactions,
- The extremely small size of Pt particles within the one dimensionalzeolite channels, which limits the extent of the alkane hydrogenolysis,
- The size and morphology of the zeolite channels, which inhibit bimolecular and hydrogen transfer reactions generally involved in the mechanism of coke formation,
- The stabilizing effect of KL support against the sintering of Pt crystallites due to the dimensions of the channels and possibly to the interaction between the Pt particles and the zeolite channels,
- And, the space inside the L-zeolite was similar to that of a cyclic, six carbon species. Therefore, the adsorbed hexane curls around on itself in the zeolite cage in order to maximize its Van der Waals interactions. This preorganization of the *n*-hexane molecule favored ring closure, and was responsible for the high activity and selectivity of Pt/KL for aromatization.

As well as aromatization of *n*-octane, it was observed that high dispersion of Pt clusters inside the channel of KL zeolite is the important factor for the aromatization performance (Jongpatiwut *et al.*, 2003). To prepare a Pt/KL catalyst with dispersion of Pt clusters inside the channel of KL zeolite, vapor phase impregnation (VPI) is the best preparation methods compared to both incipient wetness impregnation (IWI) and ion-exchange method (IE). The reasons supporting this statement were as follows: 1) IWI method provided the Pt/KL catalyst with Pt clusters inside the channels; however, at high temperature reduction treatment, the growth of Pt clusters inside the channel was displayed and Pt/KL catalyst prepared by ion exchange method resulted in high fraction of Pt particle external to the L zeolite and rapid deactivation by coke formation 2) as for the catalyst prepared by VPI method, the Pt clusters were located inside the channel and more resistant to agglomerate at high temperature (Jacobs *et al.*, 1999; Jacobs *et al.*, 2001).

However, the unique behavior exhibited for *n*-hexane in terms of selectivity and catalyst life were not presented for *n*-octane (Huang *et al.*, 1992) because the selectivity for *n*-octane aromatization still lowered and quickly dropped due to pore plugging after a few hours on stream (Jongpatiwut *et al.*, 2003). The expected products of this reaction are ethylbenzene (EB) and o-xylene (OX) from a direct six-membered ring closure; nevertheless, the product distribution shows benzene and toluene as major aromatics products with small quantities of EB and OX. Since the pore size of the KL zeolite is approximately 0.71 nm, larger than the critical diameter of EB but smaller than that of OX, OX diffuses much slower than EB. As a result, OX would preferentially convert to benzene and toluene before escaping from the pore of zeolite. In the study, it was proposed that pore length of the zeolite should have a great impact on product distribution and catalyst life. The idea of short channel KL zeolile has been previously discussed by Treacy (1999) to minimize the problem of Pt entombment due to Pt agglomeration and coking. Furthermore, the zeolite with small particle size provides advantages over the zeolite with large particle size by enhancing the ratio of surface area to mass, diffusion rates, and resistance to deactivation by pore plugging.

2.2 The Structure of LTL Zeolite

The crystal structure of zeolite L was determined initially by Barrer and Villiger (Barrer and Villiger, 1969). The structure of zeolite L is hexagonal (space group P6/mmm) with unit cell constants a=18.4 °A and c=7.5 °A. The linkages of the cancrinite cages (ε-cages) by double 6-rings (D6R) leaded to the formation of column in the c-direction. And thus give rise to 12-membered rings with a free diameter of 7.1 °A of one dimensional pores leading to cavity of about 0.48x1 .20x1 .07 nm as shown in Figure 2.4. Typically, Si/Al ratio in the framework is 3.0 (KO and Ahn, 1999; Tsapatsis *et al.*, 1994).

Figure 2.4 Schematic of L zeolite structure

The formula in terms of oxide is 0.9 to $1.3M_{2/n}O$: Al_2O_3: 5.2 to $6.9SiO_2$: yH_2O, when M represents an exchangeable cation of valence.

2.4 The Effect of Sulfur on Pt/KL Catalyst

It is also known that one of the most serious drawbacks exhibited by the Pt/KL catalysts is their low sulfur tolerance which are very sensitive to even traces of sulfur (e.g. parts per billion) in the aromatization reforming catalysts (Hughes *et al.*, 1986; Meriaudeau *et al.*, 1997). To achieve aromatization, the feed has to be reduced the amount of sulfur to extremely low levels. Therefore, the development of Pt/KL catalysts which is able to withstand higher sulfur concentrations than those used to day appears as an attractive goal (Jacobs *et al.*, 1998). In previous works, Pt/KL catalysts poisoned by sulfur have been characterized by TEM (Jacobs *et al.*, 1998; McVicker *et al.*, 1993), EXAFS (Jacobs *et al.*, 1998; Vaarkamp *et al.*, 1992), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO (Tamm *et al.*, 1988; Jacobs *et al.*, 1999, 2000). The obvious results of the studies demonstrated that that Pt particle growth is accelerated in the presence of sulfur, leading to zeolite pore plugging and significant losses in catalytic activity due to the loss of active platinum surface by adsorption of sulfur (Jongpatiwut *et al.*, 2002). Consequently, these deactivate the catalyst after prolonged operation (Lee *et al.*, 1998). By mechanisms which are not fully understood, sulfur promotes Pt crystal growth and movement of Pt out of the zeolite channels; hence, sulfur behaves as a structure blocker. Moreover, as the particle size grows, larger ensembles are formed, favoring hydrogenolysis over dehydrocyclization and effecting to the reaction selectivity resulting in lower product selectivity (Vaarkamp *et al.*, 1992; Kao *et al.*, 1993; Paal *et al.*, 1996). On the other hand, other authors have proposed that the K cations directly participate in the aromatization process and they, rather than Pt, are preferentially poisoned by sulfur (Fukunaga and Ponec, 1995).

2.5 The Effect of Second Metals (Promoters) on Pt/KL Catalyst

In the reforming process, it was observed however that catalyst comprising a second metal in addition to platinum as a promoter (so-called bimetallic catalyst) had better catalytic properties (Furcht *et al.*, 2001; Carvalho *et al.*, 2004). The extensive academic studies were performed to clarify the role of the different modifying metals such as Re, Sn, Ir, and Ge which are frequently used in naphtha reforming process. These bimetallic catalysts seem to be more stable (Bruch and Mitchell, 1983; Lanh *et al.*, 1984), more selective, more resistant to coking (Bertolaccini and Pellet, 1980; De Jongste and Ponec, 1980), and sintering (Charosset *et al.*, 1979), and apparently they have better activity (Passos *et al.*, 1998) than the monometallic, only Pt, ones.

Bimetallic catalyst is often regarded as alloys, although alloying would mean an intimate mixing of all components, which would create new phases. In another approach, two ideas have been put forward to account for properties of bimetallic catalysts: the 'geometrical' and 'electronic' theories (Coq *et al.*, 1995; Ponec *et al.*, 1995). In the geometrical theory, since undesirable processes in the alkane aromatization such as hydrogenolysis reaction and coke formation were known to require relatively large clusters or ensembles of adjacent metal atoms whilst desirable reaction which aromatization can occur on single isolated atoms (Biloen *et al.*, 1977; Coq and Figueras, 1984; Vogelzang *et al.*, 1981)). Therefore, to inhibit the hydrogenolysis reaction and improve the catalyst resistance to deactivation, the particle size of Pt clusters must be decreased. The active platinum surface can be diluted into smaller ensembles by the addition of an inactive species such as Sn, Au, or Pb. In

1994, Lee and Lee found that Pt-Sn/γ-Al_2O_3 prepared by simultaneous impregnation showed a better catalytic behavior toward C8-aromatics formation than Pt/γ-Al_2O_3. The added Sn did not affect electronically on Pt because the mole ratio of *o*-xylene/ethylbenzene over various Pt-Sn catalytic with different mole ratio of Sn/Pt was shown to be almost constant. Since it has been proposed that the alternation of the EB:OX ratio by the presence of tin in the catalyst was due to an alternation to favor the weaker C-H bonds in the -CH_2-group rather than the stronger bonds of the -CH_3 groups. Therefore, the remarkable increase in catalytic activity and selectivity of the dehydrocyclization is by the structure change of Pt by adding Sn. That is, the existence of Sn around Pt leads to the increase of the number of small ensembles composed of Pt, which causes rapid change in activity and selectivity of the catalyst.

For *n*-octane reforming over alumina-supported Pt, Pt-Sn and Pt-W catalysts, it was found that the addition of Sn and W increased in the activity and stability to Pt/Al_2O_3 and also beneficial changed in selectivity during *n*-C8 dehydrocyclization. The results showed that tin was the best modifier of the metallic function, because it decreased hydrogenolysis and modifies the acid function, tuning and balancing it in order to produce more cyclization to C6 ring closure including to decrease cracking to C3-C5 and condensation to carbonaceous deposits. On the other hand, tungsten (W) increased the activity in hydrogenolysis of the catalyst. This can occur through the formation of hydrogen-tungsten compounds, being favored hydrogenolysis, hydrocrackinge and other hydrogenation reactions (Rangel *et al.*, 2000).

However, it was found that not only does tin modify the stability and selectivity of the Pt function by ensemble effect, but also does it modify the Pt function by an electronic effect. By this way, tin in metallic form (in solid solution, in small bimetallic clusters, alloyed with Pt, or as Sn^{2+} ions in intimate contact with Pt atom) gives its electron to the holes of the 5d band of platinum atoms. Of this is the case, small amounts of tin (lower than the detection limit) should affect the properties of platinum. In fact, 15 atom% of tin was sufficient to fill the hole of the 5d band of platinum. On the basic of the electronic effect, it is possible to explain the promotion effect of tin by assuming that coke precursors are not adsorbed on the surface of the doped platinum crystals, but rather they move to the support, avoiding deactivation of the active site. A lower coke formation can also occur because condensation reactions are inhibited, and lower amount of polymers are formed. For the same reason, C-C bond hydrogenolysis does not occur, again because the hydrocarbon cannot be strongly adsorbed on the catalyst (Ertl *et al.*, 1997). In 1995, Shi and Davis showed that tin alters the property of the platinum for alkane dehydrocyclization by applying reversible alkane adsorption/desorption for the Pt-Sn-SiO_2 catalyst whereas irreversible adsorption applies for the Pt-SiO_2 catalyst. The data shown that tin causes the alkane to be bound to the metal surface less tightly than when tin is absent.

Cho and Ryoo (2004) prepared Pt-Sn nanoparticles supported on KL zeolite (Pt-Sn/KL) by ion exchange method and controlled the Sn/Pt ratio at 0.1, 0.2, and 0.4, respectively. They found that no pore blockage was observed when Pt-Sn nanoparticles was formed inside the KL zeolite channel, since the amount of xenon adsorption per unit cell for the Pt-Sn/KL catalyst was the same as that of KL zeolite. Furthermore, from EXAFS, incorporation of Sn into Pt nanoparticle could not cause an increase of particle size of Pt corresponding with no increase of the coordination number of the Pt-Sn. The chemical state of Sn in the Pt-Sn/KL catalyst seems to be Sn^{2+} referred from the obtained Pt-Sn distance which is around 0.279 nm. The results of the XANES analysis suggested that electron transfer occurred from Sn to Pt and resulted in the significant change in the d band structure. Catalytic performance of the Pt-Sn/KL catalyst over n-hexane aromatization was improved with mainly the Pt ensemble effect by an incorporation of tin because the formation of dehydrogenated species required for isomerization, hydrogenolysis and coke formation was suppressed, resulting in the high selectivity to benzene. Also, the change of electronic structure of the nanoparticles may affect the adsorption characteristics of reactants such as hydrogen and similarly benzene.

There have been several attempts to increase the sulfur tolerance of the Pt/KL catalysts. One possible approach to increase sulfur tolerance could be the addition of promoters. They may act as anchoring sites for Pt particles, thus preventing their growth. They may also act as sulfur getters, thus protecting Pt, albeit temporarily, from sulfur poisoning (Jacobs *et al.*, 1999). Few authors have studied the addition of rare earth elements (e.g. Dy, Tm, Ce, Yb) as promoters (Li *et al.*, 1994; Fang *et al.*, 1997; Grau *et al.*, 1998; Jongpatiwut *et al.*, 2002). Li *et al.* have indicated that the addition of rare earth elements may have a positive effect on the aromatization activity and the sulfur resistance of Pt/KL catalysts. To support this idea, there were some results reported that adding rare earth (RE) element in the Pt/KL zeolite is better than that on the catalyst without RE in term of selectivity. For example, in the case of *n*-hexane aromatization, heavy rare earth elements added to Pt/KL catalyst have effect to electronic donation to Pt particles and blocking the accumulation of active Pt particles, and thus can remarkably increase the ability of resistant sulfur poisoning and the aromatic selectivity of *n*-hexane conversion on the Pt/KL catalyst. In the presence of sulfur, the Ce-promoted Pt/KL catalyst showed a higher resistance to metal agglomeration and a lower rate of coke formation than the unpromoted Pt/KL for n-hexane aromatization (Jongpatiwut *et al.*, 2001). Furthermore, addition of Tm onto the KL catalyst results in an increase of the active site number, that is, an increase of the dispersion of the active Pt particles, which results in a more slowly loss of the catalytic activity of the Pt-Tm/KL catalyst. More importantly, Jacobs et al. demonstrated that one of the considerable effects of Tm is to capture sulfur, hence guarding the Pt particles from poisoning (Fang *et al.*, 1996; Jacobs *et al.*, 1999). However, adding only the rare earth element onto the catalyst does not ensure a good performance, it has to include method of preparation and pretreatment. In agreement of previous studies, the resulting parameters showed that the VPI method is the best preparation due to the fact that it gave the highest metal dispersion.

