

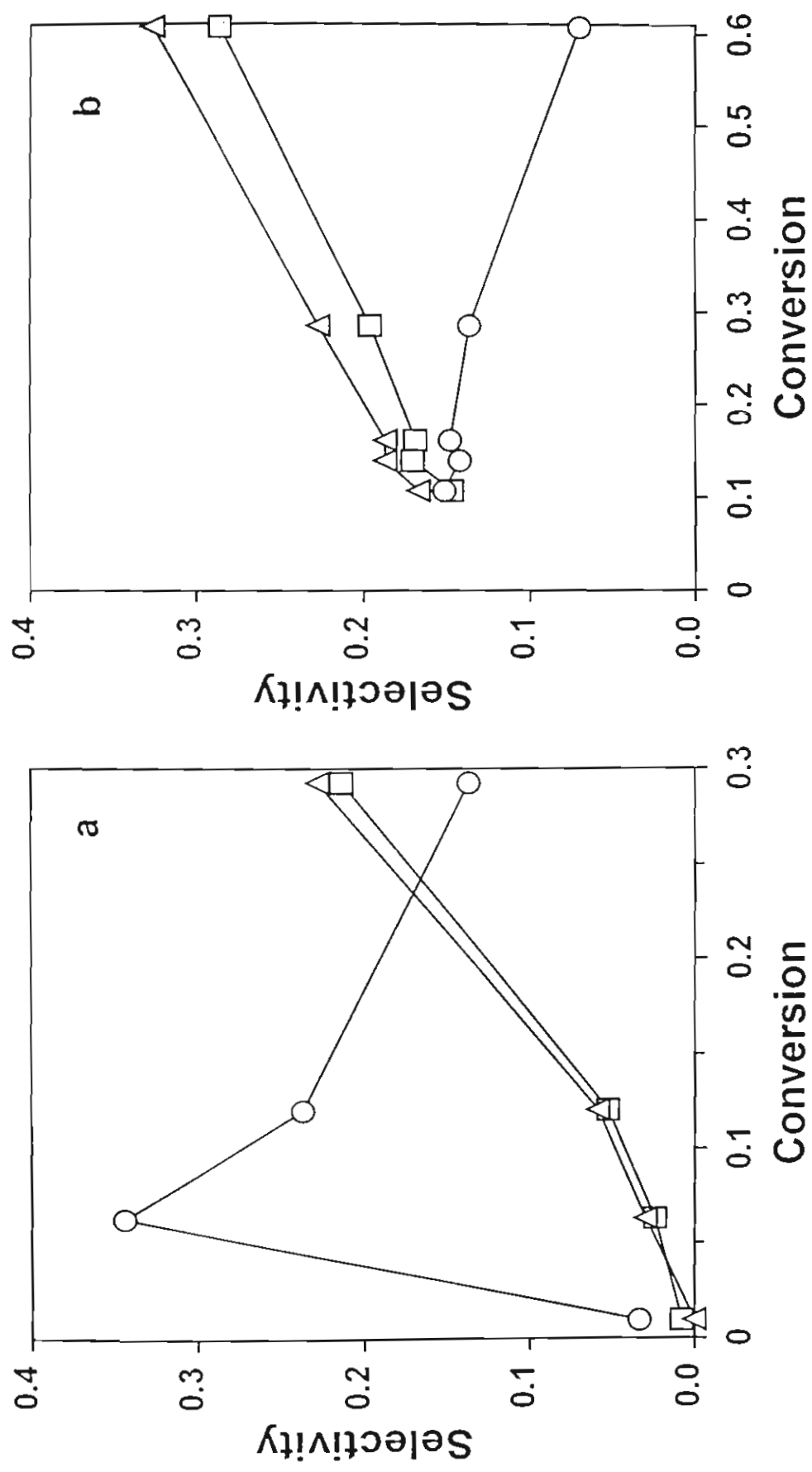


FIG. 5.

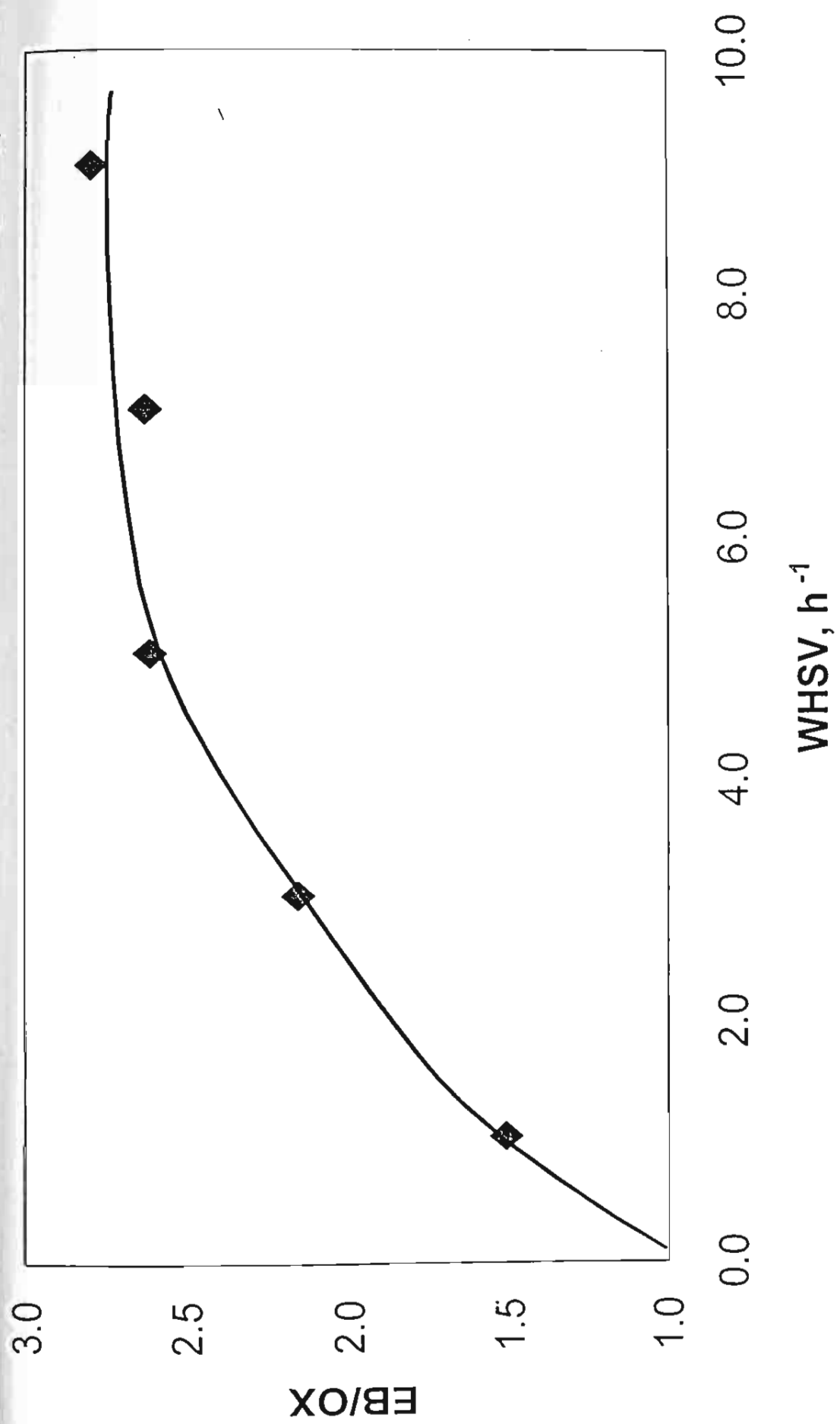


FIG. 6.

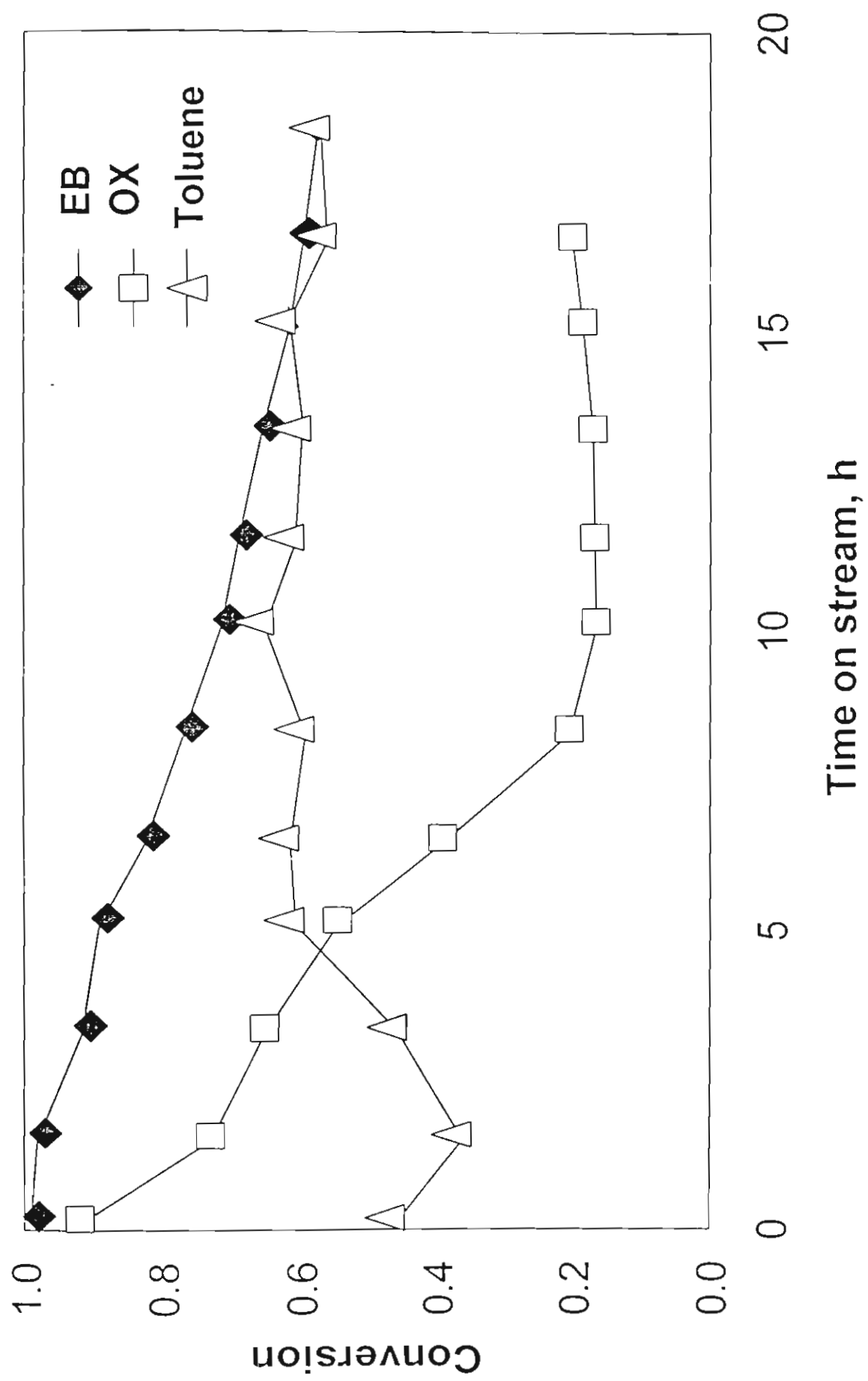


FIG. 7.

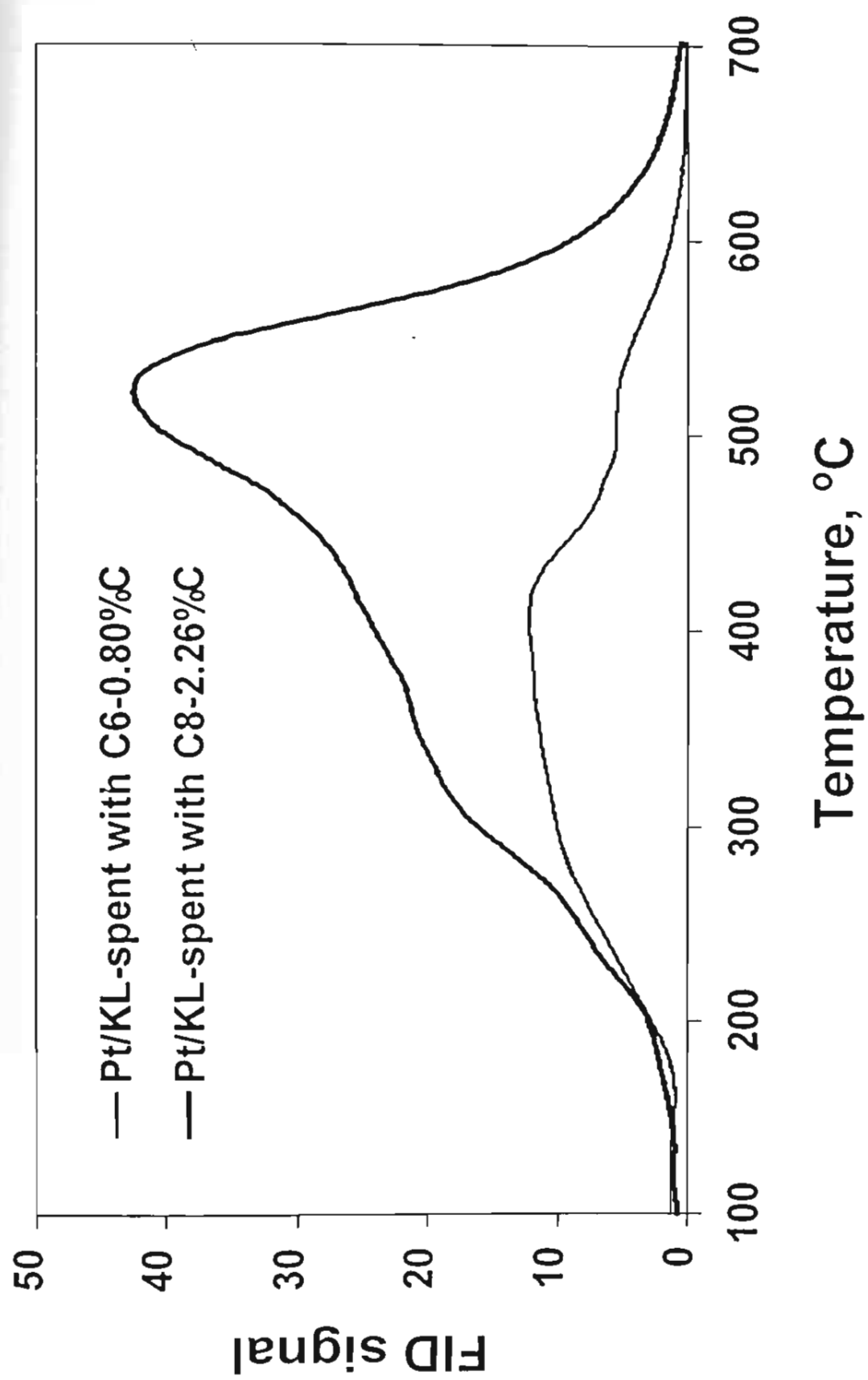


FIG. 8.

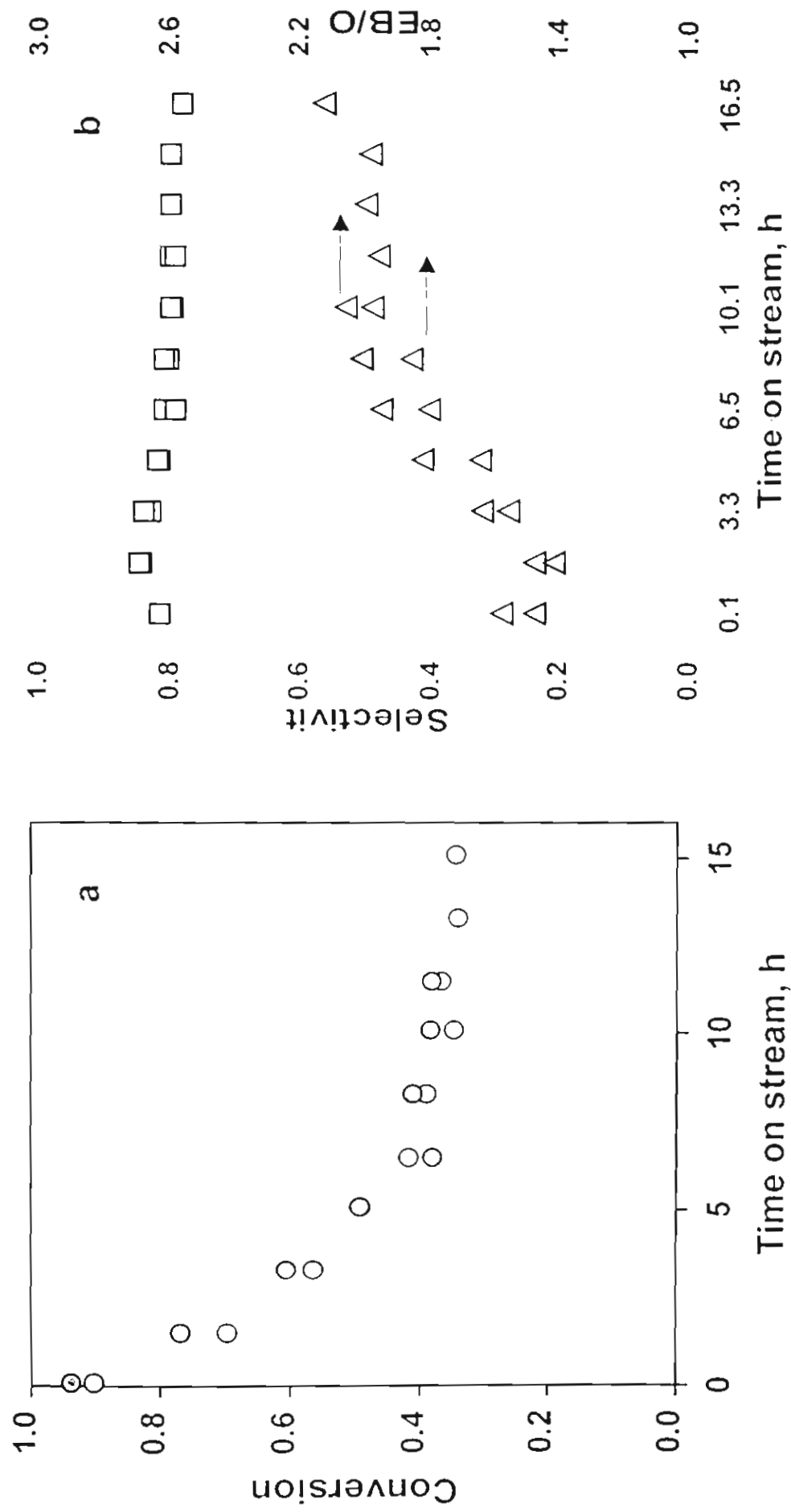


FIG. 9.

Table 1

Analysis data of fresh and spent Pt/KL catalysts.

Catalyst	%Pt	H/Pt	Coke after C6 rxn	Coke after C8 rxn	I-C4 adsorbed on catalyst after C6 rxn*	I-C4 adsorbed on catalyst after C8 rxn*
Pt/SiO ₂	1	0.2	-	-	-	-
Pt/KL-VPI	1	0.9	0.8	2.3	70	35
Pt/KL-IWI	1	0.6	1.5	2.1	-	-

Table 2

Product distribution of n-hexane and n-octane aromatization over different catalysts.
 Reaction conditions: 500°C, H₂/n-C6 (or n-C8) molar ratio 6:1, WHSV 5 h⁻¹.

	Feed: n-hexane			Feed: n-octane		
	Pt/SiO ₂	Pt/KL-IWI	Pt/KL-VPI	Pt/SiO ₂	Pt/KL-IWI	Pt/KL-VPI
Conversion, % (after 10 h on stream)	18.8	71.1	90.6	16.8	30.1	37.7
Products selectivity, %						
C1-C5	8.8	22.4	12.2	7.1	34.0	29.4
Hexenes	78.7	5.9	0.7	3.5	1.2	0.7
Total aromatics	15.1	85.6	93.6	48.8	60.2	69.2
Benzene	15.1	85.6	93.6	0.0	27.4	27.7
Toluene	-	-	-	0.9	22.8	28.3
Heptenes	-	-	-	34.8	2.6	3.0
Octenes	-	-	-	5.4	1.4	1.9
Ethylbenzene	-	-	-	21.5	5.9	6.5
m-Xylene	-	-	-	1.2	1.1	1.2
p-Xylene	-	-	-	0.4	0.3	0.2
o-Xylene	-	-	-	24.8	2.8	3.0

Table 3

Product distribution of n-octane aromatization over Pt/KL-VPI at various reaction temperatures.

Reaction conditions: H₂/n-C8 molar ratio 6:1, WHSV 5 h⁻¹.

	Reaction Temperature, °C				
	300	350	400	450	500
Conversion, %	0.2	1.0	6.3	12.1	29.3
Products selectivity, %					
C1-C5	1.4	1.4	4.2	9.4	28.9
Hexenes	3.9	16.8	7.0	5.5	1.5
Benzene	0.0	0.0	3.0	5.9	22.7
Toluene	0.0	18.2	19.0	24.0	25.5
Heptenes	66.6	45.2	24.9	22.4	4.5
Octenes	28.1	15.2	7.6	9.2	3.1
Ethylbenzene	0.0	0.0	20.6	15.7	8.6
m- and p-Xylene	0.0	3.3	2.8	1.9	1.4
o-Xylene	0.0	0.0	11.0	6.1	3.8

Table 4

Product distribution of n-octane aromatization over Pt/KL-VPI at various WHSV.
Reaction conditions: 500°C, H₂/n-C8 molar ratio 6:1.

	WHSV, h ⁻¹				
	1.0	3.0	5.0	7.0	9.0
Conversion, %	60.7	28.5	16.1	14.0	10.7
Products selectivity, %					
C1-C5	34.5	28.5	26.4	26.7	24.1
Hexenes	0.65	1.9	2.7	2.8	3.1
Benzene	32.5	22.6	18.7	18.7	16.7
Toluene	23.3	26.1	25.1	24.8	25.1
Heptenes	1.0	3.1	4.6	4.3	5.1
Octenes	1.0	4.0	7.4	8.2	10.4
Ethylbenzene	3.5	8.2	9.6	9.2	10.0
m- and p-Xylene	1.1	1.6	1.6	1.6	1.6
o-Xylene	2.4	3.9	3.7	3.5	3.6

Table 5

Product distribution of different feeds over Pt/KL-VPI catalysts.

Reaction conditions: 500°C, H₂/reactant molar ratio 6:1, WHSV 5 h⁻¹

	Reactant				
	n-Octane	Ethylbenzene	o-Xylene	Toluene	n-Heptane
Conversion, %	37.7	71.5	16.7	64.9	36.4
Products selectivity, %					
C1-C2	27.0	20.1	11.8	15.4	21.6
C3-C5	2.4	0.0	0.0	0.0	6.2
Hexenes	0.7	0.00	0.0	0.0	7.5
Benzene	27.7	46.5	6.4	84.3	28.5
Toluene	28.3	32.9	78.9	-	33.1
Heptenes	3.0	0.0	0.0	0.0	2.3
Octenes	1.9	0.0	0.2	0.0	0.0
Ethylbenzene	6.5	-	0.2	0.0	0.0
m- and p-Xylene	1.4	0.0	1.8	0.0	0.0
o-Xylene	3.0	0.2	-	0.0	0.0

การประชุมวิชาการ

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n-HEXANE AROMATIZATION TO BENZENE ON Pt/KL AND PtYb/KL CATALYSTS PREPARED BY CVD METHOD

**Thitiporn Thongsrikate¹, Siriporn Jongpatiwut¹,
Thirasak Rirksomboon¹, Somchai Osuwan¹, and Daniel E. Resasco²**

¹The Petroleum and Petrochemical College, Chulalongkorn University

²School of Chemical Engineering and Materials Science, The University of Oklahoma, USA

ABSTRACT

The catalytic performances on n-hexane aromatization of Pt/KL and PtYb/KL catalysts were investigated at various temperatures using sulfur-free, 0.6 ppm and 2.5 ppm sulfur-containing feedstocks. The incipient wetness impregnation (IWI) and chemical vapor deposition (CVD) were used to prepare both types of the catalysts. The results from FT-IR and chemisorption studies revealed that the CVD catalysts had a high dispersion with a majority of small Pt clusters inside the L-zeolite channels, especially when operated at 400°C. This morphology resulted in high catalyst stability and selectivity to benzene formation, even in the presence of sulfur, in contrast to IWI, which showed lower selectivity and more rapid deactivation. Although the addition of Yb promoter did not play an important role in the absence of sulfur in the feed, under sulfur-containing feed it improved the catalytic performance at 400°C.

INTRODUCTION

Platinum supported on potassium form of L-zeolite exhibits very high activity and selectivity on n-hexane aromatization over the other nonacidic zeolite catalysts [1]. There has been the number of research work investigating the reasons of the excellent performance of this monofunctional catalyst. Several work groups believed that zeolite geometry has influenced on the increased selectivity and activity in one-six-ring closure that led to benzene formation [2]. Furthermore, KL-zeolite support lacked of any acidity and stabilized the formation of extremely small platinum clusters [3]. However, the most important feature of zeolite is to inhibit coke formation by bimolecular interaction [4]. Besides, the presence of K⁺ can be related to both the high aromatization activity and selectivity. The K⁺ on L-zeolite can stabilize an intermediate of the aromatization. This property will be diminished by interaction with sulfur [5].