2.6 Catalyst Deactivation for Reforming

A catalyst is defined as a substance, which accelerates the rate of a chemical reaction without itself getting "affected" or "changed". This definition suggests an infinite life for the catalyst. In practice, this is really not true. All catalysts deactivate, though at different rates, and have finite lives. The deactivation is often a result of side or parallel reactions or poisoning. We will now examine the deactivation of catalysts in detail (Viswanathan, 2002). Causes for catalyst deactivation at least five main reasons for catalyst deactivation are recognized.

1. Poisoning (Chemical effect)
2. Fouling, coking, carbon deposition etc. (Mechanical effect)
3. Thermal damage (Thermal effect)

4. Loss of catalytic phases (Chemical effect)
5. Attrition (Mechanical effect)

2.6.1 Poisoning

Poisoning of catalytic sites occurs from strong chemisorption of impurities, reactants, products or by products. Catalyst poisons from strong adsorptive bonds with the catalyst surface, blocking active centers. Therefore, even very small quantities of catalyst poisons can influence the adsorption of reactants on the catalyst. The term catalyst poison is usually applied to foreign materials in the reaction system, e.g. sulfur, nitrogen, oxygen. Catalysis of feed containing several hundred ppm sulfur, was also of interest because: (1) aromatization activity is decreased with sulfur bearing feeds regardless of the method of catalyst manufacture and (2) little is known about the effects of catalyst pretreatment on the catalyst deactivation by sulfur poisoning (Jao et al., 1995).

Poisoning effects are very specific. A reactant is one reaction can be a poison for another reaction over a different catalyst; e.g., CO is a reactant in Fischer-Tropsch catalysis (iron oxide catalyst) and is a poison in NH_3 synthesis.

The adsorbed poison can affect the catalyst in the following manner:

(i) physically block the active center
(ii) electronically modify the adjacent active centers
(iii) restructure the surface
(iv) block interaction between two adsorbed species and
(v) prevent diffusion of the adsorbed species.

As poisons function through strong chemisorption, they are very selective. It is worth enough to know that different catalysts are poisoned by different agent.

Types of Poisoning

Poisoning can be classified into three types, viz., selective and anti-selective poisoning. The three types of poisoning are classified based on the relationship between catalyst activity loss and the concentration of the poison in the feed or the relative surface coverage by the poison (Figure 2.5).

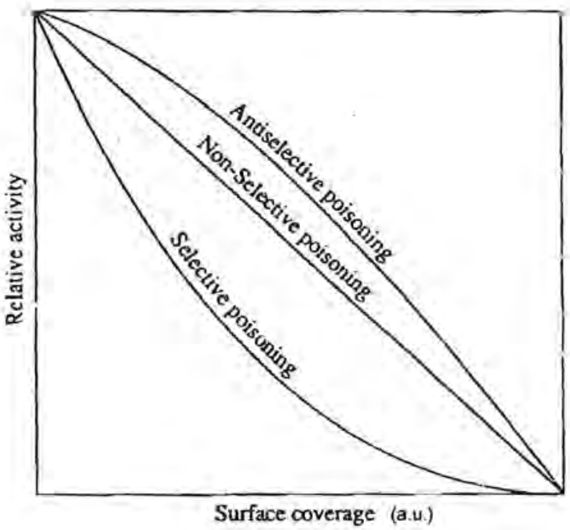


Figure 2.5 Three different types of poisoning generally observed in the case of heterogeneous catalysts

(i) Selective poisoning: Occurs when the activity of the catalyst decreases rapidly in the beginning with increasing surface coverage by the poison and the deactivation rate slow down at higher coverage.

(ii) Non-selective poisoning: Occurs when the loss in catalyst activity is proportional to poison coverage.

(iii) Anti-selective poisoning: Occur when the initial loss in activity is less and the loss becomes more pronounced with increasing surface coverage by the poison.

2.6.2 Fouling

Fouling of a catalyst takes place when carbonaceous material or extraneous metal oxides are deposited on the catalyst. Carbonaceous materials are the major causes of deactivation in most reactions. These can be coke (polynuclear aromatics or large oligomeric molecules; C/H > 0.5) or carbon. Coke deposits lower the activity of catalysts by one or more of the following effects:

(1) adsorb strongly on the active sites (metal, acid centres),

(2) physically envelope the active centre (a metal crystallite),

(3) plug the micro and meso pores of the catalysts and

(4) damage the physical texture or shape of the catalyst through growth of the carbonaceous materials.

The major effects of fouling noticed during the reaction are:

(i) activity loss; temperature of reactor is continuously increased to compensate for loss is activity and

(ii) increase in pressure drop across the bed.

2.6.2.1 Coking

The mechanism of coke formation will depend on the type of catalyst, the reactants, the reaction conditions and the reactor feed composition. In addition, Matín *et al.* (2005) also show that the characteristics of the coke depend on the deactivation process, and that coke on the industrial catalyst could be successfully described and defined. Generally, two types of nature of coke have been recognized. The soluble coke extracts of spent catalysts is rich in alkylated mono- and di-aromatics with low percentage of polyaromatics whereas the nature of insoluble coke is highly polyaromatic (aromaticity, $f_a > 0.95$) (Sahoo *et al.*, 2003). A soluble can be extracted using solvent (C/H = 0.5 to 1) and an insoluble coke (C/H => 1) which is not soluble in organic solvents. Both types of coke are burnt off into CO_2 at elevated temperatures. Catalysts, like those used in HDS, have long cycle length (cycle length = period of operation between two successive regeneration) of 1 to 5 years due to the mild operating conditions (H_2 atmosphere, high pressures and moderate temperature of < 400°C). On the other hand, cracking catalysts deactivate in seconds due to the heavy nature of the feed and severe operating conditions (atmospheric pressure > 500°C). Many factors influence the formation of coke on catalysts. Because of pore filling by the coke, the pore volume of the catalyst decreases faster than its surface area. Possible effects of fouling by carbon (or coke) on the functioning of supported metal catalyst are illustrated in Figure 2.6 (Bartholomew, 2001).

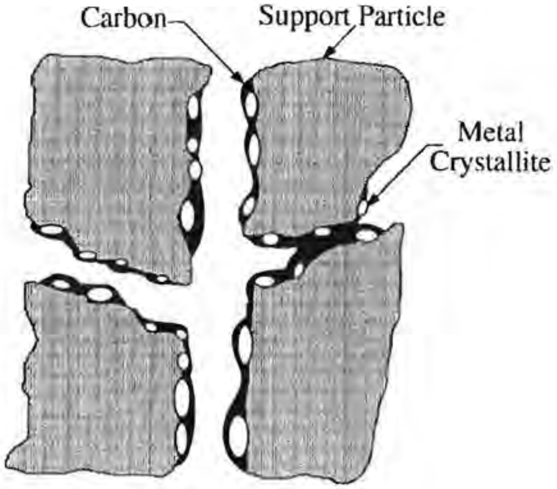


Figure 2.6 Conceptual model of fouling, crystallite encapsulation and pore plugging of a supported metal catalyst due to carbon deposition

The activity loss itself is more rapid in the beginning and becomes slower after some time. In some catalyst with long lives, the activity may decrease asymptotically with time after the initial rapid loss (Figure 2.7).

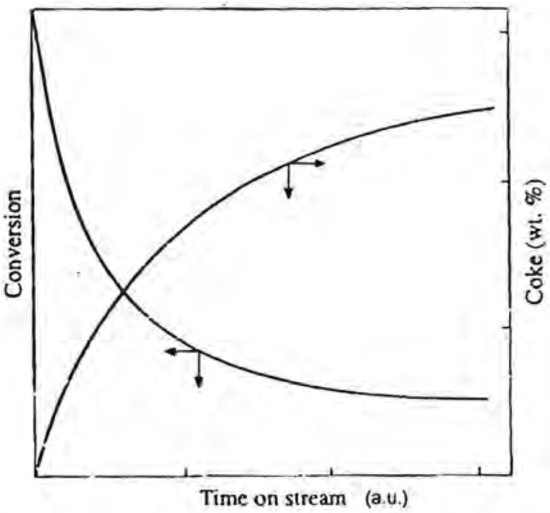


Figure 2.7 Relationship between catalyst activity loss and coke deposition with during of run

2.6.2.2 Metal Deposition

Metal deposition is a major problem in petroleum refining processes where heavy oil feeds are used. The major metallic impurities present in these oils are V and Ni, which are present as organometallics. The large metal content in the feed causes deactivation of HDS catalysts when desulfurization of residua is carried out. The metal complexes break down at the high pressures and hydrogen atmosphere, the metals react with the H_2S in the system and transform into S deposits. These deposits affect the activity of the catalyst, besides leading to plugging of the bed and causing large pressure drop across the bed.

When the metal feed containing feeds are used in FCC processes, the deposited V destroys the zeolite component of the catalyst causing again rapid deactivation. The Ni in the feed leads to excessive dehydrogenation resulting in increased H_2 in the gas and also increased coke lay down on the catalyst. Examination of the metal concentration profiles in individual particles of FCC catalysts reveals that while V is uniformly distributed throughout an individual particle, Ni is deposited mostly at the periphery.

Metal can also come from the plumbing (corrosion of pipes, tube etc.) of the reactors. These deposits are mainly iron oxide scales which deposit on the top layers of the catalyst bed. For example, in the case of HDS reactors, these are periodically skimmed off from the top of the bed to keep the pressure drop within limits.

2.6.3 Thermal Degradation

Catalyst activity loss due to thermal damage is often a serious problem in supported metal catalysts (Pt-Al_2O_3, Ni-Al_2O_3 etc.) and oxide catalysts with large surface areas (SiO_2-Al_2O_3, zeolite, iron-molybdate etc.)

The major thermal damages to the catalysts are:

(1) Loss of metal surface area due to crystallite growth (sintering of metal),

(2) Loss of support surface area due to pore collapse (sintering of support), and

(3) Transformation of the catalytic phase into a non-catalytic phase.

2.6.3.1 Sintering of Metals

Sintering occurs because small crystallites always tent to lower their surface free energies by minimizing their specific surface areas.

Various mechanisms have been proposed for the sintering of metals. These are:

1. Crystallite migration
2. Atomic migration
3. Spreading and splitting and
4. Vapor transport

In crystallite migration, entire (small) crystallites migrate and fuse to form bigger thermodynamically more stable crystallites. This is a likely scenario when the dispersion levels are moderately high and metal-support interactions are weak. Similarly, atoms can migrate and coalesce into small crystallites at high dispersion levels. Spreading and splitting are expected to occur when the metal-support interaction is large and the contact angle between the support and the metal is small. This can be expected in the case of low melting elements. Sintering through vapor transport will occur at high temperatures. In the case of Pt group metals; this is a major sintering pathway in oxidizing conditions when metal oxides with lower vapor pressures are formed.

The rate of sintering of supported metals depends on many parameters such as the nature of the atmosphere, the nature of the support and the presence of impurities. The rate of sintering increases with temperature. The activation energy values for sintering depend on the nature of the metal, the support and ambient atmosphere. E_a values of 13 to 97 kJ mol^{-1} have been reported for Pt-Al_2O_3 at different sintering conditions. The typical sintering behavior of metal catalyst is presented in Figure 2.8. The surface area loss is initially rapid, but becomes progressively less at longer times reaching a nearly constant value after a certain period, the magnitude of this value being smaller at higher temperatures.

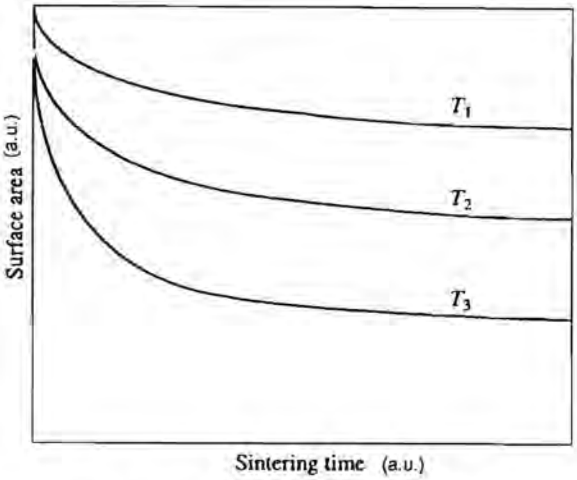


Figure 2.8 Influence of sintering temperature on metal surface area: $T_3 > T_2 > T_1$

In H_2, the resistance to sintering of the metals is in the order: Ru > Ir > Rh > Pt > Pd > Ni > Cu > Ag. This order is found to be nearly in the order of the melting points of the elements. As for O_2, the resistance to sintering in the case of Pt group metal is in the decreasing order: Rh > Pt > Ir > Ru. This order is related to the vapor pressure of the oxides of the above metals, the higher the vapor pressure, the faster the sintering. Thus, sintering takes place in reductive atmospheres through metal species, while it takes place via the oxide species in oxidizing atmospheres.

Supported-metal interactions also play a role in determining the sintering rate of supported catalysts. Strong metal support interaction stabilizes the supported metal from sintering. For example, the interaction of most metals (and many oxides) is stronger with an alumina surface than with a silica surface. As a result, alumina supported catalysts are generally more sinter resistant than silica supported catalysts. Sintering increases in the order: $Pt\text{-}Al_2O_3 < Pt\text{-}SiO_2 < P\text{-}C$.

Impurities such as Cl_2, and S in the gas phase or support increase metal atom mobility. Other impurities such as O_2, Ca and Cs appear to decrease metal atom mobility. Similarly, surface defects and the pore system in the support can reduce sintering rate by impeding the migration of metal particles.

2.6.3.2 Sintering of Supports

A supported metal catalyst can also deactivate due to the sintering of the support. When the support sinters, the supported metal particles come closer making easier to sinter. Besides when supports sinter, the nature of the surface can undergo modifications resulting in weakened metal support interactions. Sometimes the sintering support may also trap metal particles inside their closed pores preventing their accessibility to the reactants

Supports can sinter through one or more of the following mechanisms:

1. Surface diffusion,
2. Solid-state diffusion,
3. Evaporation/condensation of volatile atoms/molecules,
4. Grain boundary diffusion, and
5. Phase transformation.