Since Pt/KL catalysts are very sensitive to a trace amount of sulfur resulted in the loss of active sites and pore blockage, therefore various preparation methods of Pt/KL were applied to increase its sulfur resistance. The proper metal loading method has significant effects on the dispersion and location of platinum particles in zeolite that, intern, impact on the catalytic activity and stability of Pt/KL. It was found that the Pt/KL catalysts prepared by CVD method showed a higher fraction of small Pt clusters locating inside the zeolite channel than that of IWI method which resulted in higher aromatization performance in the both clean and sulfur-poisoned conditions [6].

Recently, the promotion of rare earth elements to Pt/KL as a promoter was widely investigated. One of the advantages of the rare earth promoter such as Tm on Pt/KL is an

increasing sulfur resistance of Pt/KL because Tm can act as sulfur getter [4]. Another advantage is that Tm can increase the degree of Pt dispersion in KL so that PtTm/KL has more active sites resulting in higher activity than that of unpromoted catalyst [7]. The decrease in the agglomeration rate of Pt on PtTm/KL after the reaction was also observed.

From the above discoveries, it is interesting to study the effects of adding another rare earth element into Pt/KL catalyst on n-hexane aromatization performance. In this research, the rare earth element used was ytterbium (Yb). Two preparation methods, IWI and CVD, were employed. The reaction testing was performed at the reduction and reaction temperatures of 400°C and 500°C under clean and sulfur containing feedstock at sulfur concentrations of 0.6 and 2.5 ppm. The catalysts were characterized using a diffuse reflection infrared fourier transform spectroscopy (DRIFTS) of adsorbed CO and hydrogen chemisorption to provide the dispersion and location of Pt particles.

EXPERIMENTAL SECTION

Catalyst Preparation

The impregnation technique was employed to prepare the catalysts. Two impregnation methods were used in this work: incipient wetness impregnation (IWI) method and chemical vapor deposition (CVD) method. In the case of promoted catalyst, PtYb/KL, the catalyst was separately impregnated in the sequence of ytterbium and platinum, respectively. The catalysts were characterized by H₂ chemisorption and FTIR of adsorbed CO. Prior to incorporation of Pt metal, the zeolite powder was calcined under a flow of air (100 ml min/g zeolite) at 400°C for 5 h.

For the IWI procedure, the freshly calcined support was quickly transferred to an inert atmosphere and impregnated dropwise while grinding with an aqueous solution of platinum tetramine platinum (II) nitrate. To achieve incipient wetness, a liquid solid ratio of 0.69 ml/g was used. After impregnation, the sample was dried for 12 h at 110°C and then calcined for 2 h in air at 350°C. This sample was designated as IWI.

The second method employed was CVD. After quickly transferring the freshly calcined support to an inert atmosphere, platinum acetylacetonate Pt(AcAc)₂ was physically well mixed with KL, and then a solid mixture was transferred to a continuous-flow reactor. The reactor was operated under atmospheric pressure and a low flow rate of helium (< 10 ml/min). The catalyst was slowly heated to 130°C for subliming the Pt(AcAc)₂. At this point, the sample was light yellow in color, indicating that the Pt(AcAc)₂ did not decompose during the course of preparation. To decompose the platinum precursor the sample was heated to 350°C in flow of air and calcined for 2 h. This sample was designated as CVD.

Catalyst Characterization

All of catalysts prepared were characterized by infrared spectroscopy of adsorbed CO and chemisorption.

FTIR was performed on Nicolet Avatar 360 spectrometer equipped with a DTGS detector. Experiments were conducted in a diffuse reflectance cell, Spectra-Tech that allowed in-situ thermal pretreatment performance. For each IR spectrum, taken at a resolution of 8 cm⁻¹, 128 scans were added. Samples were in-situ reduced under H₂ flow at either 400°C or 500°C for 1.30 h. Prior to each spectrum, the catalyst was cooled down and purged in He for 30 min. The background was recorded at this time. Then the catalyst was exposed to a flow of 3 % CO in He for 30 min at room temperature and purged in He for 30 min, to remove the contributions from gas phase and weakly adsorbed CO, prior to obtaining the scans.

Chemisorption measurement was carried out by Autosorb-1-c. The experiments were conducted on pellet samples in a static volumetric adsorption Pyrex system, equipped with a high capacity, high vacuum pumping station. First, the catalyst was loaded into the quartz tube and performed a reduction under hydrogen flow for 1 h at 500°C. Second, the hydrogen at the platinum surface was removed by helium flow at the reduction temperature for 30 min and then evacuated for 1.5 h. After that the catalyst was cooled to 40°C and evacuated at the same time. At this step, all hydrogen was removed from the surface of platinum, which was reabsorbed hydrogen incrementally. The hydrogen was incrementally dosed at 40 °C at elevated pressure. The extrapolation back to zero pressure method was used to calculate the adsorbed volume. To quantify the amount of reversibly adsorbed hydrogen, after obtaining the first isotherm, the sample was evacuated for 5 min at 40 °C to removed the weakly adsorbed (physisorbed) and a second isotherm was determined. The irreversible H/Pt was obtained by subtracting the two isotherms.

Activity and Selectivity Measurements

A catalyst of 0.4 g was used for reaction testing. The operating temperature and pressure were maintained at 400°C or 500°C and 1 atm in the continuous flow reactor, respectively. The reaction was operated under a hydrogen flow. A liquid n-hexane was injected by a syringe pump through a tee connection prior to entering the reactor. In all experiments, the hydrogen/n-hexane ratio was kept constant at 6. Prior to reaction, the catalyst was slowly heated in flowing hydrogen at 100 ml/min/g catalyst for 2 h to a temperature of 400°C or 500°C and reduced for 1 h at that temperature. The reaction testing was conducted at the same temperature with the reduction temperature, for 9 h, at a weight hourly space velocity (WHSV) of 5 h⁻¹.

The thiophene was mixed with n-hexane feed at the sulfur concentration 0.6 ppm and 2.5 ppm for testing the sulfur tolerance of the catalysts. To prevent the contamination from sulfur, the reaction line from feed point to the entrance of the reactor including reactor and syringe was separately used from that for free sulfur reaction runs.

RESULTS AND DISCUSSION

Catalyst Characterization

The degree of metal dispersion results obtained on the pellet samples after reduction at either 400°C or 500°C are reported in Table 1.

Table 1 Degree of Metal Dispersion Characterized by Using Hydrogen Chemisorption Measurement

Type of catalyst	Preparation method	Reduction temperature (°C)	Dispersion (%)
Pt/KL	IWI	500	70.19
Pt/KL	CVD	400	90.31
Pt/KL	CVD	500	70.99
PtYb/KL	CVD	500	80.75

All of catalysts show a high degree of metal dispersion, particularly for the ytterbium promoted catalyst at a given reduction temperature. Interestingly, CVD catalysts exhibit the higher degree of metal dispersion than the IWI catalysts. For CVD method, a decrease in metal dispersion is observed as the reduction temperature is increased.

The FTIR of adsorbed CO has been widely used to characterize the distribution and location of Pt particles [2]. The results in this work are consistent with the previous work [4] that Pt/KL catalysts display complex bands which typically extend from 2080 cm^{-1} to much lower wave numbers (e.g., as low as 1930 cm^{-1}). The evidence of bands at low wave numbers is explained by EXAFS experiments of Mojet and Koningsberger [8]. They revealed that small Pt particles decomposed upon CO exposure and led to small $\text{Pt}(\text{CO})_2$ entities which were stabilized by the basicity of the zeolite pore walls.

However, the position of band cannot be used directly as an indicator of the dispersion. There are some complications such as electronic effects, dipole-dipole interactions and interaction of CO with the zeolite which can modify the frequencies. Therefore, the extension of the band position to the lower wave numbers was ascribed from the secondary effects as mentioned above. The interpretations of the results in this work are based on three important regions that are believed to correspond with three variations of morphology of Pt clusters [9]:

- (1) Bands below 2050 cm^{-1} are assigned to Pt-CO species arising from the disruption of small Pt clusters inside the L-zeolite channels.
- (2) Bands between 2050 and 2075 cm^{-1} are associated with larger Pt clusters in the near-surface region of the L-zeolite.
- (3) Bands at around 2080 cm^{-1} are generally assigned to larger Pt particles on the external surface of the L-zeolite.

The variations in the morphology of the catalyst resulted from the different procedures of metal loading are illustrated by the various bands shown in Fig 1. All of them display the major bands below 2050 cm^{-1} that demonstrate the small Pt clusters inside the channels. The bands around 2050 – 2075 cm^{-1} , corresponding to the larger Pt clusters in the near-surface region of the L-zeolite are obviously pronounced for the IWI catalysts. Furthermore, the bands around 1970 cm^{-1} , which are assigned to the highly dispersed cluster in zeolite, are more pronounced for the CVD catalysts than that of IWI catalysts.

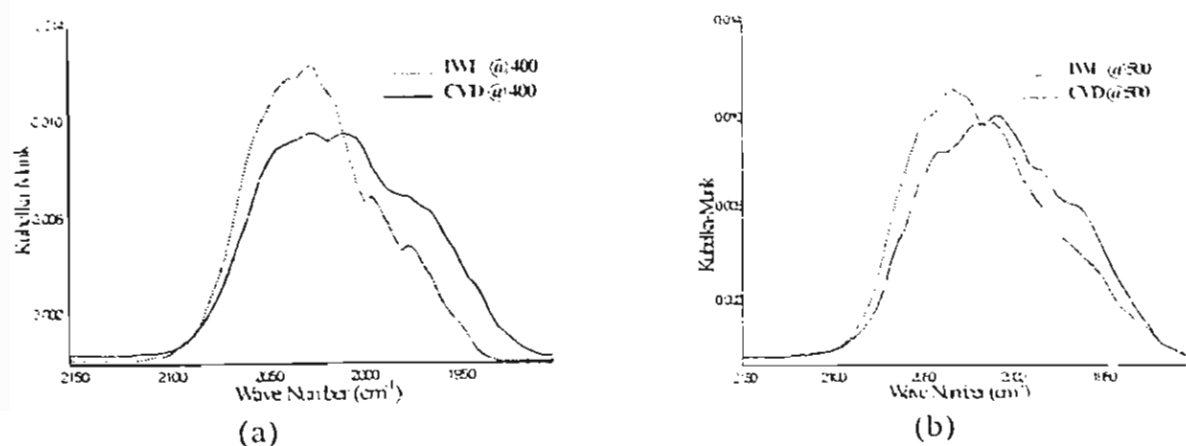


Fig. 1 FTIR Spectra of Adsorbed CO on Pt/KL of IWI and CVD Catalysts after Reduction at (a) 400°C and (b) 500°C .

According to Fig. 2a, the spectra of adsorbed CO in the presence of 0.6 ppm sulfur at 400°C indicate that almost Pt outside the channels were poisoned as shown by the drop of bands in the region of 2010 – 1970 cm^{-1} . For a distinguishable shoulder around 1930 cm^{-1} , it may be because the low concentration of sulfur poisoned only small amount of Pt inside the channels. This probably leads to increasing the electron density of support resulted in stabilization of small particles inside the channel. However at high temperature condition, 500°C (Fig. 2b) the spectra display the large decreases in the region of 2010 and 1970 cm^{-1} , including the drastic drop in the shoulder between 1950 – 1930 cm^{-1} . This demonstrates the growth of Pt cluster inside the channels while the major bands extend to the wave number

around $2050\text{--}2030\text{ cm}^{-1}$ which evidenced the migration of large Pt cluster toward the pore mouth resulting in the partial blockage of channels in the longer reaction time.

By increasing sulfur concentration to 2.5 ppm (Fig. 3), the deactivation of catalysts by sulfur poisoning is clearly observed. The bands around $1950\text{--}1930\text{ cm}^{-1}$ disappear and the greater fractions of bands above 2050 cm^{-1} are found. The distributions to high wave numbers in the region of $2080\text{--}2060\text{ cm}^{-1}$ indicate that major cluster growth to the large cluster which migrated to outside of the channel resulting in loss in its activity and selectivity and the pore mouth blockage.

The stability of ytterbium promoted catalysts to sulfur poisoning was also examined. From the results in Figs. 2 and 3, PtYb/KL catalysts show the higher degree of metal dispersion and the lower fraction of the large Pt clusters aggregate out of the pores in comparison with the Pt/KL, CVD catalysts.

The study of thermal treatment by FTIR provided that catalysts were more stable at a lower temperature even in the presence of sulfur. This can be confirmed by the shift of spectrum to lower wave numbers after reduction at 400°C in compared with after reduction at 500°C .