2.6.3.3 Thermal degradation of supported catalysts

The manner in which supported catalysts can undergo thermal damage into non (or less) –active catalyst are:

1. Reaction of the metal with the support to produce an in active compound; e.g., Ni/alumina or Co/alumina, which form inactive spinels,
2. Segregation of the metal or carrier components (e.g., in bimetallic catalysts),
3. Metal or carrier transitions (e.g., γ-alumina to α-alumina), and
4. Reaction of the carrier with the reactants etc. (e.g., SiO_2 or TiO_2 are used in SCR catalysts and not Al_2O_3 as the latter support reacts with SO_3 in the exhaust gas).

2.6.4 Loss of Catalytic Phases by Vapor Transport

Catalytic phases can sometimes be lost through reaction with one of the reactants or products. For example, loss of Ni as Ni-carbonyl has been noticed when using Ni catalysts for reactions involving CO under reductive conditions. Similar, when Rh-Pt gauze is used in the oxidation of NH_3 to NO (temp > 900°C), loss of Pt occurs as Pt-oxide. In fact, addition of Rh decreases Pt loss besides decreasing surface restructuring. Another example is in the aromatization of small alkanes into aromatics over ZnO-ZSM-5. The loss in activity of the catalyst is mainly attributed to the loss of Zn.

2.6.5 Mechanical Failure of Catalysts

This is important cause of failure of industrial catalysts. Mechanical failure can happen in two ways:

1. During the reaction due to changes in the catalyst brought about by side reaction or
2. Due to the inherent low mechanical strength of the catalyst.

Stream reforming and stream cracking catalysts sometimes undergo mechanical failure due to growth of carbonaceous particles inside the pellets. Rimg tables of iron molybdate used in the oxidation of methanol to formaldehyde are known to undergo mechanical failure (break-up) due to the formation of iron and molybdenum oxide phases. In the case of FCC processes abrasion between particles takes place and catalyst fines tend to be generated. These leave the system through the flue gas and along with product. The loss of catalyst is compensated by addition of catalyst (make-up) which can exceed 1 ton per day in a typical FCC unit. Besides, during attrition, the more valuable component for activity (zeolite) may be preferentially lost leading to rapid loss of catalyst activity. At the same time, if the fluidized particles are too hard, they may also damage the reactor internals by abrasion. In slurry reactors, attrition can lead to loss of the catalyst (sometimes expensive) which may also be difficult to separate from the products. In fixed-bed reactors, mechanical failure may take place through crushing of the pellets/extrudates.

2.7. Prevention of Catalyst Deactivation

As the catalyst is the heart of a process, it is necessary to keep it working for as long as it is possible. Though some catalysts may be regenerated through burning (or washing with solvents) of the coke or poison, frequent regeneration entail loss of productivity and a slow decline in the performance of the catalyst with each regeneration. It is necessary, therefore, to maximize the cycle length (active period) of the catalyst before resorting to regeneration. The prevention of catalyst deactivation will depend on the identification of the reasons for deactivation. Some typical reasons for deactivation and methods for prevention of catalyst activity loss are presented in Table 2.1.

Table 2.1 Typical reasons for deactivation and methods for prevention of catalyst deactivation

Cause	*Solutions*
Poisoning	Purity feed; use guard beds; use additives which selectively react with/deactivate the poison; change reaction conditions
Coking	Avoid coke precursors in feed; avoid free radical reaction; avoid free space; passivate metal surfaces; add water, hydrogen; use shape selective zeolities; add promoters; change operating conditions.
Sintering	Use promoters/stabilizers; lower reaction temperature; avoid specific impurities
Loss of catalytic phase	Avoid impurities which an cause volatilization; alter operating conditions; add promoters
Mechanical failure	Improve mechanical strength of catalyst; alter reaction conditions; improve catalyst formation

Poisoning is a major cause for deactivation of metal catalysts. In the case of Pt-Al_2O_3 used in the reforming of naphtha to aromatics, S compounds in the feed are the major poisons. These are removed by hydrodesulfurization of the feed prior to contacting with the catalyst; the feed, which usually contains 10-15 ppm of S is desulfurized to < 1 ppm. In the case of methanation catalysts (supported Pd/Ni), a guard bed of ZnO is usually used to remove S to the required specifications. Additives that selectively passivate or react with the poisons are used with FCC catalysts. Ni is passivated with Sb or Bi containing additives and V is neutralized by Sn containing additives.

Coking is a universal phenomenon in the case of heterogeneous catalysts operated at high temperatures. Coking is not easy to avoid, though it is possible to minimize it by decreasing the concentration of coke precursors like unsaturates and high boiling aromatics. Coke deposition is reported to be lowered by adding promoters like Re and Ir to Pt-Al_2O_3 catalysts. Besides, these promoters also keep the catalyst active at higher coke contents than possible with Pt-Al_2O_3. Again, the above promoters also lower the sintering rate of the active component, Pt. Chloride ions present on the support increase its acidity, besides decreasing the sintering of Pt. As moisture causes the elimination of chloride ions from the support, besides poisoning the acid centers and enhancing the sintering of the support, tight control of the moisture in the system is mandatory. However, a small amount of moisture (20 to 40 ppm) is kept in the system to create and maintain the desired Brönsted acidity in the catalysts.

CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Gases

- The ultra high purity (UHP) hydrogen was used for *n*-octane reaction testing, FID detector, and H_2 chemisorption measurement.
- The high purity (HP) nitrogen was used for purging the glove box during catalyst preparation.
- The high purity (HP) helium was used for purging catalysts after reaction testing, for the catalyst preparation during sublimation, and H_2 chemisorption measurement.
- The zero grade air was used for FID detector and catalyst preparation during calcination and pretreatment.
- The 5% oxygen balanced in helium was used for the temperature-programmed oxidation (TPO) measurement.
- The 5% hydrogen balanced in argon was used for the temperature-programmed reduction (TPR) measurement.

All gases were supplied from TIG, Thailand.

3.1.2 Chemicals

- *n*-Octane (C_8H_{18}) of min. 99% purity was obtained from Merck, Germany.
- The commercial K-LTL zeolite (HSZ-500, $SiO_2/Al_2O_3 = 6$, surface area = 280 m^2/g) was obtained from Tosoh, Japan.
- Platinum (II) acetylacetonate ($[CH_3COCH{=}(CO\text{-})CH_3]_2Pt$) was obtained from Aldrich, USA.
- Tin (IV) bisacetylacetonate dichloride $[CH_3COCH{=}(CO\text{-})CH_3]_2SnCl_2$) was obtained from Aldrich, USA.

- Thulium 2, 4-pentanedionate ($Tm[CH_3COCHCOCH_3]_3$) of 99.9% purity was supplied by Alfa, USA.
- Cerium (2,4-pentanedionate ($Ce[CH_3COCHCOCH_3]_3$) of 98% purity was supplied by Alfa, USA.
- Thiophene (C_4H_4S) of 98% purity was supplied by Fluka, USA.

3.2 Equipment

- JEOL JEM-2000FX transmission electron microscope (TEM)
- Temperature programmed reduction (TPR)
- Temperature programmed oxidation (TPO)
- Catalytic testing system consisting of cylinders, mass flow controllers, furnace and tube reactors
- Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/Al_2O_3 "S" deactivated column

3.3 Methodology

3.3.1 Catalyst Preparation

The bimetallic Pt-Sn supported on the commercial KL zeolite was prepared by vapor-phase co-impregnation (VPCI) which was introduced following previously published method (Trakarnroek *et al.*, 2006). For this method, the nominal percentage of platinum is 1 wt%. Prior to impregnation, the commercial KL zeolite was dried in an oven at 110°C overnight and calcined at 500°C in flowing dry air of 100 cm^3/min.g for 5 h. In the case of co-impregnation, the dried support was mixed physically with weighed platinum (II) acetylacetonate (Aldrich) and tin (IV) bisacetylacetonate dichloride (Aldrich) precursors under nitrogen atmosphere. The mixture was then loaded in a tube reactor before being subjected to a helium flow of 5 cm^3/min·g. The reactor was gradually ramped to 40°C and held for 3 h, and ramped again to 60°C and held for 1 h. After that it was further ramped to 110°C where the mixture was held for 1 h to sublime the $Pt(AcAc)_2$. After being cooled down to room temperature, it was ramped to 350°C in flowing air for 2 h to decompose the platinum precursor. The resulting materials were stored in the oxidic form.

In the part of trimetallic PtSnRE/KL, the catalysts were firstly prepared vapor-phase impregnation of RE into KL zeolite, then co-impregnated Pt and Sn. After that, the preparation followed by the same procedures and using the same conditions.

3.3.2 Catalytic Activity Testing

The catalytic activity studies were conducted at atmospheric pressure in a 0.5 inch diameter glass tube reactor equipped with an internal K-type thermocouple for temperature measurements. To avoid unwanted contamination, independent systems were used for runs using clean feeds and runs using sulfur-containing feeds. In the continuous-flow reactor 0.2 g of fresh catalyst was used in each run. Prior to reaction, the catalyst was slowly ramped in flowing H_2 for 2 h up to 500°C and in-situ reduced at that temperature for 1 h. The *n*-octane feed was continuously injected from a syringe pump, keeping in all the experiments hydrogen to *n*-octane molar ratio of 6:1. For the sulfur deactivation studies, thiophene was pre-mixed in *n*-octane at the proper amount to obtain 2.5 ppm S in the reaction mixture. The equipment for sulfur-free and sulfur-containing feed was completely segregated. The products were analyzed by gas chromatography using a Shimadzu 17A-GC equipped with an HP-PLOT/Al_2O_3 "S" deactivated capillary column. The GC column temperature was programmed to obtain an adequate separation of the products. The temperature was first kept constant at 40°C for 10 min and then, linearly ramped to 195°C and held for 30 min. The schematic of the experiment set up is shown in Figure 3.1 (Jongpatiwut *et al.*, 2001; Trakarnroek *et al.*, 2006).

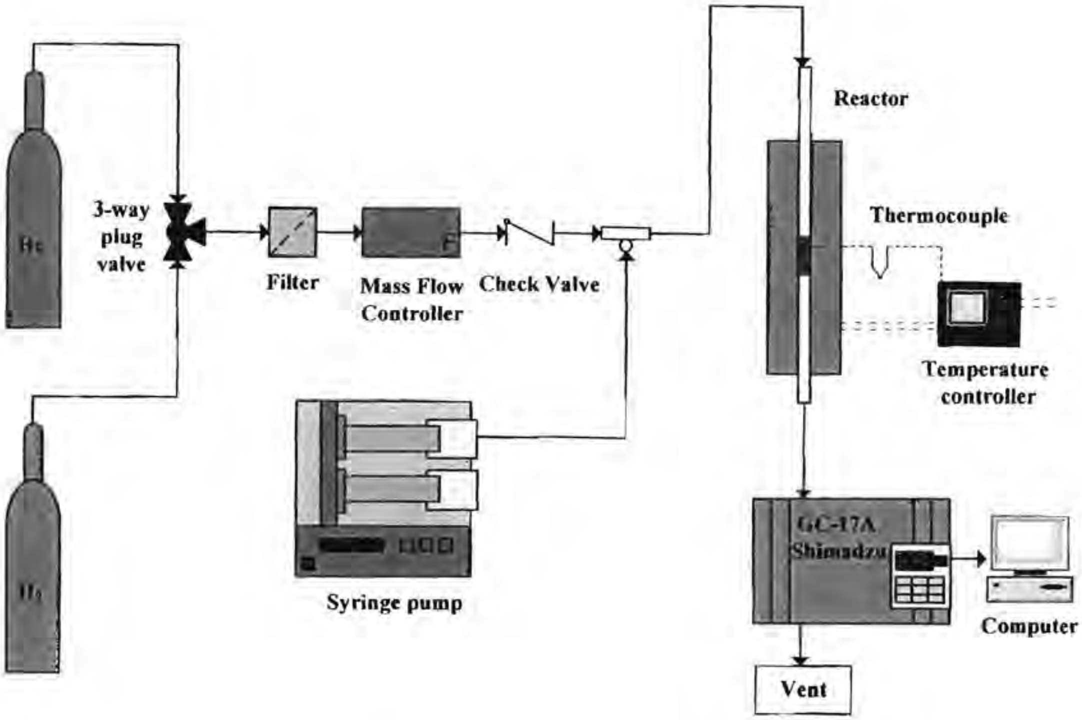


Figure 3.1 Schematic of the experimental set-up for *n*-alkane aromatization

3.3.3 Catalyst Characterization

3.3.3.1 *Hydrogen Chemisorption*

This technique was employed to characterize the bimetallic PtSn/KL and trimetallic PtSnRE/KL catalyst dispersion including Pt agglomeration. Hydrogen uptake and degree of dispersion were determined by using a pulse technique. Prior to the pulse chemisorption, the sample is reduced in H_2 atmosphere at 500°C for 1 h. Consecutively, it was purged with N_2 at 500°C for 30 min and cooled down to 50°C in flowing N_2. H_2 pulses (purged H_2, 20 μl) were injected onto the sample at 50°C until the saturation was observed.

3.3.3.2 *Transmission Electron Microscopy (TEM)*

This technique was employed to characterize metal size distribution of the bimetallic PtSn/KL and trimetallic PtSnRE/KL catalysts. The TEM images of the catalysts were acquired in a JEOL JEM-2000FX electron microscope. The pre-reduced catalyst samples were ultrasonicated for 5 min in isopropanol until a homogeneous suspension was formed. In each determination, one drop of this mixture was placed over a TEM copper grid and subsequently dried before the analysis.