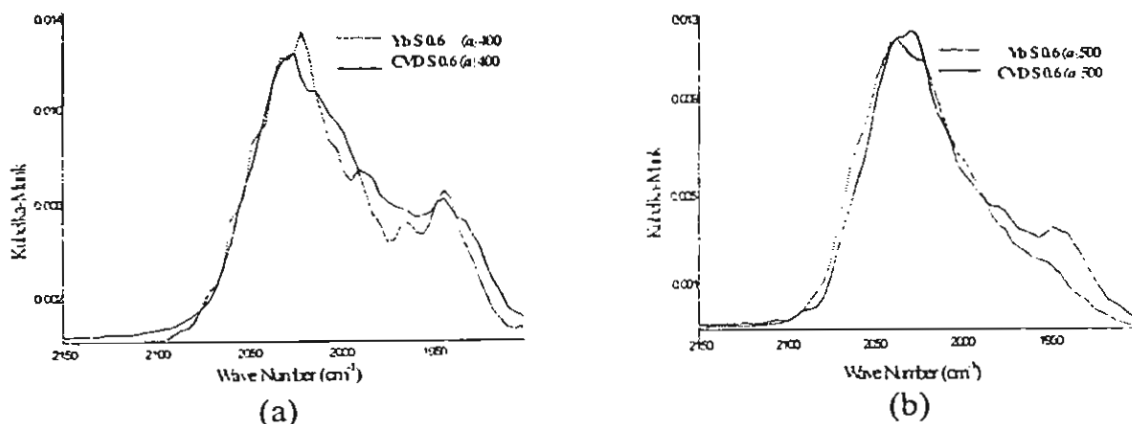


Fig. 2 FTIR Spectra of Adsorbed CO on Pt/KL and PtYb/KL after Spent in 0.6 ppm Sulfur at (a) 400°C and (b) 500°C

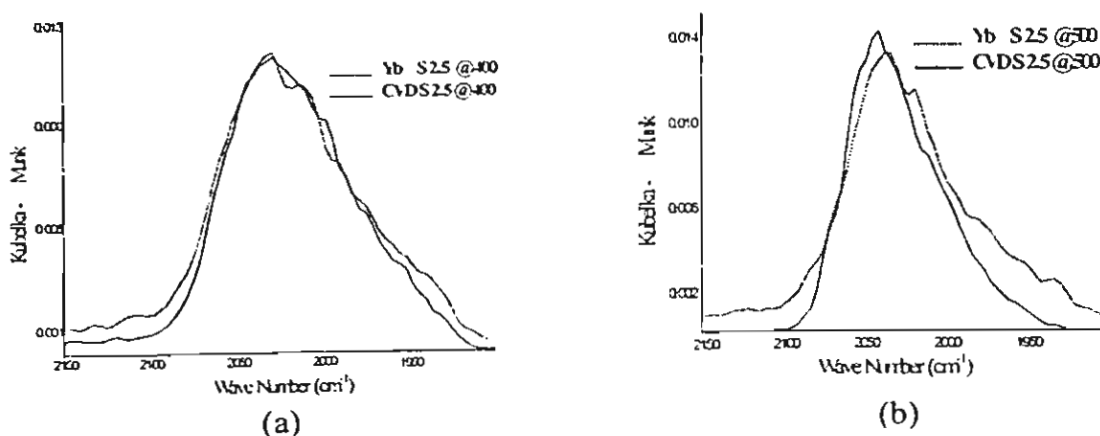


Fig. 3 The FTIR Spectra of Adsorbed CO on Pt/KL and PtYb/KL after Spent in 2.5 ppm Sulfur at (a) 400°C and (b) 500°C

Catalytic Activity Measurements

As illustrated in Fig. 4, the CVD catalysts show the higher benzene selectivity and n-hexane conversion than the IWI catalysts at both temperatures, 400°C and 500°C. A much lower conversion of IWI catalyst than CVD catalyst at 500°C in comparison with at 400°C illustrates that the activity of IWI catalyst is decreased at high temperature that is confirmed by the FTIR results. This demonstrates the high sensitivity to high temperature of IWI catalyst.

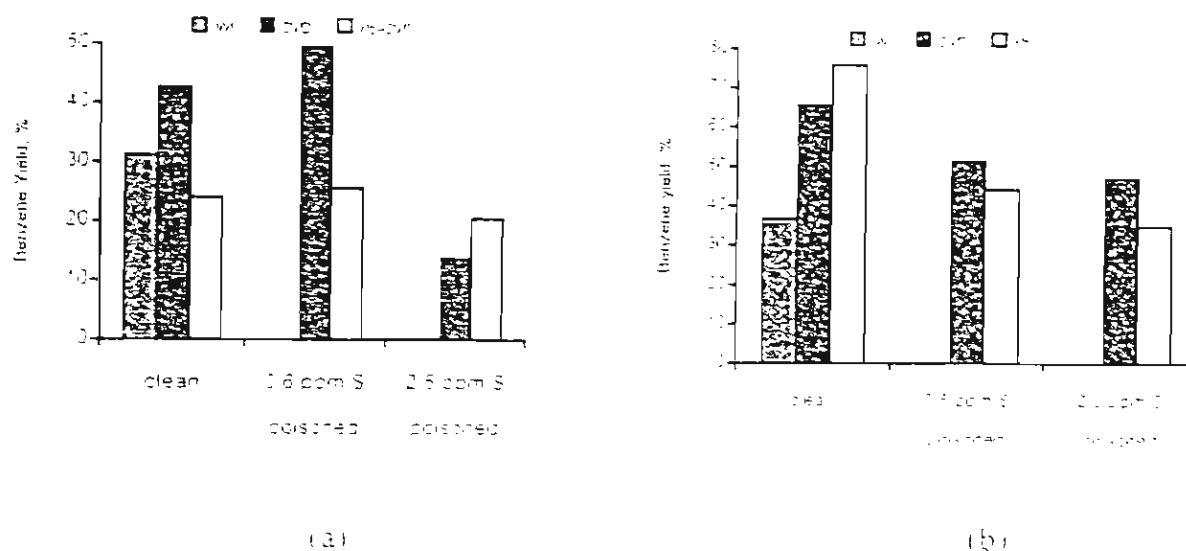


Fig. 4 Benzene Yield of Pt/KL Prepared by IWI and CVD Methods under Sulfur Free and Sulfur Containing Feeds at (a) 400°C and (b) 500°C

The EXAFS, MCP-ring opening and TEM experiments performed by Jacobs *et al.* [6] showed that the IWI procedure incorporated small clusters into the L-zeolite. This fraction of small particles located near the mouth of pore, agglomerated to fill and partially block the channels. Therefore it implies that CVD catalysts have higher thermal stability than IWI catalysts due to the high dispersion of Pt particles from CVD method. Significantly, the CVD catalysts give the higher benzene yields than IWI catalysts as shown in Fig. 4.

As mentioned above, it can be concluded that CVD preparation method is more preferable than IWI method. The reasons are as follows:

1. The catalyst prepared by CVD method has smaller Pt particles than the catalyst that prepared by IWI method
2. The CVD catalysts have higher fraction of Pt particles located inside the channels of zeolite than IWI catalysts.

The important description for the advantage of CVD method is that Pt particles in CVD catalysts are small enough to allow for the diffusion of reactants and products around the cluster during the aromatization of n-hexane resulting in the high activity and selectivity. Moreover, EXAFS information [6] ascribed that CVD catalysts displayed the lower Pt-Pt coordination and higher Pt coordination to L-zeolite oxygen atoms in comparison with IWI catalysts.

PtYb/KL has the selectivity as high as Pt/KL catalyst at both temperatures (Fig. 5). It is indicated that the addition of ytterbium does not change the property in high selectivity of Pt/KL catalyst. However, at 500°C PtYb/KL shows higher conversion than Pt/KL at the initial stage (Fig. 6b). This can be described with FTIR spectra that PtYb/KL is sensitive to a thermal treatment. At 400°C, PtYb/KL has lower conversion than Pt/KL as shown in Fig. 6a.

This may be due to the slow adsorption of reactant on active site at low thermodynamic environment. Ytterbium may have some undesirable effects on the adsorption of n-hexane on Pt, resulting in the low conversion of PtYb/KL at 400°C. According to the selectivity and the conversion of catalysts, PtYb/KL gives higher benzene yield than Pt/KL at the initial of reaction at 500°C (Fig. 4b) while, at 400°C, it provides lower benzene yield than Pt/KL.

As shown in Fig. 7, it is illustrated from the minor amount of hexenes produced from the large cluster outside the channels when ytterbium is promoted to the catalysts. This conforms to FTIR spectra of adsorbed CO at low frequency in Fig. 8 as demonstrated that Pt cluster in PtYb/KL is small size located inside the channels of L-zeolite.

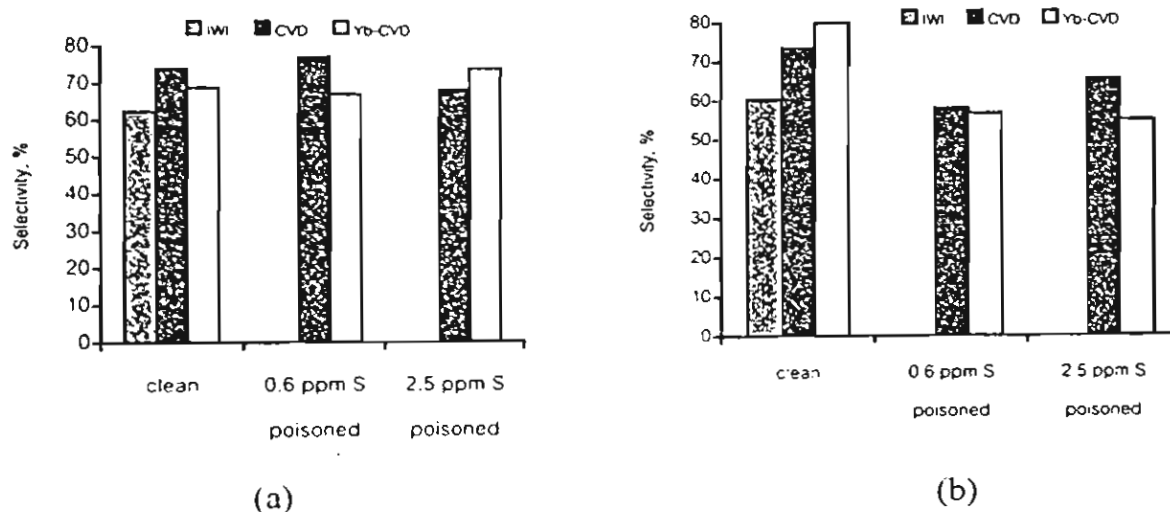


Fig. 5 Benzene Selectivity of Pt/KL Prepared by IWI and CVD Methods under Sulfur Free and Sulfur Containing Feeds at (a) 400°C and (b) 500°C

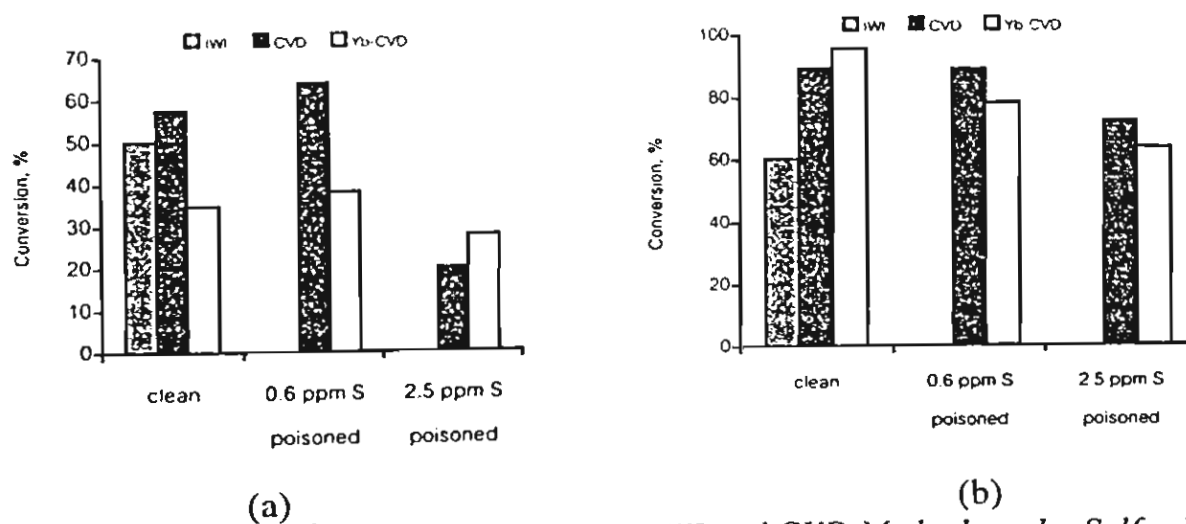
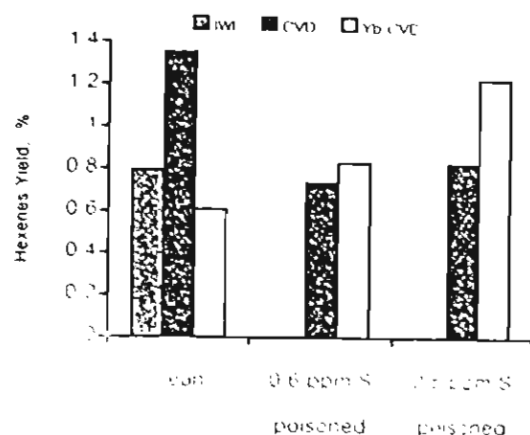
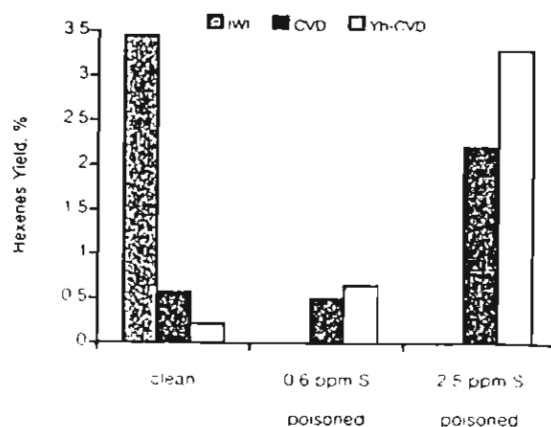