3.3.3.3 *Temperature Programmed Reduction (TPR)*

This technique was employed to investigate the reducibility of samples. Temperature programmed reduction was performed on the fresh catalysts. For each run, the samples were weighted 50 mg. TPR runs were conducted using a heating rate of 10°C/min in a flow of 5%H_2/Ar (30 ml/min) up to 800°C. An ice trap was used to eliminate water during the operation.

To prove that sulfur would break metal interaction, mild decoking was firstly operated at 350°C for 30 min in a flowing of 5% H_2/Ar in order to remove coke deposited on the spent catalysts. For each run, the spent samples were weighted 50 mg and placed in a quartz reactor. Afterward, the decoking catalyst was further employed in temperature programmed reduction (TPR) up to 800°C to see the reducibility of the catalyst after mild decoking.

3.3.3.4 *Temperature Programmed Oxidation (TPO)*

This technique was employed to analyze the amount and characteristics of the coke deposited on the catalysts during reaction and obtain information about how the coke distributes over the catalyst. TPO of the spent catalysts was performed in a continuous flow of 2% O_2 in He while the temperature was linearly increased with a heating rate of 12°C/min. The oxidation was conducted in a ¼ in. quartz fixed-bed reactor after the spent catalyst has been dried at 110°C overnight, weighted (30 mg), and placed between two layers of quartz wool inside the quartz tube. The sample was further purged at room temperature by flowing 2% O_2 in He for 30 min before the TPO was stared. The CO_2 produced by the oxidation of the coke species was converted to methane using a methanizer filled with 15% Ni/Al_2O_3 and operated at 400°C. The evolution of methane was analyzed using an FID detector.

3.3.3.5 *X-Ray Photoelectron Spectroscopy (XPS)*

XPS data were achieved on a Physical Electronics PHI 5800 ESCA system using monochromatic Al*Kα* X-ray anode operated at 350 W and 15 kV. The base pressure of the main chamber was kept at about 1.0×10^{-8} Torr. The electron takeoff angle was 45° with respect to the sample surface, and pass energy of 23 eV was typically used for the analysis. The energy scale of the instrument was calibrated using the Ag $3d_{5/2}$ line at binding energy of 368.3 eV. The binding energy values reported below are all referenced to the Fermi level. Quantification of the surface composition was carried out by integrating the peaks corresponding to each element with aid of the Shirley back ground subtraction algorithm, and then converting these peak areas to atomic composition by using the sensitivity factors provided for the each element by the PHI 5800 system software. The reduction treatment was carried out under a hydrogen flow at 500°C for 1 h. After that, the sample was transferred into the XPS holder under a He flow to avoid any contact with air.

3.3.4 Product Obtained from *n*-Octane Aromatization Analysis

The products was analyzed in a Shimadzu GC-17A gas chromatograph equipped with a capillary HP-PLOT/Al_2O_3 "S" deactivated column, using a temperature-programmed mode, to obtain optimal product separation, by starting at 40°C for 10 min. Then, the temperature was ramped up to 195°C with a heating rate of 5°C/min and held at 195°C for 30 min. Helium was sent to carry the effluent of each reaction cycle through the column to obtain the product separation. The activity data were reported in terms of total *n*-octane conversion and product selectivity defined as weight of each individual product per weight of *n*-octane converted including product yield which was defined as conversion multiplied by selectivity.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Fresh Catalysts

Table 4.1 shows a list of mono-, bi-, and trimetallic Pt-Sn-(RE) catalysts which were supported on the commercial KL zeolite. The rare earth (RE) elements investigated in this work are Thulium (Tm) and Cerium (Ce). The catalysts were prepared by vapor-phase impregnation method with different orders of impregnation.

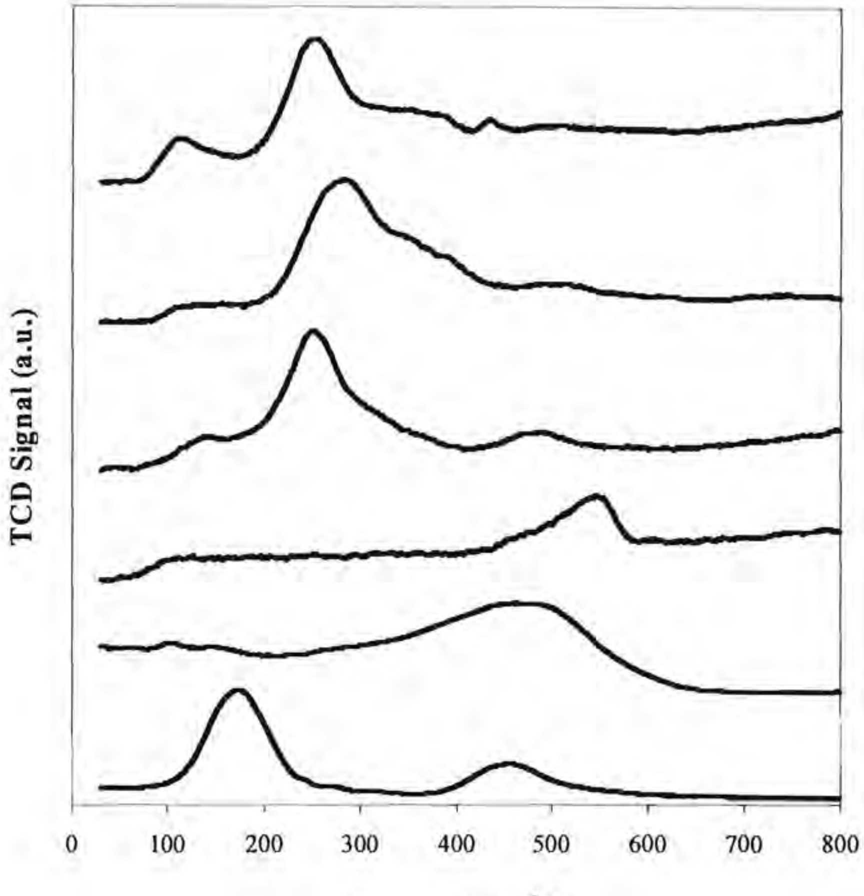
Table 4.1 List of mono-, bi-, and trimetallic Pt-Sn-(RE)/KL catalysts investigated in this work

Catalyst	wt% Pt	wt% Sn	wt% RE	Order of Impregnation
Pt/KL	1	0	0	Pt
Sn/KL	0	1	0	Sn
Tm/KL	0	0	0.15	Tm
Ce/KL	0	0	0.15	Ce
PtSn/KL	1	1	0	(Pt+Sn)
PtSn/Tm/KL	1	1	0.15	Tm, (Pt+Sn)
PtSn/Ce/KL	1	1	0.15	Ce, (Pt+Sn)

To determine the effect of promoters on the reducibility of catalysts, the PtSn/KL and PtSnRE/KL catalysts were characterized by TPR. TPR experiments were carried out to investigate the reducibility of samples. Figure 4.1 shows the TPR profiles of the mono-, bi-, and trimetallic Pt-Sn-(RE) supported on commercial KL zeolite. For the monometallic, Pt/KL catalyst with a board reduction peak centered at ca. 180°C represented the reduction of Pt (IV) to Pt° (Ostgard *et al*., 1992; Zheng *et al*., 1996; and Rodriguez *et al*., 2005). Moreover, the reduction temperature of Tm showed at 530°C while the profile of Ce in supported KL zeolite was not shown. In contrast, the TPR of Sn exhibited one broad reduction peak starting at 350°C with the maximum around 550°C (Trakarnroek *et al*., 2007). When the profiles of both monometallic Pt and Sn catalysts were combined, the resulting profile did not match any profiles of the bimetallic PtSn/KL catalysts. Since the TPR profiles of the bimetallic PtSn/KL consisted of the broad peak which can be deconvoluted into three main peaks centered at 140°C, 255°C, and 480°C. These peaks correspond to Pt (IV) to Pt^o (Pt rich phase), Pt-Sn alloy phase, and Sn^o (Sn rich phase), respectively. As for trimetallic catalysts, 0.15 wt% of Ce or Tm, were integrated with PtSn/KL, the TPR profiles can be also deconvoluted into four main peaks. The additional peak was Pt-RE alloy phase centered at 358°C. From Figure 4.1, it indicated that alloy peaks of PtSn/RE/KL are broader than PtSn/KL. It might be due to the metal interaction of Pt-Sn and Pt-RE. In addition, it was observed that reduction temperatures of trimetallic catalysts shift to higher temperature because of the alloy phase of the third promoters but it was still in the range of reduction temperature at 500°C.

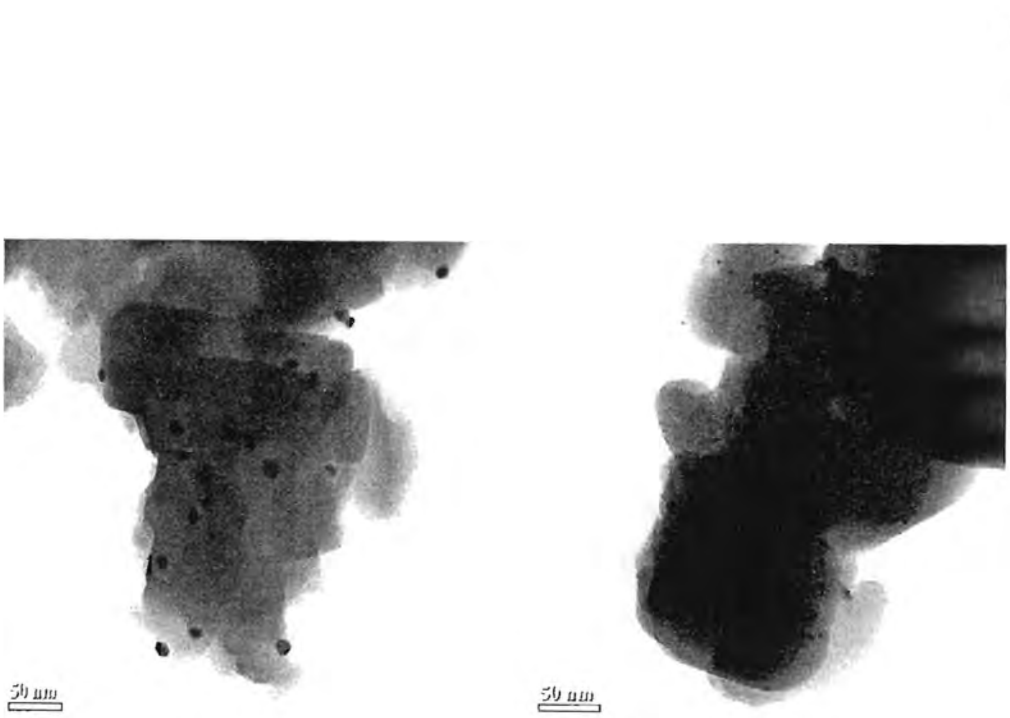
Table 4.2 Deconvolution of TPR profiles of PtSn/KL and PtSn/RE/KL catalysts

Catalysts	Area of each TPR temperature (%)			
	100-220°C Pt rich phase	180-320°C Alloy phase of Pt-Sn catalyst	250-470°C Alloy phase of PtRE catalyst	360-580°C Sn&RE rich phase
PtSn/KL	11.56	70.43	0	18.01
PtSn/Tm/KL	6.49	50.65	22.22	20.64
PtSn/Ce/KL	8.67	47.75	26.21	17.37



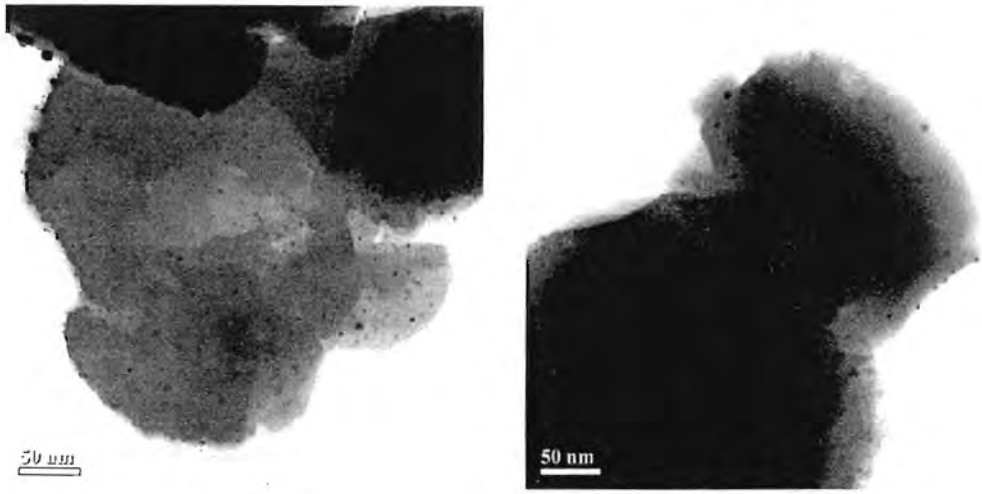
* TPR profile of Ce disappeared for supported KL zeolite.

Figure 4.1 TPR profiles of the mono-, bi-, and trimetallic Pt/KL, PtSn/KL, and PtSnRE/KL catalysts prepared by vapor-phase impregnation method



Pt/KL

PtSn/KL



PtSn/Tm/KL

PtSn/Ce/KL

Figure 4.2 TEM images of particle size distribution obtained by TEM of the Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts.

Table 4.3 Analysis of fresh catalysts

Catalyst	wt% Pt	wt% Sn	wt% RE	H/Pt ratio after reduction at 500°C	Average metal size (nm) (measured from TEM)
Pt/KL	1	0	0	1.32	6.91-13.06
PtSn/KL	1	1	0	0.14	1.18-3.53
PtSn/Tm/KL	1	1	0.15	0.14	1.29-6.45
PtSn/Ce/KL	1	1	0.15	0.16	2.63-6.05

TEM images of particle size distribution obtained by TEM of the Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts were depicted in Figure 4.2. Pt particles outside the zeolite were detected. The results showed that the addition of tin and rare earth elements enhanced the dispersion of metal and also decreased the particle size of metal compared with the unpromoted Pt/KL catalyst. The average particle size of the metal was reported in Table 4.3. It was found that the metal size was decreased to less than 2 nm for PtSn/KL and PtSn/Tm/KL catalysts. However, there are some parts of metal clusters which have a larger particle size than 2 nm for such catalysts as observed in the histogram. Unfortunately, the particles inside the pore of zeolite were not visible. TEM images are the evidence for external particles outside the pore of zeolite because of the limited performance of the TEM machine.

The results of hydrogen chemisorptions are listed in Table 4.3; the unpromoted Pt/KL catalyst exhibited higher H/Pt ratio than PtSn/KL and PtSn/RE/KL catalysts. The addition of tin and rare earth elements caused a strong decrease in the H/Pt ratio since Sn may partially cover the Pt resulted in low hydrogen adsorption (Passos *et al.*, 1998).

X-ray photoelectron spectra of the Pt4d, Sn3d, Tm4d, and Ce3d levels were recorded in order to obtain information about the oxidation states of the metal phased (Pt and/or Sn, RE) on the surface. The peak positions have been corrected for sample charging by using the Si2s peak as a standard at 154.7 eV. Figure 4.3(a) and 4.3(b) showed the Pt4d XPS spectra of the calcined and reduced Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts.

Table 4.4 XPS Binding energy of each type of PtSn/KL and PtSnRE/KL catalysts

Catalysts	$Si2s^a$ (eV)	$Pt4d_{5/2}{}^b$ (eV)	$Sn3d_{5/2}{}^b$ (eV)
Pt/KL	154.7	314.6 (50) 317.2 (50)	-
R_Pt/KL	154.7	314.6 (61) 317.1 (39)	-
PtSn/KL	154.7	314.6 (44) 317.2 (56)	487.3 (100)
R_PtSn/KL	154.7	314.6 (62) 317.2 (38)	485.4 (41) 486.9 (59)
PtSn/Tm/KL	154.7	314.3 (44) 317.1 (56)	487.4 (100)
R_PtSn/Tm/KL	154.7	314.6 (69) 317.1 (31)	485.3 (50) 486.3 (50)
PtSn/Ce/KL	154.7	314.6 (46) 317.1 (54)	487.3 (100)
R_PtSn/Tm/KL	154.7	314.6 (72) 317.1 (28)	485.3 (50) 486.3 (50)

[a] Values reported in eV, and reference to a value of Si2s – 154.7 eV.

[b] Values in parentheses indicate the percentage of the species.

Although the most intense photoemission lines of Pt were those arising from the Pt 4f levels, it was not impossible since there is an overlapping with Al 2p peak (Hoang *et al.*, 2007). As a result, we determined Pt in the levels of 4d instead in this work. In the case of Pt catalyst, it was found that there were two overlapping signals detected at 314.6 eV and 317.1 eV, corresponding to Pt^0 and Pt^{2+} in an oxide environment, respectively. During the calcinations, Pt seemed to be reduced partially. The peaks due to metallic Sn and oxided Sn were found at 485.3 eV and 486.3 eV, respectively. Unfortunately, discrimination between Sn(II) and Sn(IV) is not possible by means of the XPS studies alone. Calcined samples showed oxided Sn only. Upon H_2 reduction at 500°C, more metallic Pt (BE at 314.6 eV) and reduced Sn

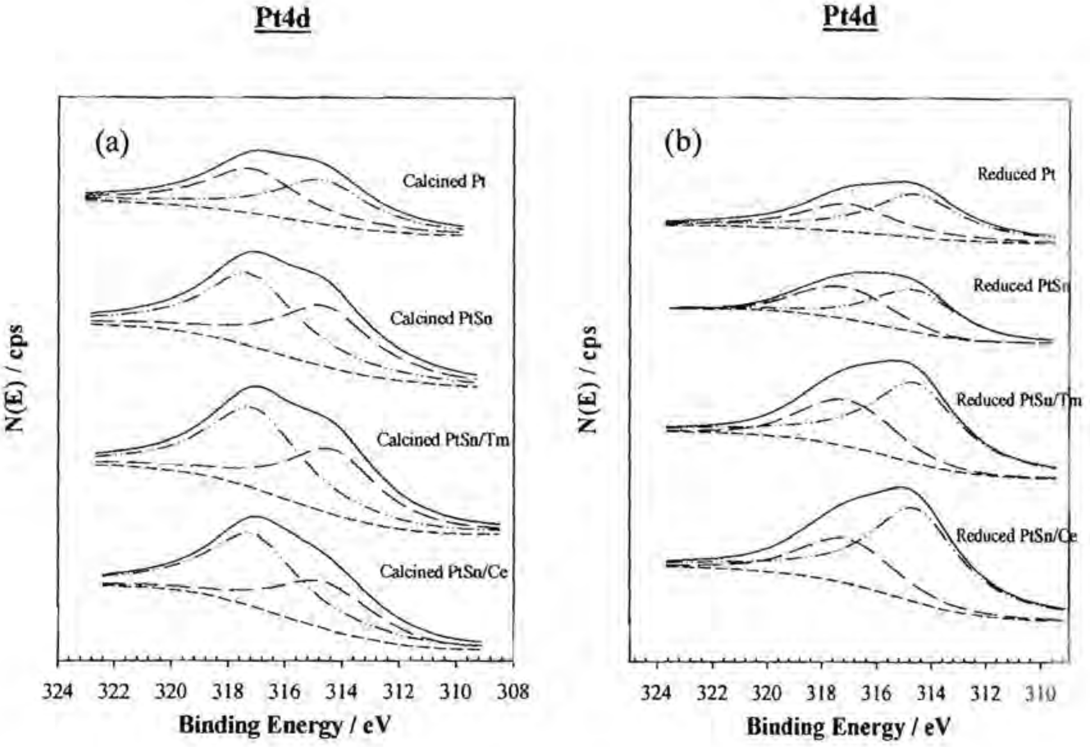


Figure 4.3 XPS Pt $4d_{5/2}$ spectra of the (a) calcined and (b) reduced PtKL, PtSn/KL, and PtSnRE/KL catalysts

species (BE at 485.3 eV) were observed. On the basis of both TPR and XPS data, it can be concluded that the TPR peak of bi- and trimetallic catalysts at temperature around 280°C was associated with the partial reduction of Pt and also with the partial reduction of Sn, so-called Pt-Sn alloy. As for the case of trimetallic PtSn/RE/KL catalysts, Ce and Tm, there were some parts of them were reduced at binding energies 885.1 eV and 175.9 eV, respectively. Their TPR profiles displayed broader peaks which might be due to Pt-RE interaction. This was concordant with XPS data showing more reduced Pt than Pt/KL and PtSn/KL catalysts.

Table 4.5 XPS reference data according to NIST database

Peak	$4d_{5/2}$ (eV)	Peak	$3d_{5/2}$ (eV)
Pt	314.6	Sn	485.2
PtO	317.2	SnO_x	486.1-487.2

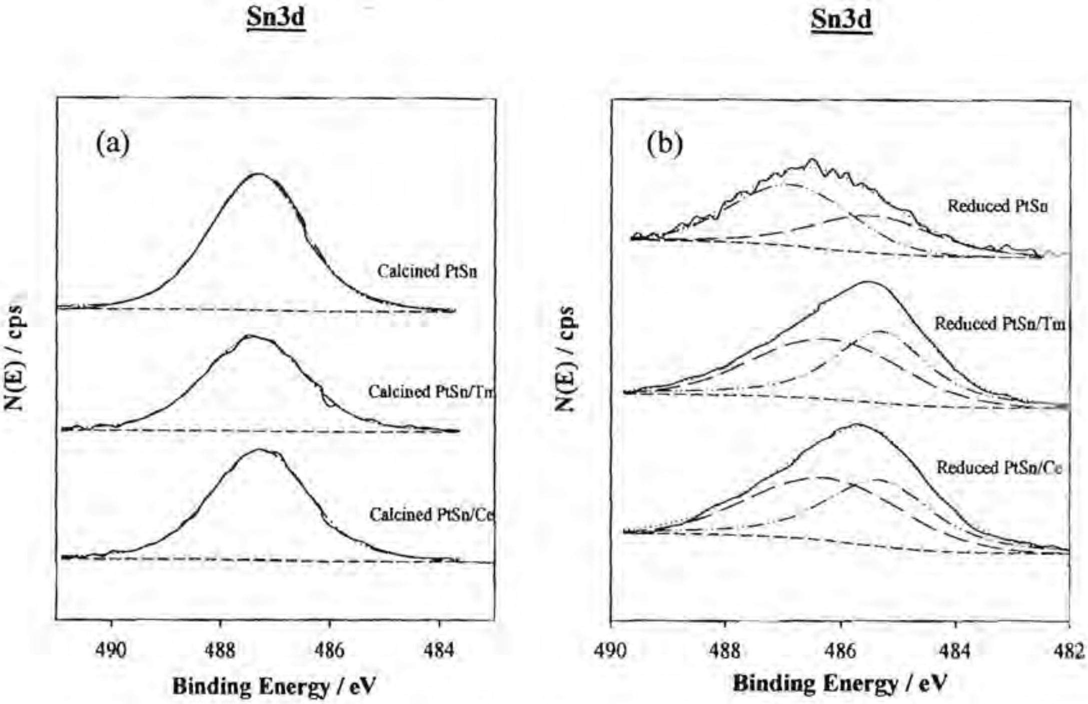


Figure 4.4 XPS Sn $3d_{5/2}$ spectra of the (a) calcined and (b) reduced PtSn/KL, and PtSnRE/KL catalysts

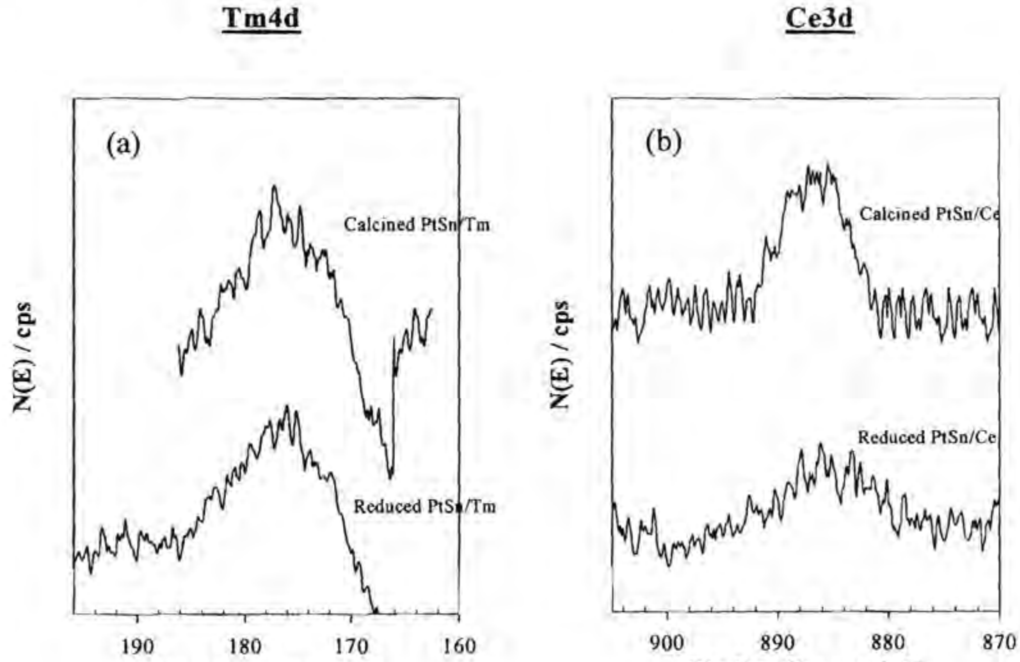


Figure 4.5 XPS (a) Tm 4d5/2 and (b) Ce 3d5/2 spectra of the calcined and reduced PtSnRE/KL catalysts

4.2 Catalytic Activity Testing: *n*-Octane Aromatization

4.2.1 Sulfur-free Feed

All catalysts were tested for *n*-octane aromatization at 500°C and atmospheric pressure. The variations of *n*-octane conversion with time on stream for the mono-, bi-, and trimetallic catalysts are illustrated in Figure 4.6 (a). It was found that Pt/KL exhibited a rapid deactivation due to coke plugging inside the pores because of the restricted diffusion out of the pore of C8-aromatic products (EB and OX) (Jongpatiwut *et al*., 2005). Moreover, the presence of a promoter (Sn) caused a decrease in the initial activity due to the decrease in the platinum adsorption capacity as measured by hydrogen chemisorption. In a previous study, it was observed that the addition of the promoter such as tin improved the stability of the Pt/KL catalyst by inhibiting the adsorption of dehydrogenated species which is the intermediate for formation of coke (Hill *et al*., 1998, Cortright *et al*., 1994, 2000).