Fig. 6 n-Hexane Conversion of Pt/KL Prepared by IWI and CVD Methods under Sulfur Free and Sulfur Containing Feeds at (a) 400°C and (b) 500°C

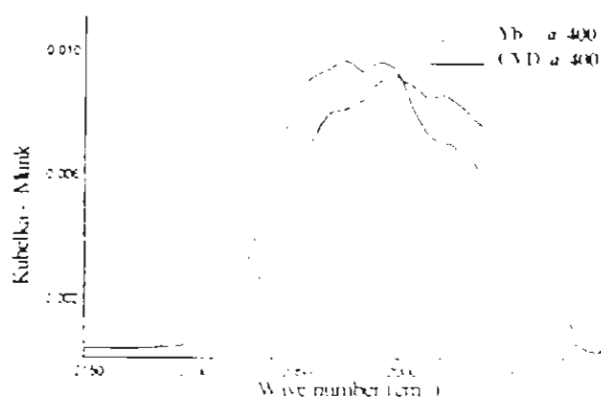


(a)

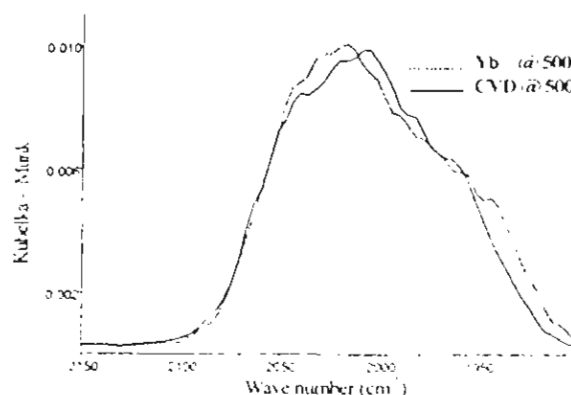


(b)

Fig. 7 Hexenes Yield of Pt/KL Prepared by IWI and CVD Methods under Sulfur Free and Sulfur Containing Feeds at (a) 400°C and (b) 500°C



(a)



(b)

Fig. 8 FTIR Spectra of Adsorbed CO on Pt/KL and PtYb/KL after Reduction at (a) 400°C and (b) 500°C

The reason of the high degree dispersion of PtYb/KL can be described that ytterbium oxide is not reduced at 500°C and it can penetrate between the Pt particles resulting in the increase in Pt dispersion [6]. The drop in the selectivity and conversion of PtYb/KL after 4-5 h to the similar conversion with that of Pt/KL can be described by following assumption. After reduction at 500°C, the anchoring of ytterbium in the zeolite pore walls might not be strong enough. Therefore ytterbium oxides are removed from the surface and block some part of channels and thus reduce the catalytic activity of PtYb/KL.

Since sulfur poisoning is the main cause of Pt/KL deactivation, the scrutiny in the stability of catalysts to the sulfur poisoning is necessary. Thiophene was used as a source of sulfur when it was decomposed. Thiophene was mixed with n-hexane to attain the sulfur concentrations of 0.6 ppm and 2.5 ppm.

In the presence of 0.6 ppm sulfur, at 500°C, the benzene selectivities of Pt/KL and PtYb/KL are slightly decreased and the conversion of the n-hexane is not significantly changed when compared with the catalysts in the absence of sulfur (Figs. 5b and 6b). It can be presumed that Pt/KL and PtYb/KL catalysts prepared by CVD method demonstrate strong sulfur tolerance under the reaction conditions due to less poisoned active sites. However, the increase in amount of hexenes yield (Fig. 7b) indicates that the catalysts have some ensemble of Pt particles and would migrate out of the pore thus losing their characteristics or would block the channels in the longer reaction time. Moreover the poisoned Pt/KL has lower

hexenes yield than the poisoned PtYb/KL. This is because the Pt clusters outside the pore were poisoned before were ones inside the pore. In the case of PtYb/KL, ytterbium has a stronger positive charge than Pt thus it could act as sulfur getter [2]. At 400°C, as shown in Figs. 5a and 6a, the selectivity of poisoned catalyst rarely changes but the conversions of Pt/KL and PtYb/KL catalyst significantly increase in the presence of sulfur. The reason of the better conversion under sulfur condition at this temperature is interesting to find out.

In the presence of 2.5 ppm sulfur, at 500°C, the deactivation of catalysts is clearly observed (Fig. 4b). PtYb/KL has higher deactivation rate than Pt/KL as indicated by the lower selectivity, conversion, benzene yield and higher hexenes yield than Pt/KL (Figs. 5b, 6b, and 7b). The deactivation of PtYb/KL may be occurred from the low ability of ytterbium to anchoring in the pore system of L-zeolite at higher temperatures. This assumption can be observed from the high catalytic performance of PtYb/KL in the initial reaction time, under both clean and sulfur conditions. At 400°C, the poisoned PtYb/KL has higher n-hexane conversion and benzene yield than the poisoned Pt/KL (Figs. 4a and 6a). Thus it can be summarized that ytterbium performs better in the presence of sulfur at 400°C. However, the increase in hexenes yield of poisoned PtYb/KL indicates that the Pt clusters begin to grow after all of ytterbium particles are poisoned. PtYb/KL should be further investigated using a longer reaction time.

CONCLUSIONS

The Pt/KL catalysts, prepared by CVD method under helium flow, exhibited a high fraction of Pt clusters located inside zeolite channels. The CVD catalysts gave higher conversion, selectivity and stability than the conventional IWI catalysts. It was found that ytterbium attributed to the increase in the metal dispersion inside the channels of zeolite. The highly disperse of Pt in L-zeolite resulted from the addition of Yb led to the high performance of the PtYb/KL but only in the initial of reaction. At 400°C, PtYb/KL gave lower conversion than Pt/KL under the free sulfur conditions but in the presence of sulfur, especially at a high concentration (i.e., 2.5 ppm), PtYb/KL yielded a significant increase in conversion.

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FINAL PROGRAM & ABSTRACTS

n-HEXANE AROMATIZATION TO BENZENE ON Pt/KL AND Pt/Ce-KL PREPARED BY VPI METHOD

Banchong Lertrojanchosut, Siriporn Jongpatiwut, Thirasak Rirksomboon,
and Somchai Osuwan

The Petroleum and Petrochemical College, Chulalongkorn University
Phya Thai Rd., Bangkok 10330, THAILAND, banchong@thaioil.co.th

Daniel E. Resasco

School of Chemical Engineering and Materials Science, The University of Oklahoma,
Norman, Oklahoma 73019, U.S.A., resasco@ou.edu

1. ABSTRACT

The performance of Pt/KL and Pt/Ce-KL catalysts for the n-hexane aromatization reaction was studied at various temperatures using sulfur-free and sulfur-containing feedstocks. Examination of the product distribution as a function of conversion and selectivity for the Pt/KL catalyst prepared by vapor phase impregnation (VPI) indicated that this catalyst had much higher aromatization activity than that prepared by incipient wetness impregnation (IWI) technique. Moreover, FT-IR of adsorbed CO results showed that VPI method yielded small Pt clusters located inside the zeolite channels while the IWI technique presented larger clusters, some of them located outside the channels. When using clean feeds, the addition of Ce to the Pt/KL did not result in any enhancement of catalytic activity, but when using sulfur-containing feeds Ce exhibited interesting effects. In the presence of 0.6 ppm and 2.5 ppm of sulfur, both the Pt/KL and Pt/Ce-KL catalysts exhibited a loss in n-hexane conversion and benzene selectivity due to the agglomeration of Pt clusters. However, the activity and selectivity retention under sulfur was both a function of the presence of the promoter and the reaction temperature. It was observed that at 500°C, the Ce-promoted catalyst exhibited an improved performance. By contrast, at 400°C the presence of Ce resulted in lower activity and selectivity compared to the unpromoted Pt/KL catalyst.

2. INTRODUCTION

Pt/KL zeolite catalysts, which consist of Pt supported on a non-acidic zeolite L, have been recognized as a new generation of alkane reforming catalysts because they show an exceptionally high activity and selectivity for the n-hexane aromatization. The catalysts differ from conventional, bifunctional catalysts because they only exhibit the metallic function. In fact, Lane et al. (1991) clearly showed that the Pt/KL catalyst benefits from the absence of acid-catalyzed hydrocracking, resulting in higher liquid yields. A key feature of the catalyst is a low coking rate, which is attributed to the particular structure of the zeolite channels. Tauster and Steger (1990) speculated that a linear orientation of the alkanes in channels of zeolite L favors adsorption of n-hexane on a Pt cluster at a terminal carbon. However, this high terminal-cracking index was later found to be a typical characteristic of clean Pt, and it is the geometry of the zeolite, preventing coke formation, that allows the Pt to remain clean and selective for aromatization (Iglesia and Baumgartner, 1993). In addition to these purely geometric effects, there is evidence that supports the hypothesis that Pt inside the KL zeolite is electronically modified. Several years ago, Larsen and Haller (1989) used competitive benzene/toluene hydrogenation to study the importance of electronic effects on differently cation-exchanged Pt/KL catalysts. More recently, Mojet et al. (1999) have advanced a new method of XANES analysis for studying the electronic modification of Pt by changing support alkalinity, which seems to confirm the modification of the position of the electronic levels of Pt inside the zeolite. Regardless the fundamental reason behind the unique characteristics of Pt/KL, it is well known that in order to be active and selective, Pt must be in the form of very small clusters inside the channels of the zeolite. A shortcoming of the Pt/KL catalysts is their extremely high sensitivity to even minute concentrations of sulfur (e.g., parts per billion), thus requiring very expensive and complicated sulfur-removal operations. Consequently, finding effective catalysts in the presence of sulfur is an attractive research challenge. The effect of heavy rare earth (RE) metals on sulfur resistance was investigated by Fang et al (1997). They examined a series of Pt-RE-KL catalysts containing 0.2 wt% of different kinds of RE and concluded that the addition of RE is beneficial to the aromatic selectivity. More recently, Jacobs et al. (2000) demonstrated that addition of a RE such as Tm could indeed result in improved performance under sulfur. However, the amount and method of incorporation of Tm is critical. For example, while the sequential vapor phase impregnation method with a small amount of Tm yielded a catalyst with improved catalytic properties, other methods such as coimpregnation of Pt and Tm hindered the dispersion of Pt, causing blocking of the L-zeolite channels and a higher deactivation rate under

reaction. Therefore, the present work attempts to further investigate the effects of preparation methods on the aromatization activity and sulfur resistance of RE-promoted Pt/KL catalysts.

3. EXPERIMENTAL

3.1 Catalyst preparation

The platinum-supported catalysts were prepared with 1 wt % loading of platinum (Pt), with and without 0.15 wt % loading of cerium (Ce) by two methods; incipient wetness impregnation (IWI) and vapor phase impregnation (VPI) whereas the platinum-cerium zeolite catalysts were only prepared by the VPI method. Prior to addition of the metal, the K-LTL zeolite was dried in an oven at 110°C overnight and calcined at 400°C in a dry air flow of 100 cm³/min.g for 5 h.