In terms of product selectivity, the results revealed that PtSn/KL and PtSn/RE/KL yield were higher selectivity to total aromatics and C8-aromatics selectivity than Pt/KL. Based on a previous study, it was found that the addition of Sn improved the stability of the Pt/KL catalyst by inhibiting the adsorption of dehydrogenated species which was the intermediate for formation of coke. Since Sn addition broke the Pt ensemble into the smaller metal clusters; consequently, the coke and hydrogenolysis reactions which favored to occur on large metal cluster were inhibited (Passos *et al*., 1998). Furthermore, as shown in Table 4.6, the predominant aromatics products on bi- and trimetallic catalysts were C8-aromatics (EB and OX) with the small amount of benzene and toluene which are undesired products from hydrogenolysis reaction. Therefore, the addition of promoted metal caused a decrease in the hydrogenolysis products and increase in C8-aromatics products. Additionally, from previous studies, it was believed that tin decreased the hydrogenolysis reaction by the electronic effect since some electrons of tin were transferred to Pt when PtSn alloy phase was formed. Consequently, C-C bond hydrogenolysis does not occur because the hydrocarbon cannot be strongly adsorbed on the catalyst surface (Trakarnroek *et al*., 2007). Not only was the hydrogenolysis reaction decreased by the electronic effect, but also the formation of OX molecules was also enhanced

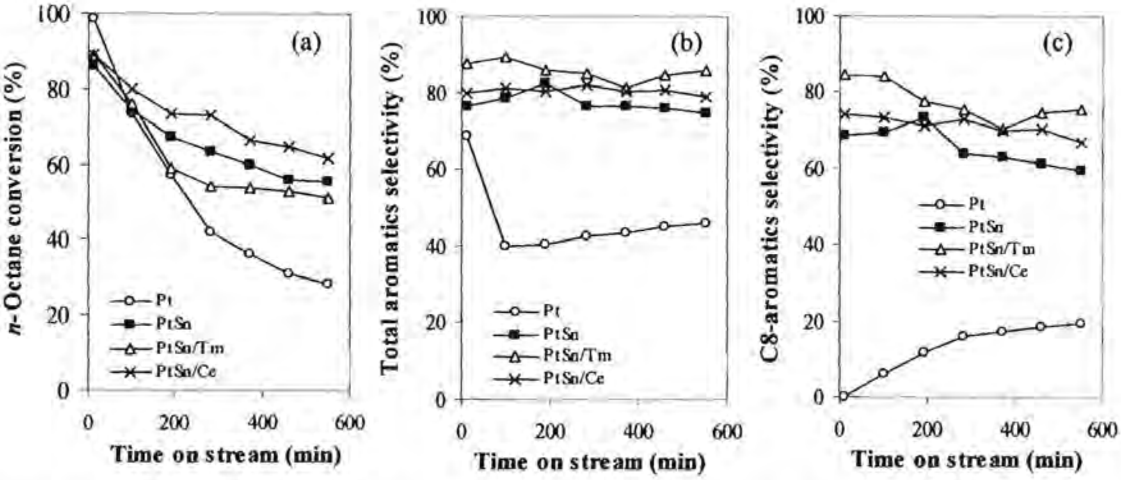


Figure 4.6 The variations of (a) *n*-octane conversion (b) total aromatics selectivity and (c) C8-aromatics selectivity vs. time on stream under clean *n*-octane feed over Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts. Reaction conditions: WHSV = 5h^{-1}; H_2/HC molar ratio = 6; temperature = 500°C; pressure = 1 atm

as shown in Table 4.6. Westfall *et al.* (1976) and Lee *et al.* (1993) informed that the molar ratio of EB/OX may be an indirect index, indicating that electron density of Pt by the addition of Sn. Dehydrocyclization of *n*-octane produced EB and OX by a mechanism that involved the direct formation of a six-membered carbon ring (Davis *et al.*, 1969). The bond strength of primary hydrogen in $-CH_3$ is only greater than that of secondary hydrogen in $-CH_2$. Therefore, it was expected that the six-membered ring intermediate would lead to an almost equal amount of EB and OX (Meriaudeau *et al.*, 1997). However, Sn would alter the ability of Pt to rupture the C-H bond and favor the rupture of the weaker C-H bond of the secondary hydrogen of the $-CH_2$ groups over those of the primary hydrogen of the $-CH_3$ groups. Therefore, the EB/OX ratio was decreased when Sn was employed (Trakarnroek *et al.*, 2007). From Table 4.6, it was found that the EB/OX ratio of Pt was significantly high as a result of no electrons being transferred from Sn to Pt atoms. Contrarily, the bi- and trimetallic catalysts exhibited the EB/OX ratio less than unity while the Pt was greater than unity. The reason that gave the ratio of Pt/KL was greater than one because the critical size of the OX molecule is larger than that of EB which means the speed of transport through the pores is slower for OX than for EB. Hence, OX is much easier to convert to smaller molecules such as benzene, toluene and methane by secondary hydrogenolysis. From Figure 4.6, the result showed that bi- and trimetallic catalysts obtained similar trends on both *n*-octane conversion and product selectivity. That means the addition of rare earths elements as the third metal did not significantly affect the catalytic activity and product selectivity in the case of sulfur-free feed.

4.2.2 Sulfur-containing Feed

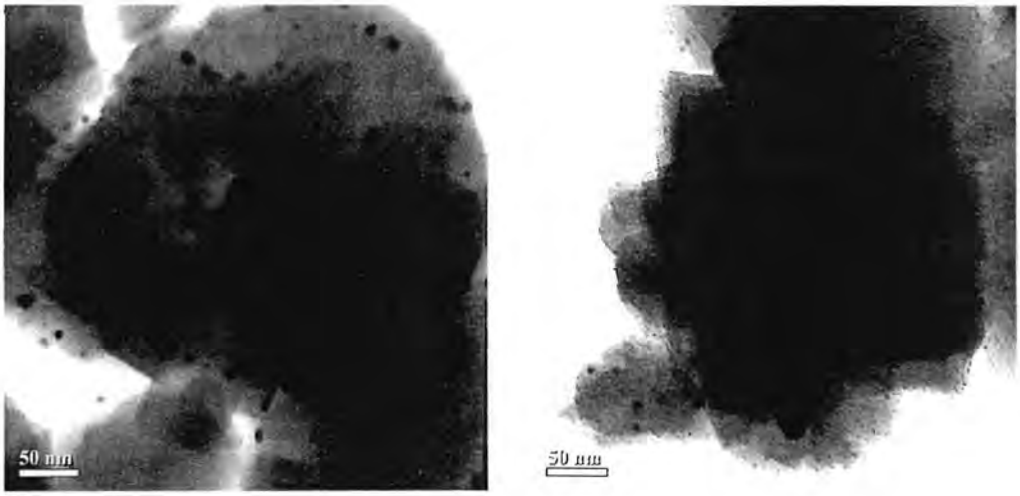
As mentioned before, the high sensitivity of Pt/KL catalysts to sulfur is a major serious problem. They are much more sensitive to sulfur than conventional bifunctional reforming catalysts such as Pt/Al_2O_3 and PtRe/Al_2O_3 (Meriaudeau *et al*., 1997). In order to study the sulfur resistance of Pt/KL, PtSn/KL and PtSn/RE/KL catalysts, 2.5 ppm sulfur was added to the feed. The catalytic activity and C8-aromatics selectivity of sulfur-containing feed are obviously lower than clean feed. Figure 4.7(a) shows the *n*-octane conversion versus time on stream. PtSn/RE/KL catalysts showed higher conversion than mono- and bimetallic catalysts, while C8-aromatics selectivity in Figure 4.7(b) was not significantly different. In agreement with previous study, the presence of sulfur led to instantly weak bonding between metal and support, and then formation of Pt agglomeration and ultimately accelerating the seepage of Pt to the exterior surfaces which blocked the zeolite channel (McVicker *et al*., 1993, M.M.J Treacy, 1998). This induced larger Pt ensembles or clusters required for hydrogenolysis reaction in place of smaller ensembles being suitable for dehydrocyclization. This coincided with Table 4.6; it was found that hydrogenolysis products were increased for PtSn/KL and PtSn/RE/KL catalysts in sulfur-containing feed. Anyhow, Pt/KL did not correspond to the above mention. The reason could be because unpromoted Pt/KL was poisoned and rapidly deactivated which led to lower adsorption of hydrocarbons. Moreover, EB/OX ratio of Pt/KL exposing with sulfur as shown in Table 4.6 are much lower than that of clean feed while it did not have noticeable difference for bi- and trimetallic catalysts. Due to the fact that Pt inside the zeolite channel migrated to near pore mouth or outside the pore of zeolite, the probability to occur OX increased since there was no restricted diffusion out of the product inside the channel. In the case of bimetallic catalyst, sulfur might break Pt-Sn alloy; which plays an important role for product selectivity, due to

Table 4.6 Properties of Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts tested for *n*-octane aromatization after 550 minutes time on stream under sulfur-free and 2.5 ppm sulfur-containing feeds; reaction conditions: WHSV = 5h^{-1}; H_2/HC molar ratio = 6; temperature = 500°C; pressure = 1 atm

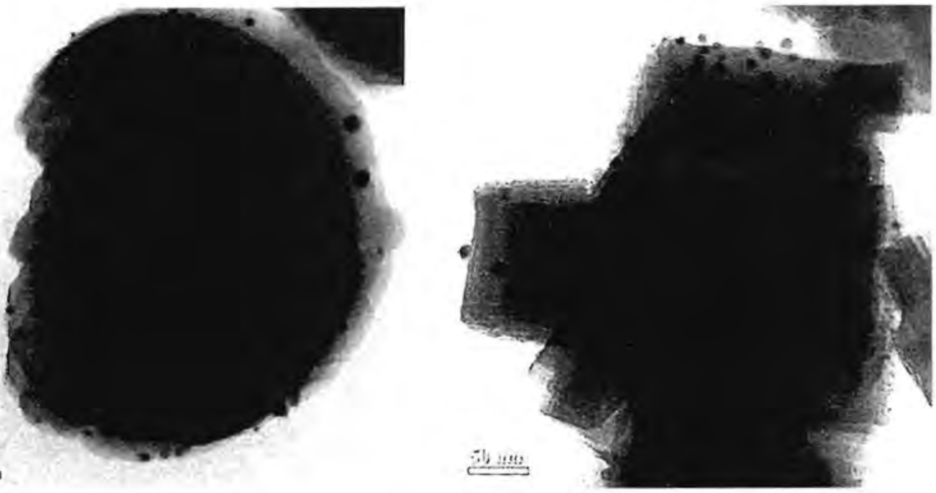
Feed	Sulfur-free feed				Sulfur-containing feed			
Catalysts	Pt/KL	PtSn/KL	PtSn/Tm/KL	PtSn/Ce/KL	Pt/KL	PtSn/KL	PtSn/Tm/KL	PtSn/Ce/KL
Conversion (%)	24.5	56.1	51.3	61.8	19.4	25.8	46.7	48.6
Product distribution (%)								
C1-C5	22.9	7.1	1.6	5.1	10.5	20.2	25.9	38.5
Total enes (C6-C8enes)	30.7	16.9	12.4	13.9	26.3	34.4	19.8	19.9
Total aromatics	46.4	76.1	86.0	80.9	63.2	45.4	54.3	41.6
Total aromatics (%)								
Benzene	16.7	4.1	0.04	3.1	0.1	0.1	2.4	2.8
Toluene	6.9	10.8	10.0	7.5	17.7	17.0	10.8	9.4
C8-aromatics	22.8	61.2	75.6	70.3	44.9	28.3	41.1	29.4
EB	14.9	25.8	32.4	27.6	19.8	13.2	21.1	13.9
m-.*p*-Xylene	1.6	1.7	0.0	1.6	0.0	0.0	0.0	1.9
o-Xylene	6.3	33.8	43.2	41.0	25.0	15.0	20.0	13.6
EB/OX ratio	2.35	0.76	0.75	0.67	0.79	0.88	1.05	1.02
Hydrogenolysis products	46.5	21.9	12.0	15.8	28.8	37.3	39.1	50.7

4.3 Characterization of Spent Catalysts

TEM images of particle size distribution obtained by TEM of the Pt, PtSn, and PtSn/RE catalysts after running of reaction at 550 minutes are shown in Figure 4.8.



Pt/KL PtSn/KL



PtSn/Tm/KL PtSn/Ce/KL

Figure 4.8 TEM images of particle size distribution obtained by TEM of the spent Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts

It was clearly seen that the particle size of spent catalysts was bigger than fresh ones. The reason of this could be because sulfur might induce metal particle size growth and resulted in lower metal dispersion which caused lower catalytic activity and C8-aromatics selectivity in Figure 4.4 (McVicker *et al.*, 1992). Although, TEM images could not indicate the existence of the metal inside the zeolite channel as mentioned before, the performance on both *n*-octane conversion and C8-aromatics selectivity for Pt/KL and PtSn/KL catalysts in this experiment agreed with previous investigations (Jongpatiwut *et. al.*, 2005, Trakarnroek, 2007) and was evident the presence of very fine particles inside the zeolite channel.

The spent catalysts were also characterized by TPO to quantify the amount of carbon deposited on the catalysts during the reaction in terms of percent weight of carbon. The coke formation obtained after reaction with feeds containing sulfur-free and sulfur-containing over Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts are illustrated in Table 4.7.

Table 4.7 TPO analysis of spent Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts under clean and 2.5 ppm sulfur-containing feed

Catalysts	Coke deposited after reaction 550 minutes TOS (wt%) **Sulfur-free feed**	Coke deposited after reaction 550 minutes TOS (wt%) **2.5 ppm Sulfur-containing feed**
Pt/KL	2.9	1.1
PtSn/KL	2.1	1.8
PtSn/Tm/KL	1.3	1.7
PtSn/Ce/KL	2.0	2.1

In the case of non-sulfided samples, the monometallic Pt/KL catalyst was more deactivated by coke than bimetallic PtSn/KL and trimetallic PtSn/RE/KL catalysts. This agrees with the catalytic activity of clean feed in Figure 4.6 (a). Pt/KL rapidly deactivated by coke plugging inside the pore of KL zeolite because of the restricted diffusion out of the pore of C8-aromatic products (EB and OX) (Jongpatiwut *et al.,* 2005). Contrarily, Sn-promoted on the catalysts have less amount of coke due to the fact that tin decreased the number of contiguous platinum atoms and then

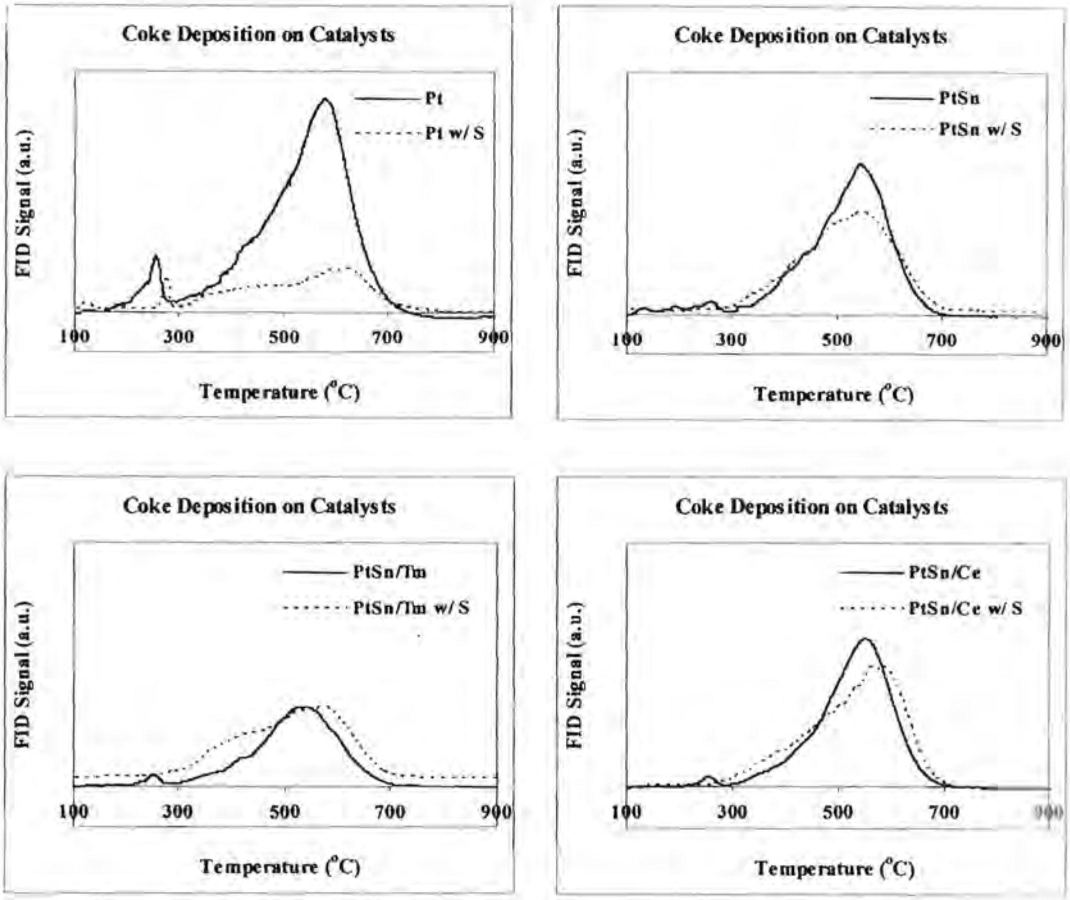


Figure 4.9 TPO profiles of spent Pt/KL, PtSn/KL, and PtSn/RE/KL catalysts under clean and sulfur-containing feeds

the multipoint adsorption of hydrocarbon molecules on the surface is hampered. Consequently, coke formation can be reduced (Paal *et al.*, 1997). However, coke formation in Table 4.7 was regarded as there was no significant change in carbon remained on the PtSn/KL and PtSnRE/KL catalysts for both clean and sulfur-containing feeds. While activity profiles of catalyst with sulfur-containing feed in Figure 4.7(a) remarkably dropped as compared with those of clean feed in Figure 4.6 (a). That means the quantity of coke deposition in promoted catalysts was not affected by the presence of sulfur. From Figure 4.9, the peaks occurred at low temperature were corresponded to TEM images indicating some Pt particles outside the pore of zeolite. Therefore, coke deposited on these clusters was firstly burned out at low temperature. The amount of Pt at exterior zeolite channel for clean feed exhibited higher than that of sulfur-containing feed. Also, Pt/KL showed the highest quantity of these clusters. Presumably, external Pt was poisoned by adsorbing with sulfur. It quickly deactivated, then Pt could not adsorb hydrocarbons which are coke precursors. As a result, the coke deposition peaks for external Pt in sulfur-exposing feed were lower than clean feed.

To prove that sulfur would segregate Pt-Sn and Pt-RE alloys, the spent catalysts were characterized by TPR after mild decoking at 350°C for 30 minutes. From Figure 4.10, there are three main peaks which correspond to Pt phase, metal interaction phase, and RE and Sn phase, respectively. The result displayed that TPR profiles showed the Pt-Sn interaction for the catalysts spent with sulfur-free feed but no Pt-Sn signal was observed on the spent catalysts with sulfur-containing feed. This demonstrates that the presence of sulfur induced the rupture of Pt-Sn alloy resulted in lower C8-aromatics selectivity which is shown in Figure 4.7(c).

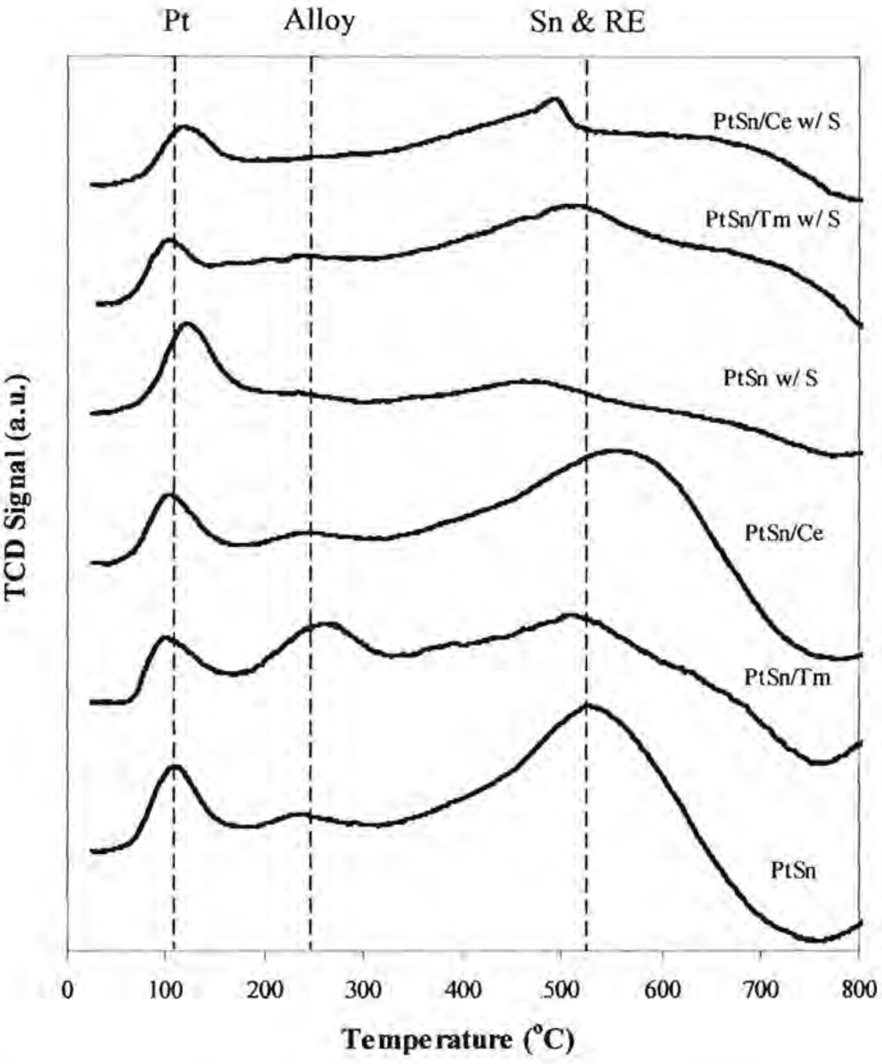


Figure 4.10 TPR profiles of the spent PtSn/KL and PtSn/RE/KL catalysts under clean and 2.5 ppm sulfur-containing feed after mild decoking at 350°C for 30 minutes

Since tin is inactive, it does not bond with sulfur. Therefore, it interacts with Pt instead. As a result, C8-aromatics products decreased while hydrogenolysis products increased. Interestingly, 1Pt shows

. To illustrate, sulfur does not adsorb on tin (Borgna *et al.*, 1994, Garetto *et al.*, 1996) because it is inactive, so it may interact with Pt atoms instead. The low thiotolerance of *n*-hexane reforming displayed by Pt–Sn catalysts cannot therefore be explained only by the characteristics of the sulfur adsorption on the metal fraction. Probably, the sensitivity to sulfur poisoning was enhanced because the formation of coke is suppressed over Pt–Sn/Al_2O_3 (Borgna *et al.*, 2000). It has been reported that coke formation may protect the metal against sulfur poisoning (Pieck *et al.*, 1996); this protective effect for sulfur adsorption would be negligible on the Pt–Sn catalyst.

It can be concluded that sulfur accelerates the Pt particle growth, and that the catalyst deactivation results in part from the blockage of KL channel by large Pt particles. On the other hand,

TPO

From previous works, they found that sulfur affects both nature and location of the coke deposit. It has been proposed that coke is more dehydrogenated and occurred mainly on the support on sulfided catalysts. It has been reported that coke deposition may protect the metal against sulfur poisoning since sulfur prefer bonding with rhenium instead of active Pt (Pieck *et al.*, 1996); this protective effect would be negligible on Pt-Sn catalyst due to the fact that sulfur does not adsorb on tin (Borgna *et al.*, 1994, Garetto *et al.*, 1996) because it is inactive atom, so it therefore interacts with Pt atoms instead. As a result, Pt metal growth increases leading to lower product selectivity.

Based on Jacob's and Jongpatiwut's work in 1998 and 2002, respectively, it was seen that during the first several time on stream (< 20 hours) in sulfur feed, less coke pronounced on unpromoted Pt/KL than RE-promoted Pt/KL. Additionally, the results of TPO in this research agree with previous studies that catalysts employing with RE can be observed indistinguishable amount of coke formation between clean and sulfur-exposing feed. That means the quantity of coke deposition in RE-catalysts is not affected by the presence of sulfur. Thus, sulfur was the predominant effect in deactivation instead of coke formation.

Sulfur containing feed

At the end of 550 minutes time on stream, it is very interesting that C8-aromatics selectivity of Pt is higher than that obtained with sulfur-free feed. This could be because sulfur accelerates Pt agglomeration outside the pore, leading to lower pore restriction and lower hydrogenolysis reaction, respectively.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

It was found that for sulfur-free feed, the addition of Sn improved the catalytic activity and selectivity of *n*-octane aromatization on Pt/KL catalyst. The result showed that bi- and trimetallic catalysts obtained similar trends on both *n*-octane conversion and product selectivity. That means the addition of rare earth elements as the third metal did not significantly affect the catalytic activity and product selectivity.

In the presence of sulfur, the sulfur resistance of PtSn/KL was low. The catalytic activity gradually decreased as a function of time on stream and gave similar extent with Pt/KL. The reason could be because sulfur does not adsorb on tin, it therefore interacts with active Pt instead. As a result, metal interaction broke. This induced the deactivation by Pt particle growth. However, there was somehow different results in the activity when RE-promoted catalysts was used in sulfur-containing feed. *n*-Octane conversion of PtSn/RE/KL catalysts was higher than that obtained from mono- and bimetallic catalysts, while C8-aromatics selectivity of all catalysts was not significantly different. It was clearly seen that RE helps retart the adsorption of sulfur on active site by acting as sulfur anchoring or sulfur getter. Consequently, it temporarily prevents Pt agglomerization. As a result, sulfur tolerance increased.

5.2 Recommendation

In this work, for trimetallic catalysts, we have done experiment with the preparation of sequential RE impregnation, then co-impregnation of Pt and Sn. The results exhibited in a good way for the catalytic activity but not for the selectivity. However, it is an interesting idea to vary ratio of added Pt, Sn, and Tm including preparation methods to see how they effect to catalytic activity and selectivity of sulfur-free and sulfur-containing feeds.

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2. Nawarat, U., Rirksomboon, T., **Jongpatiwut, S.,** Dokjampa, "Ethylation of Benzene with Ethanol over Commercial HZSM-5 Catalysts", 13th Asian Pacific Confederation of Chemical Engineering Congress, Taipei, Taiwan, 5-8 October, 2010.
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24. Trakarnroek, S., **Jongpatiwut, S.**, Rirksomboon, T., Osuwan, S., and Resasco, D. E "Effect of Pore Length of Pt/KL Zeolite Catalyst on n-Octane", *Research Advances in Rational Design of Catalysts and Sorbents,* IFP-Lyon, France, 14-16 December 2005.
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26. Resasco, D.E., Do, P, Santana, R., **Jongpatiwut, S.**, Santikunaporn, M., Beltramone, A., "Combined deep hydrogenation and ring opening of poly-aromatic hydrocarbons for diesel quality improvement", *229th ACS National Meeting*, San Diego, CA, USA, 13-17 March 2005.

27. Dokjampa, S., **Jongpatiwut, S.**, Rirksomboon, T., Osuwan, S., and Resasco, D. E "Comparative Study of the Hydrogenation of Tetralin on Supported Ni, Pt, and Pd Catalysts", *Proceedings of the AIChE Annual Meeting*, Cincinnati, USA, 30 October-4 November 2005.

28. Danuthai, T., **Jongpatiwut, S.**, Rirksomboon, T., and Osuwan, S., , Resasco, D. E "A Comparative Study of N-Octane Aromatization over Modified Mfi- and Mel-Type Zeolite Catalysts", *Proceedings of the AIChE Annual Meeting*, Cincinnati, USA, 30 October-4 November 2005.