In the IWI method, tetraammineplatinum (II) nitrate was weighed and dissolved in deionized water and then impregnated in dried support by slowly adding drops of solution. Next, the mixture was dried in an oven at 110°C overnight. The cool mixture was loaded into a quartz tube and calcined at 350°C in a dried air flow of 100 cm³/min.g for 2 h and left cool to room temperature. The resultant catalyst (Pt/KL) was stored in a desiccator. The VPI catalysts were prepared by physically mixing weighed platinum(II) acetylacetonate and dried support under nitrogen atmosphere. The mixture was then loaded into the reactor tube under helium flow of 2 cm³/min. The mixture was slowly ramped to 40°C and held there for 3 h, and ramped again to 60°C and held again for 1 h. After that, further ramped to 100°C, at which temperature the mixture was held for 1 h to sublime the Pt(AcAc)₂. After sublimation, the mixture was ramped to 130°C and held for 15 minutes to ensure that all of Pt(AcAc)₂ was sublimed. The reactor was cooled to room temperature. After that it was ramped to 350°C in flow of air for 2 h and calcined at that temperature to decompose the platinum precursor. Finally, the Pt/KL prepared by VPI method was stored in a desiccator. In the case of the platinum-cerium zeolite catalyst (Pt/Ce-KL), it was prepared using the same procedure as described above, but the calcined support was first physically mixed with cerium(III) 2,4-pentanedionate (Ce(AcAc)₃) and the mixture was then ramped up step by step up to 130°C. After calcined in dry air flow, Ce/KL was obtained and was, as before, mixed with Pt(AcAc)₂ and calcined in a dried air flow to obtain the VPI Pt/Ce-KL.

3.2 Catalyst characterization

The Pt/KL and Pt/CeKL catalysts were characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) Nicolet AVATAR 360 FT-IR E.S.P., equipped with a DTGS detector using CO as a probe. Experiments were conducted in a diffuse reflectance cell and the samples were reduced *in-situ* in a flow of H₂ at either 400°C or 500°C for 1.5 h. For each spectrum, taken at a resolution of 8 cm⁻¹, 128 scans were added.

3.3 Catalytic activity measurement

The catalytic activity studies were conducted at atmospheric pressure in a 0.5-inch stainless steel tube with an internal K-type thermocouple for temperature measurement. The reactor was a single pass and continuous-flow type. To avoid unwanted contamination, independent systems were used for clean n-hexane runs and for sulfur deactivation studies. 0.40 g of catalysts was used in each run. Prior to reaction, the temperature was slowly ramped in flowing H₂ at 100 cm³/min.g for 2 h up to 400°C or 500°C and *in-situ* reduced at that temperature for 1 h. n-Hexane was added by infusion with a syringe pump. In all experiments, the hydrogen/n-hexane molar ratio was kept at 6. The products were analyzed in a Shimadzu GC-17A equipped with a capillary column HP-PLOT/Al₂O₃ "S" Deactivated.

4. RESULTS AND DISCUSSION

The fresh and spent catalysts were characterized by DRIFTS of adsorbed CO in the range 2100-1950 cm⁻¹ to determine the morphology and location of Pt clusters. As shown in Figure 1, after reduction at 400°C, a band at 1970 cm⁻¹ was clearly evident on the spectrum of the Pt/KL prepared by VPI method, while the band was much less pronounced on the spectrum of the Pt/KL catalyst prepared by the IWI method. As described in previous studies (Stakheev *et al.*, 1995 and Jacobs *et al.*, 1999), this band has been ascribed to the formation of Pt carbonyls stabilized inside the L-zeolite channels. Since these carbonyls can only be formed from very small Pt clusters, the presence of this band indicates a very high degree of dispersion. Accordingly, a comparison of the

two spectra shown in Fig. 1 indicates that the VPI method results in a higher dispersion than that prepared by the IWI method. When the reduction temperature was increased to 500°C, the spectra for the two catalysts (not shown) were similar, but for the IWI catalyst the spectrum shifted to higher wavenumber. By contrast, the spectrum of the VPI catalyst did not shift. This difference in the sensitivity of the spectra to an increase in reduction temperature gives further information about the morphology of the Pt clusters. At higher reduction temperatures, Pt clusters can be more easily agglomerated on the IWI catalyst than on the VPI catalyst. That is, the VPI catalyst had a higher resistance to metal particle growth than the IWI catalyst. On the study of the Ce-promoted catalyst, it was found that at 400°C the spectra were very similar to those of Pt/KL. However, as shown in Figure 2, after reduction at 500°C, the Pt/Ce-KL sample exhibited higher intensity at low wavenumbers than the Pt/KL sample. This could either be due to a higher fraction of small particle located inside the zeolite or to a direct interaction of the adsorbed CO with Ce ions. The first explanation would be in line with the hypothesis that Cerium anchors Pt clusters in the zeolite, inhibiting agglomeration (Fang et al., 1997).

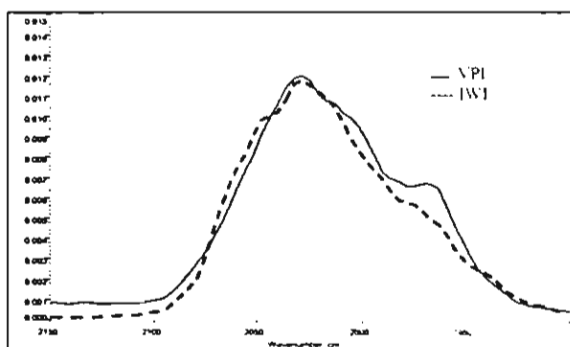


Figure 1 DRIFTS spectra of CO adsorbed on Pt/KL prepared by VPI and IWI method reduced at 400°C.

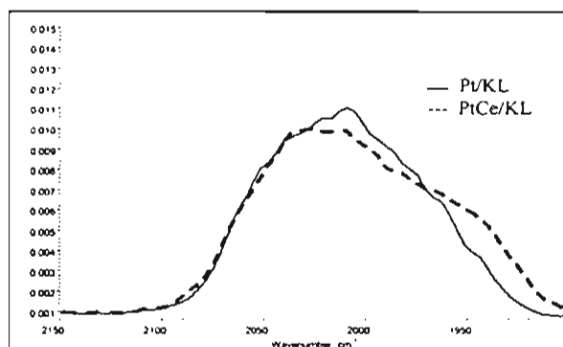


Figure 2 DRIFTS spectra of CO adsorbed on VPI Pt/KL and Pt/Ce-KL catalysts reduced at 500°C.

DRIFTS has also been used to analyze the catalysts after exposure to reaction in clean and 2.5 ppm sulfur containing feeds. As illustrated in figures 3 and 4, the intensities of the bands for the poisoned catalysts are significantly lower than those for the catalysts used under clean feeds. However, an important difference is observed in the degree of intensity reduction. The drop in intensity observed on the Pt/Ce-KL after poisoning is much less pronounced than that on the unpromoted Pt/KL catalyst.

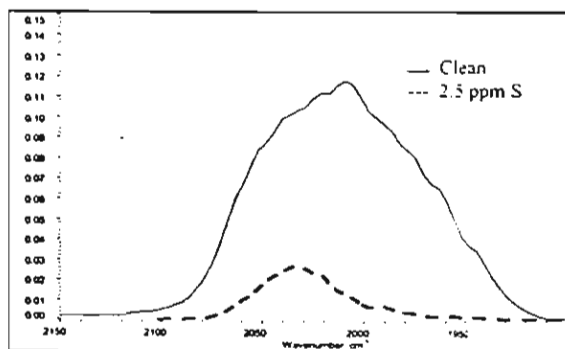


Figure 3 DRIFTS spectra of CO adsorbed on Pt/KL after the catalysts were exposed to 9 h of reaction at 500°C with or without sulfur.

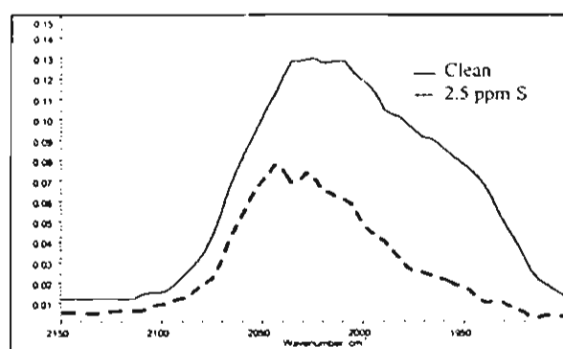


Figure 4 DRIFTS spectra of CO adsorbed on Pt/Ce-KL after the catalysts were exposed to 9 h of reaction at 500°C with or without sulfur.

This important difference might be due to the proposed ability of cerium to prevent Pt agglomeration. Another possible explanation for the resistance of the Ce-containing catalyst to sulfur poisoning is the cerium may act as a sulfur getter, guarding the poisoning of Pt. Such a sulfur-scavenging ability was demonstrated for the case of Tm by Jacobs *et al.* (2000) studying Pt/Tm-KL catalysts.

Figure 5 shows the evolution of n-hexane conversion with reaction time. It is observed that the conversion decreased with time, especially on the IWI catalyst at 500°C. In contrast to the IWI catalyst, the conversion of the VPI catalyst at the same temperature was constant during the first 4 h and only later started to decrease

slowly. The selectivity values obtained on the VPI catalyst were also higher at both temperatures than those obtained on the IWI catalysts. Another indication of the improved performance of the VPI catalyst can be clearly seen in a plot of hexenes yield versus time, as illustrated in Figures 6. It is seen that the IWI catalyst produces higher amounts of by-product hexenes than the VPI, particularly at 500°C. The production of hexenes is typically observed when there is Pt cluster growth (Bellatreccia *et al.*, 1995). This behavior is consistent with the FTIR observations, which indicated that Pt on the IWI catalyst agglomerated more easily than on the VPI catalyst.

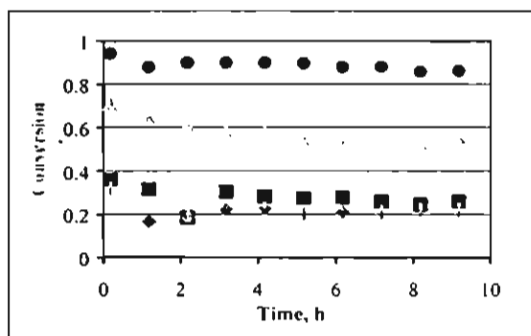


Figure 5 Conversion of Pt/KL prepared by different methods, (○) IWI at 400°C, (□) IWI at 500°C, (△) VPI at 400°C, and (◇) VPI at 500°C.

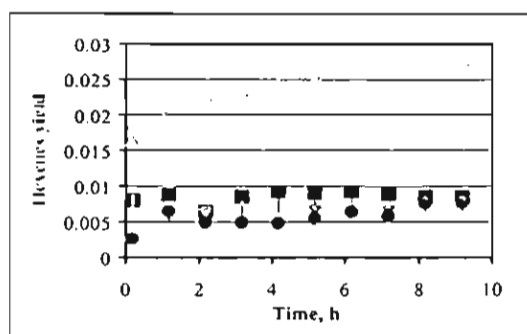


Figure 6 Hexenes yield of Pt/KL prepared by different methods, (○) IWI 400°C, (□) IWI 500°C, (△) VPI 400°C, and (◇) VPI 500°C.

Depending on the reaction conditions, different trends can be observed when 0.15 % wt of Ce is added as a promoter to the Pt/KL by the VPI method. For example, Figure 7 shows the effect of Ce addition on conversion of Pt/KL at 400°C and 500°C using clean feeds. In this case, it can be observed that the conversions obtained on Pt/KL and Pt/Ce-KL are not significantly different, especially at 400°C, at which temperature the conversions on both catalysts fall almost on the same curve. Similarly, the selectivity was almost unchanged at 400°C by the addition of Ce. At 500°C with clean feeds, the addition of Ce had a negative effect on aromatization, not so much on selectivity, which is almost unaffected, but on total conversion, which as shown in Fig. 7 dropped about 10 % in comparison to the unpromoted VPI Pt/KL catalyst.

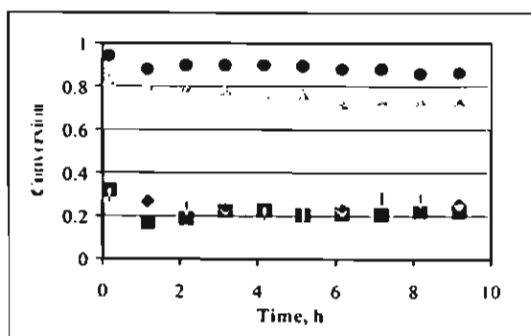


Figure 7. Conversion of VPI Pt/KL and Pt/Ce-KL, (○) Pt/KL at 400°C, (□) Pt/KL at 500°C, (△) Pt/Ce-KL at 400°C, and (◇) Pt/Ce-KL at 500°C.

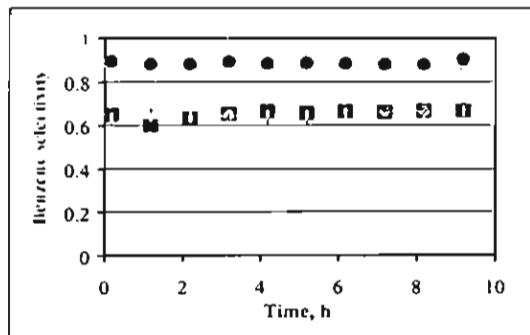


Figure 8 Benzene selectivity of VPI Pt/KL and Pt/Ce-KL, (○) Pt/KL at 400°C, (□) Pt/KL at 500°C (△) Pt/Ce-KL at 400°C, and (◇) Pt/Ce-KL at 500°C.

An interesting effect of Ce appears when sulfur is present in the feed. As shown in Figures 9 and 11, the drop in conversion over the Pt/KL catalyst exposed to the sulfur-containing feed was significant in comparison to the same catalyst under clean conditions. At the same time, the selectivity towards benzene was almost unchanged, although, as shown in Figure 12, the yield towards hexenes, which are always in relatively low concentration, was shown to increase significantly.

A dramatic effect of Ce is evident by comparing Figures 9 and 10. While the activity dropped in the presence of S over the Pt/KL catalyst. There was no loss of activity on the Ce-promoted catalyst. There is however some

deactivation with time on stream. Likewise, the clear effect of Ce is observed when comparing the production of hexenes. As mentioned above, the production of hexenes is a fingerprint for Pt agglomeration and growth outside the channels of the zeolite. While the Pt/KL catalyst exhibited a clear increase in the hexenes yield during sulfur poisoning, the Ce-containing catalyst exhibited the same hexenes yield with or without sulfur.

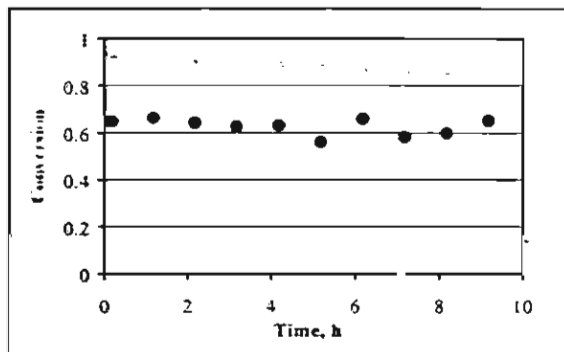


Figure 9 Effect of sulfur in feed on conversion of VPI Pt/KL at 500°C, (○) sulfur-free and (△) 0.6 ppm sulfur containing feed.

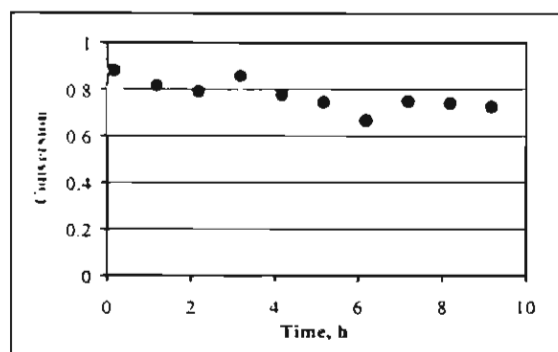


Figure 10 Effect of sulfur in feed on conversion of VPI Pt/Ce-KL at 500°C, (○) sulfur-free and (△) 0.6 ppm sulfur containing feed.

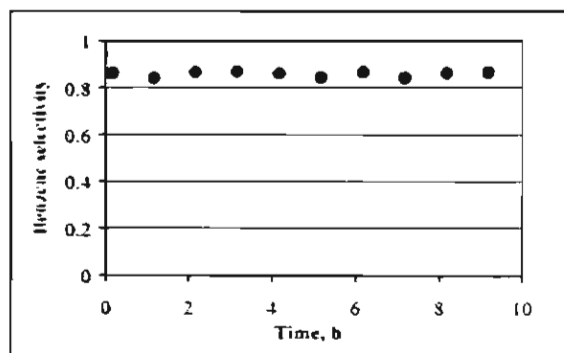


Figure 11 Effect of sulfur in feed on benzene selectivity of VPI Pt/KL at 500°C, (○) sulfur-free and (△) 0.6 ppm sulfur containing feed.

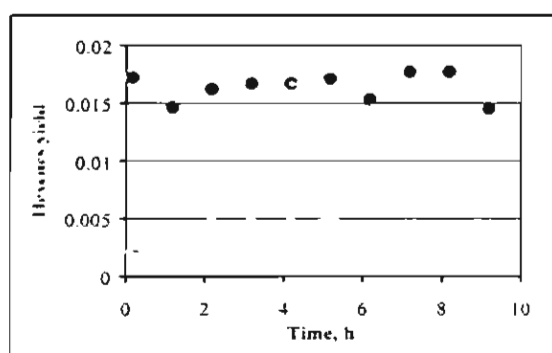


Figure 12 Effect of sulfur in feed on hexenes yield of VPI Pt/KL at 500°C, (○) sulfur-free and (△) 0.6 ppm sulfur containing feed.

An opposite effect of Ce was observed at lower temperatures. At 400°C, the promoting effect of Ce to sulfur tolerance disappeared. In fact, at this temperature under 0.6 ppm S, the activity of the Ce-containing catalyst was lower than that of the unpromoted Pt/KL (not shown).

When the sulfur concentration was increased to 2.5 ppm sulfur, the drop in activity was much more pronounced for all catalysts than with 0.6 ppm S. Surprisingly, on the unpromoted Pt/KL catalyst the initial activity at higher sulfur concentration was higher than with low sulfur concentration. However, the activity drop as a function of time was much more pronounced under the higher sulfur content (Figure 13). In addition, hexenes yield increased sharply with increasing sulfur concentration as shown in Figure 14. The activity of the Pt/Ce-KL catalyst also decreased more sharply under 2.5 ppm sulfur than under 0.6 ppm. These results indicate that Ce can have potential as a promoter for aromatization catalysts for low concentrations of sulfur in the feed. It must be noted however that under the current commercial conditions, the maximum allowed sulfur concentrations are below 0.01 ppm. Therefore, a catalyst that shows improved performance at a sulfur concentration, which is 60 times higher is indeed still promising.

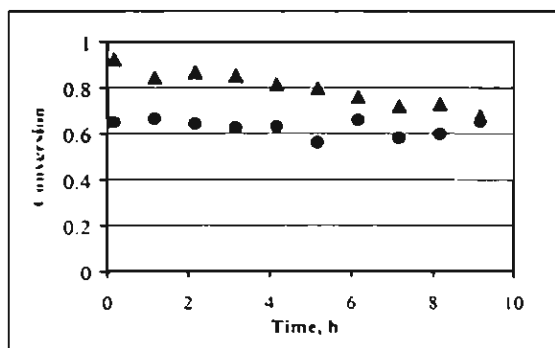


Figure 13 Effect of sulfur concentration in feed on conversion of VPI Pt/KL at 500°C, (Δ) 0.6 ppm and ($\circ$) 2.5 ppm sulfur containing feed.

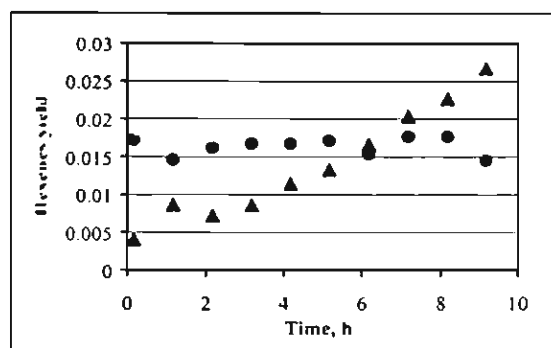


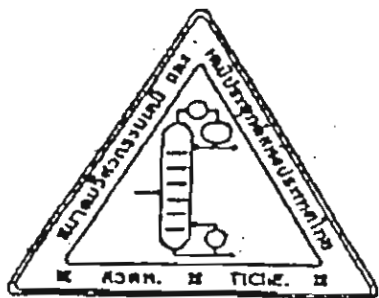
Figure 14 Effect of sulfur concentration in feed on hexenes yield of VPI Pt/KL at 500°C, (Δ) 0.6 ppm and ($\circ$) 2.5 ppm sulfur containing feed.

5. CONCLUSIONS

The alkane aromatization activity has been compared on Pt/KL and Pt/Ce-KL catalysts prepared by VPI and IWI methods. The results indicate that the method of preparation strongly affects not only the morphology and location of the Pt cluster on the L-zeolite, but also the catalytic activity, selectivity, and stability. It was shown that the Pt/KL catalysts prepared by the VPI method exhibit higher activity for n-hexane aromatization and resistance to Pt particle growth than those prepared by the IWI method. The concentration of sulfur in the feed significantly affects the performance of Pt/KL catalysts. Although the addition of Ce does not enhance the activity under sulfur-free conditions it significantly improves the catalytic performance of n-hexane aromatization under sulfur-containing feed at 500°C.

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การประชุมวิชาการ วิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย ครั้งที่ 11

ณ สุรสัมมนาการ มหาวิทยาลัยเทคโนโลยีสุรนารี

วันที่ 9 - 10 พฤศจิกายน 2544

จัดโดย

สาขาวิชาวิศวกรรมเคมี มหาวิทยาลัยเทคโนโลยีสุรนารี

และ สมาคมวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย

A Comparative Study of n-Hexane and n-Octane Aromatization over Pt/KL Catalysts

Paneeya Sackamduang*, Siriporn Jongpatiwut*, Thirasak Rirksomboon*,
Somchai Osuwan*, and Daniel E. Resasco**

* The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

** School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, OK 73019

Abstract

The catalytic performances of Pt/KL and Pt/Ce-KL catalysts on n-hexane and n-octane aromatization were investigated under clean and sulfur-containing feeds. The catalysts were prepared by two techniques; incipient wetness (IWI) and vapor-phase impregnation (VPI). It was found that VPI catalysts exhibited much higher conversion, aromatic selectivity, and stability than those of IWI catalysts for both the n-C6 and n-C8 reactions. Hydrogen chemisorption and DRIFTS of adsorbed CO results indicated that the VPI technique resulted in a higher fraction of small Pt clusters inside the L-zeolite channels. At the same conditions, the aromatization performance of catalyst on n-C8 was much less than that on n-C6. TPO and iso-butane sorption revealed that the very low activity in case of n-C8 aromatization resulted from pore plugging by coke deposit. In the presence of sulfur, the addition of cerium enhanced the catalytic performance of the Pt/KL.

Introduction

Naphtha reforming is one of the important catalytic processes in petrochemical industry because the aromatization of paraffins increases the octane number and produces valuable aromatic hydrocarbons (benzene, toluene, and xylenes). Different formulations and different kinds of catalysts were proposed in order to increase the selectivity to aromatics and to achieve better stability than do the traditional Pt/Al₂O₃ catalysts. Pt/KL zeolite catalysts, which consist of Pt supported on a non-acidic zeolite L, have been recognized as a new generation of alkane reforming catalysts because they show an exceptionally high activity and selectivity for the n-hexane aromatization (Bernard, 1980). There have been many reasons explaining how Pt/KL catalysts, which only exhibit metallic function, differ from conventional, bifunctional Pt/Al₂O₃ catalysts. Among those, some explanations ascribe the unique features of the Pt/KL catalysts to structural characteristics of the L zeolite. In addition to geometric effects, there is evidence that supports the hypothesis that Pt inside the KL zeolite is electronically modified. Moreover, there was a study showing the unique characteristics of Pt/KL catalysts to inhibit the coke formation (Iglesia et al., 1993). Regardless the fundamental reasons behind the unique characteristics of Pt/KL, it is well known that in order to be active and selective, Pt must be in the form of very small clusters inside the channels of the zeolite. Although Pt/KL catalysts are accepted for the aromatization of hexane, they display a very high sensitivity to even small concentrations of sulfur in the feed. It has been shown that in presence of less than 1 ppm sulfur, the catalysts deactivate in an hour. Therefore, development of sulfur resistant catalyst is

one of the major goals in this area. One possible approach to increase sulfur tolerance of Pt/KL catalysts was done by addition of rare earth elements (e.g., Tm, Yb, and Dy) as promoters (Fang et al., 1996, 1997, and Jacobs et al., 2000). In addition, the recent investigations have pointed out that the different preparation methods can greatly influence in the difference of size and morphology of Pt particles inside the channels of L zeolite (Ostgard et al., 1992 and Jacobs et al., 1999). In this study the effect of preparation methods was studied by focusing on conventional incipient wetness impregnation (IWI) and vapor phase impregnation (VPI). Despite the great disparity in the possible explanations proposed by several authors, most of them agreed in the uniqueness of Pt/KL catalysts to promote high aromatization of n-hexane. However, there are not many studies in the open literature related to the aromatization of large alkanes, such as n-octane (C8) but the products from that reaction are indeed very important industrial applications.

This contribution focuses on the study of catalytic performance for C6 and C8 aromatization, under clean and sulfur-containing feeds on standard Pt/KL and "novel" Ce-promoted Pt/KL catalysts. For catalyst characterizations, the fresh and spent catalysts were analyzed using FTIR of adsorbed CO and hydrogen chemisorption to provide the location and dispersion of Pt particles respectively. Temperature programmed oxidation (TPO) was applied to obtain the amount and nature of coke formation on the spent catalysts. Moreover, iso-butane sorption was employed to study pore plugging by coke formation.