29. Trakarnroek, S., Osuwan, S., Rirksomboon, T., **Jongpatiwut, S.**, and Resasco, D. E "n-Octane Aromatization over Pt/KL of Varying Zeolite Crystallite Morphology", *Proceedings of the 7th World Congress of Chemical Engineering*, Glasgow, Scotland, 10-14 July 2005.

30. Dokjampa, S., Rirksomboon, T., **Jongpatiwut, S.**, Osuwan, S., and Resasco, D. E "Hydrogenation of Monoaromatics on Nickel Catalysts", *Proceedings of Regional Symposium on Chemical Engineering 2004 in conjunction with the 14th National Chemical Engineering and Applied Chemistry*, Bangkok, Thailand, 1-3 December 2004.

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32. Trakarnroek, S., Rirksomboon, T., and Osuwan, S., **Jongpatiwut, S.**, Resasco, D. E., "Effect of zeolite crystal size on the selectivity for n-octane aromatization over Pt/KL catalysts", *Proceedings of the AIChE Annual Meeting*, Austin, TX, USA, 7-12 November 2004.

33. Herrera, J.E., Zhongrui L., **Jongpatiwut, S.**, Alvarez, W., and Resasco, D.E., "Role of Fluorine in Enhancing the Sulfur-Tolerance of Pt-Pd Catalysts used in the Hydrogenation of Diesel Fuel Components", *Proceedings of the AIChE Annual Meeting*, Austin, USA, 7-12 November 2004.

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39. **Jongpatiwut, S.**, Santana R.C., Resasco, D. E., Alvarez, W. E., Sughrue, E.L., Dodwell, G. W. "Role of F in the Sulfur Tolerance of Pt-Pd Catalysts for Hydrogenation of Polynuclear Aromatics", *Proceedings of the AIChE Annual Meeting*, San Francisco, USA, 16-21 November 2003.

40. Lertkijcharoenwong, D., **Jongpatiwut, S.,** Rirksomboon, T., Osuwan, S., and Resasco, D. E., " Regeneration of Pt/KL Catalysts Used for n-Octane Aromatization" *Proceedings of the AIChE Annual Meeting*, San Francisco, USA, 16-21 November 2003.

41. Sakulchaicharoen, N., **Jongpatiwut, S.,** Herrera, J.E., and Resasco, D. E., ,"Influence of Catalyst Support and Reaction Conditions in the Synthesis of Silicon Nanowires by Decomposition of Silane on Gold", *Proceedings of the AIChE Spring Meeting*, San Francisco, USA, 16-21 November 2003.

42. **Jongpatiwut, S.**, Resasco, D. E., Zhongrui, L., Alvarez, W. E., Sughrue, E., Dodwell, G. "Competitive Hydrogenation of Poly-aromatic Hydrocarbons on Sulfur-resistant Bimetallic Pt-Pd Catalysts", *59th Southwest Regional Meeting of the American Chemical Society*, Oklahoma, USA, 26-28 October 2003.

43. **Jongpatiwut, S.**, Sackamduang, P., Rirksomboon, T., Osuwan, S., Alvarez, W. E., and Resasco, D. E. "Aromatization of n-Hexane and n-Octane over Pt/KL and Pt/SiO_2 Catalysts", *Proceedings of the AIChE Spring Meeting*, New Orleans USA, 10-14 March 2002, pp. 1-8.

44. Sackamduang, P., **Jongpatiwut, S.**, Rirksomboon, T., Osuwan, S., and Resasco, D.E. "A Comparative Study of n-Hexane and n-Octane Aromatization over Pt/KL Catalysts" *Proceedings of the 11th National Chemical Engineering and Applied Chemistry Conference*, Nakhon Ratchasima, Thailand, 9-10 November 2001, CD ROM.

45. **Jongpatiwut, S.**, Sackamduang, P., Rirksomboon, T., Osuwan, S., Alvarez, W.E., and Resasco, D. E. "Promotion of Pt/KL catalysts with rare earth oxides for the aromatization of C6 and C8 feeds" *46th Annual Pentasectional Meeting; Oklahoma Sections of the American Chemical Society*, Oklahoma, USA, 3 March 2001.

46. **Jongpatiwut, S.**, Sackamduang, P., Rirksomboon, T., Osuwan, S., and Resasco, D. E. "Comparative Study of n-Hexane Aromatization on Pt/KL Catalysts Prepared by Vapor Phase Impregnation and Containing Rare Earth Elements: Clean, Sulfur-Containing, and Water-Containing Feeds", *Bangkok International Conference on Heterogeneous Catalysis*, Bangkok, Thailand, 7-9 January 2001.

47. Lertrojanachoosit, B., **Jongpatiwut, S.**, Rirksomboon, T., Osuwan, S., and Resasco, D.E. "n-Hexane Aromatization to Benzene on Pt/KL And Pt/Ce-KL Prepared By VPI Method" *Proceedings of the Regional Symposium on Chemical Engineering 2000*, Singapore, 10-12 December 2000, CD ROM.

48. Thongsrikate, T., **Jongpatiwut, S.**, Rirksomboon, T., Osuwan, S., and Resasco, D. E. "n-Hexane Aromatization to Benzene on Pt/KL and PtYb/KL Catalysts Prepared by CVD Method" *Proceedings of the 10th National Chemical Engineering and Applied Chemistry Conference*, Bangkok, Thailand, 26-28 October 2000, pp. 197-206.

49. Lertrojanachoosit, B., Thongsrikate, T., **Jongpatiwut, S.**, Rirksomboon, T., Osuwan, S., and Resasco, D. E. "Increased Sulfur Tolerance of Pt/KL Catalysts Containing Rare Earth Promoters for n-Hexane Aromatization", *AIChE Annual Meeting 2000*, Los Angles, USA, 12-17 November 2000.

50. Santipornvit, P., **Jongpatiwut, S.**, Rirksomboon, T., Osuwan, S., and Lobban L. L. "Ozone Degradation of Aqueous Contaminants in Bonded Admicelles" *Proceedings of the Regional Symposium on Chemical Engineering 2000*, Songkhla, Thailand, 22-24 November 1999, pp. B28-1-6.[MS]

51. **Jongpatiwut, S.**, Lertrojanachoosit, B., Thongsrikate, T., Rirksomboon, T., Osuwan, S., and Resasco, D. E., "Increased Sulfur Tolerance of Pt/KL Catalysts Containing Rare Earth Promoters for n-Hexane Aromatization", *RGJ-Ph.D. Congress I*, Karnjanaburi, Thailand, 2-4 May 2000.

52. **Jongpatiwut, S.**, Rirksomboon, T., Osuwan, S., and Lobban L. L. "Formation and Adsolubilization of Hydrocarbon and Fluorocarbon Aggregates Chemically Bonded on Silica Surface" *Proceedings of the 8th National Chemical Engineering and Applied Chemistry Conference*, Nakhonpatom, Thailand, 17-18 December 1998, pp. 358-373. [MS]

SCHOLARSHIP & AWARD

• Royal Golden Jubilee Ph.D. Scholarship (as Advisor)	2010
• TRF New Faculty Scholarship	2005-2007
• Rachadapiseksompot New Faculty Scholarship	2005
• Oklahoma Center Advancement of Science and Technology, USA	2002-2004
• Royal Golden Jubilee Ph.D. Scholarship	999- 2002
• The Best Student Award (Class IV: 1996-1998)	1998

SKILL

RESEARCH AREA:

Catalysis for Petroleum, Petrochemicals, and Renewable Energy

CHARACTERIZATION TECHNIQUE:

Chromatography: GC, HPLC

Spectroscopy: FTIR, EXAFS, XPS, MS

Others: XRD, BET, TPO/D/R, TGA, DSC, TEM, SEM, Chemisorption, AAS

COMPUTER:
Programming: Fortran, C, Access
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Education

Ph.D. (Chem. Eng.)	U. of New Brunswick, Canada	1971
M.Sc. (Chem. Eng.)	U. of New Brunswick, Canada	1968
B.Sc. (Hons.) (Chem. Eng.)	Chulalongkorn University	1964

Memberships

Science Society of Thailand
Engineering Institute of Thailand
American Chemical Society
American Institute of Chemical Engineers

Professional experience

Chulalongkorn University
Petroleum and Petrochemical Technology Consortium (1999-present)
  Director (1999-present)
The Petroleum and Petrochemical College (1992-present)
  Director (1993-2000)
  Deputy Director (1992-1993)
Department of Chemical Technology (1964-2000)
  Professor (1988-2000)
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Research interests

Catalysis and reactor design
Surfactant application and separation processes
Energy, fuel and combustion

Publications (recent)

1. Luengnaruemitchai, A., Thoa, D.T.K., Osuwan, S., and Gulari, E. (2005) "A Comparative Study of Au/MnO_x and Au/FeO_x Catalysts for the Catalytic Oxidation of CO in Hydrogen Rich Stream" ,International Journal of Hydrogen Energy, 30, 981-987.
2. Jongpatiwut, S., Trakarnroek, S., Rirksomboon, T., Osuwan, O., and Resasco, D.E. (2005) "n-Octane Aromatization on Pt-containing Non-acidic Large Pore Zeolite Catalysts", Catalysis Letters, 100(1-2), 7-15.
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4. Trakultamupatam, P., Scamehorn, J.F., and Osuwan, S. (2004) "Scaling Up Cloud Point Extraction of Aromatic Contaminants from Wastewater in a Continuous Rotating Disk

Contactor. I. Effect of Disk Rotation Speed and Wastewater to Surfactant Ratio" ,Separation Science and Technology, 39 (3), 479-499.

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EDUCATION:

- Ph.D., Chemical Engineering, The University of New Brunswick, Fredericton, Canada, 1997
  Dissertation Title: Investigation of Small Scale BLEVE Tests,
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- M.Sc., Chemical Technology, Chulalongkorn University, Bangkok, Thailand, 1990
  Thesis Title: Correlation of Heating Value and Proximate Analysis of Coals in Thailand,
  Advisor: Professor Somchai Osuwan
- B.Sc., Chemical Engineering, Chulalongkorn University, Bangkok, Thailand, 1987
- High School Diploma, Math-Sci. Program, St. John's College, Bangkok, Thailand, 1983

CURRENT POSITION:

- Associate Professor of Chemical Engineering, The Petroleum and Petrochemical College, Chulalongkorn University, 2002-Present

PROFESSIONAL EXPERIENCE:

- Deputy Director, Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials Chulalongkorn University, 2006-2011
- Deputy Director, The Petroleum and Petrochemical Technology Consortium, Chulalongkorn University under Asian Development Bank (ADB) Loan, 2002-2006
- Assistant Professor of Chemical Engineering, The Petroleum and Petrochemical College, Chulalongkorn University, 1999-2002
- Lecturer, The Petroleum and Petrochemical College, Chulalongkorn University, 1997-1999
- Research Assistant, Centre for Nuclear Energy Research, The University of New Brunswick, 1994-1996
- Programmer, Thai Chemical and Engineering Co., Ltd., 1990-1991
- Assistant Engineer, PPG-Siam Silica Co., Ltd., 1989-1990

AWARDS:

- PRC-RTG Technical Cooperation Program for Observation on Petroleum and Petrochemical Industries in People's Republic of China, Thailand International Development Cooperation Agency, Ministry of Foreign Affairs, Thailand, 2000
- Research Assistantship, Centre for Nuclear Energy Research, The University of New Brunswick, Canada, 1994-1996
- Teaching Assistantship, Chemical Engineering Department, The University of New Brunswick, Canada, 1991-1996
- Graduate Research Assistantship, The University of New Brunswick, Canada, 1991-1993
- Teaching Assistantship, Chemical Technology Department, Chulalongkorn University, Thailand, 1988-1990
- Graduate Scholarship, Graduate School, Chulalongkorn University, Thailand, 1988-1989

AREAS OF SPECIAL INTEREST:

Boiling liquid expanding vapor explosion (BLEVE), heterogeneous catalysis related to petroleum and petrochemical industry, pyrolysis of solid wastes to energy

PUBLICATIONS AND PRESENTATIONS:

59. Danuthai, T., Sooknoi, T., Jongpatiwut, S., Rirksomboon, T., Osuwan, S., and Resasco, D.E. (2011) "Effect of extra-framework cesium on the deoxygenation of methylester over CsNaX zeolites", Applied Catalysis A: General, **409–410**, 74–81.
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46. Pengpanich, S., Meeyoo, V., Rirksomboon, T., and Schwank, J. (2008) "iso-Octane Partial Oxidation over Ni-Sn/$Ce_{0.75}Zr_{0.25}O_2$ Catalysts", Catalysis Today, **136** (3-4), 214-221.
45. Jongpatiwut, S., Rattanapuchapong, N., Rirksomboon, T., Osuwan, S., and Resasco, D.E. (2008) "Enhanced Sulfur Tolerance of Bimetallic PtPd/Al_2O_3 Catalysts for Hydrogenation of Tetralin by Addition of Fluorine", Catalysis Letters, **122** (3-4), 214-222.
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43. Kuanchertchoo, N., Suwanpreedee, R., Kulprathipanja, S., Aungkavattana, P., Atong, D., Hemra, K., Rirksomboon, T., and Wongkasemjit, S. (2007) "Effects of Synthesis Parameters on Zeolite

Membrane Formation and Performance by Microwave Technique" Applied Organometallic Chemistry, **21** (10) , 841-848.

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41. Dokjampa, S., Rirksomboon, T., Phuong, D.T.M., and Resasco, D.E. (2007) "Ring Opening of 1,3-Dimethylcyclohexane on Ir Catalysts: Modification of Product Distribution by Addition of Ni and K to Improve Fuel Properties", Molecular Catalysis A: Chemical, **274** (1-2), 231-240.

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