Materials and Methods

n-Hexane (C_6H_{14}) of min. 99% and n-octane (C_8H_{18}) of min. 99% purity were obtained from Merck. The catalyst support K-LTL zeolite (HSZ-500, $SiO_2/Al_2O_3=6$, surface area = $280\text{ m}^2/\text{g}$) was obtained from Tosoh, Tetraammineplatinum(II)nitrate $Pt(NH_3)_4(NO_3)_2$ (Aldrich) and Platinum(II)acetylacetonate $[(CH_3COCH=CO-CH_3)_2Pt]$ (Aldrich) were used as Pt precursor for IWI and VPI preparation methods, respectively. Cerium (III) 2,4-pentanedionate $[CH_3COCH=CO-CH_3]_3Ce$ (Alfa Aesar) was used as Ce precursor for VPI preparation and thiophene (C_4H_4S) of 98% purity obtained from Fluka was used as sulfur-poisoned chemical.

Catalyst Preparation: Pt/KL catalysts were prepared with 1% Pt loading by two methods; incipient wetness (IWI) and vapor phase impregnation (VPI) whereas Pt/Ce-KL catalyst was only prepared by VPI method. Prior to adding the platinum metal, the support was dried in an oven at 110°C overnight and calcined at 400°C in a dried airflow of $100\text{ cm}^3/\text{min.g}$ for 5 h.

For the IWI method, the liquid to solid ratio was determined for the L-zeolite to obtain incipient wetness impregnation. The platinum precursor was weighed and dissolved in a certain amount of deionized water ($0.69\text{ cm}^3/\text{g}$ zeolite) and then impregnated in the dried support by slowly adding the solution dropwise under inert nitrogen atmosphere. Next, the mixture was dried at room temperature for 4 h before being dried in an oven at 110°C over night. The cooled mixture was then calcined at 350°C in a dried airflow of $100\text{ cm}^3/\text{min.g}$ for 2 h.

For the VPI method, the catalysts were prepared by physically well mixing weighed metal precursor and calcined support under inert atmosphere. The mixture was then slowly heated to 40°C and held there for 3 h, heated again to 60°C and held again for 1 h. After that, it was further heated to 100°C at which the mixture was held for 1 h to sublime the metal precursor. After sublimation, it was heated to 130°C and held for 15 min to ensure that the entire metal precursor was sublimed. Finally, it was calcined under a dried airflow of $100\text{ cm}^3/\text{min.g}$. In case of Pt/Ce-KL, the Ce/KL was prepared in the same fashion as described above prior to loading platinum precursor.

Catalytic Activity Measurements: Reaction tests were conducted in a 0.5-inch stainless steel tube. To avoid contamination of clean runs, one reactor was only used for sulfur free n-hexane (or n-octane) runs while the other was only used for sulfur deactivation studies (sulfur-containing feeds). Prior to reaction testing, catalyst was slowly heated to 500°C for 2 h in the flowing of H_2 ($100\text{ cm}^3/\text{min}$ per gram of catalyst). The catalyst was further reduced *in situ* in the flowing of H_2 for 1 h. In each run, the experiment was conducted using 0.40 g of catalyst. The catalyst bed was supported on a bed of quartz wool. n-Hexane (or n-octane) was added by infusion using a syringe pump through a union tee connector prior to the reactor. In all experiments, the molar ratio of H_2 to n-hexane (or n-

octane) was kept at 6.0 and reactions were conducted at 500°C , atmospheric pressure while the space velocity was kept constant at 5 h^{-1} . For sulfur poisoning studies, thiophene was mixed into n-hexane (or n-octane) feed before being injected to the reaction system. A purge valve was used to transfer a sample gas to a Shimadzu GC-17A chromatograph equipped with an FID detector. To achieve product separation, the column HP-PLOT/ Al_2O_3 "S" deactivated was chosen. The column was operated in a temperature-programmed mode by starting at 40°C for 10 min, and then the temperature was ramped to 195°C with a heating rate of $5^\circ\text{C}/\text{min}$ and held at this temperature for 30 min.

Catalyst Characterization:

Hydrogen Chemisorption Measurement: The dispersion of Pt particles (H/Pt) was identified by using a hydrogen chemisorption technique. The experiments were conducted on the Pt/KL catalysts in a static volumetric Pyrex adsorption system equipped with a high capacity vacuum pumping station (Varian SD-91) that provided vacuum in the order of 10^{-9} - 10^{-7} torr. 0.30 g of catalyst was loaded into a quartz sample cell and reduced under hydrogen at 500°C for 1 h followed by being evacuated at high temperature (300°C) for 20 min to remove all adsorbed species. Next, the catalyst was cooled down to room temperature under the vacuum. Readsorbing hydrogen was incrementally performed by a higher pressure expansion. The first isotherm obtained represented the total adsorption. After that, the catalyst was evacuated for 10 min at room temperature to remove the weakly adsorbed (physisorbed), and the second isotherm was obtained. The chemisorption isotherm that represents the H/Pt was determined by subtraction the two isotherms.

Diffuse Reflection Infrared Fourier Transform Spectroscopy of Adsorbed CO (DRIFTS of Adsorbed CO): In order to determine the distribution of Pt cluster size and location, the catalysts were characterized by a Nicolet AVATAR 360 FTIR E.S.P., equipped with a DTGS detector using CO as a probe. Experiments were conducted in a DRIFTS cell of Spectra-Tech with ZnSe windows that allowed *in-situ* thermal pretreatment. For each IR spectrum, taken at a resolution of 8 cm^{-1} , 128 scans were performed. A sample was *in-situ* reduced in a flow of H_2 for 30 min at either 400°C or 500°C for 1 h, cooled under He flow, and purged by using He at room temperature for 30 min. The N_2 was flowed in a chamber of the instrument to remove the moisture and CO_2 prior to background collection. The background was recorded at this time. The catalyst was then exposed to a flow of 3 % CO in He for 30 min at room temperature and purged in He for 30 min, prior to scanning, to remove the contribution from gas phase and weakly adsorbed CO.

Temperature-Programmed Oxidation (TPO): The amount of coke formation and the nature of coke deposition were performed by temperature

programmed oxidation. 30–40 mg of spent catalyst was loaded in a quartz fixed-bed reactor supported by quartz wool. The different conditions of spent catalysts were conducted under a flow of 5 % O₂ in He with a linearly increasing temperature from room temperature to 800°C in 1 h. The evolution of CO₂ produced by the oxidation of the carbon species was monitored by a Balzers TCP 121 mass spectrometer to obtain the profiles of partial pressure of CO₂ with temperature. After that, the pure CO₂ was introduced into the system to calibrate with 100 µl pulses in order to obtain the quantity of the CO₂ produced. The evolved CO₂ partial pressure was normalized by the total pressure and the maximum signal in the pulses of CO₂.

Kinetics of Iso-Butane Sorption: Kinetic studies were performed using a Pyrex volumetric system equipped with a 0–100 torr MKS Baratron precision gauge. Prior to each adsorption run, the sample was activated by heating in vacuum (10⁻⁶ torr) at 350°C for 2 h then the temperature of the adsorbent bed was set to 100°C. The Pyrex system was also kept constant at 100°C using heating tapes controlled by a temperature controller. 37 cm³ of iso-butane at 100 torr and 100°C were expanded to the reactor (total volume, 54 cm³). The variation of pressure was monitored by a connected computer. D/r_0^2 was calculated using the following equation (Garazi et al., 1986):

$$\frac{M_t}{M_\infty} = \frac{1+K}{K} \frac{6}{r_0} \left(\frac{Dt}{\pi} \right)^{1/2}$$

where M_t/M_∞ is the fraction approach to equilibrium, K is the ratio of amount of sorbate in the gas phase to the amount in the sorbent in equilibrium, D is the diffusivity (cm²/sec), t is time (sec), and r_0 is the particle radius (cm).

Results and Discussion

Catalytic Activity Measurements of n-Hexane: The aromatization of n-hexane was conducted in the flow reactor at 500°C for 30 h, keeping the H₂/n-hexane (molar) feed ratio of 6 and the weight hourly space velocity (WHSV) of 5 h⁻¹ over the IWI, VPI, and Ce-promoted catalysts. The activity of all catalysts was measured as evolution of conversion and product selectivity with time on stream. The main products found are benzene, hexenes, and cracking products.

(I) Effect of preparation method: As shown in Figure 1, it is clearly observed that Pt/KL catalysts prepared by vapor phase impregnation (VPI) show significantly higher in both conversion and benzene selectivity than those of incipient wetness impregnation (IWI). In addition, the VPI catalysts exhibit lower undesired hexene products than IWI catalysts (not shown). The results agreed with the observation (Jacobs et al., 1999) that the different methods of preparation caused the different Pt cluster distributions. Various characterization techniques revealed that both IWI and VPI preparation methods gave Pt clusters, which contain a very small size located inside the L zeolite

channels. However, the VPI catalysts exhibit higher fraction of small Pt particles interaction with the zeolite walls than those of the IWI catalysts. Therefore the VPI catalysts were better than the IWI catalysts for n-hexane aromatization.

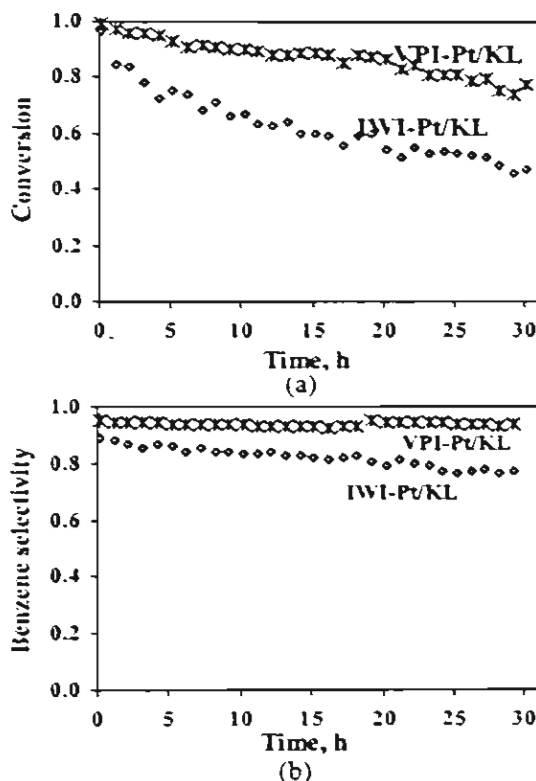
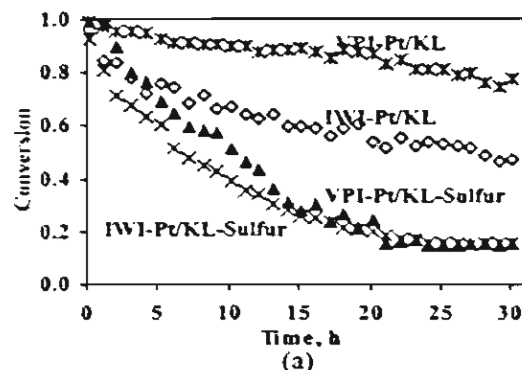


Figure 1 The variation of the (a) conversion, (b) benzene selectivity with time on stream of Pt/KL catalysts prepared by IWI and VPI methods, at 500°C, WHSV = 5 h⁻¹.

(II) Effect of sulfur in the feed: Figure 2 shows the comparison of both the IWI and VPI catalysts in sulfur-free and 2.5 ppm sulfur-poisoned conditions. The results indicate that the presence of sulfur in the feed caused drastic decreases in conversion and selectivity for both the IWI and VPI catalysts. The Pt/KL prepared by VPI method show a little better catalytic performance than those IWI catalysts at first 10 h but after that they behave the same degree of deactivation. As previously reported (Vaarkamp et al., 1992), the deactivation of Pt/KL catalysts for the aromatization resulted from the Pt agglomeration after exposing to sulfur especially the agglomeration occurred near the pore mouth that caused the block of zeolite channel.



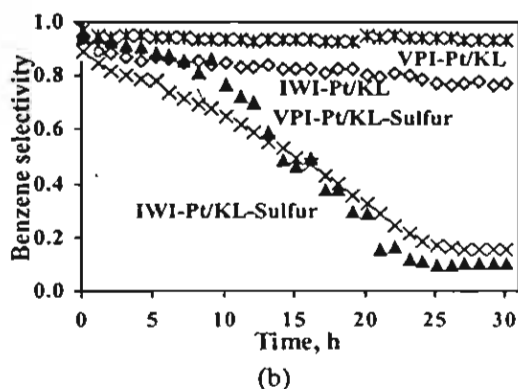


Figure 2 The variation of (a) conversion, (b) benzene selectivity with time on stream of Pt/KL catalysts prepared by IWI and VPI under clean and 2.5 ppm sulfur-containing feed at 500°C, WHSV=5 h⁻¹.

(III) *Effect of rare earth promoter.* In the presence of sulfur, the Ce-promoted catalyst exhibits significantly higher in both conversion and benzene selectivity than those of unpromoted catalyst as shown in Figure 3. The idea to increase sulfur tolerance of Pt/KL catalysts prepared by vapor phase impregnation method by adding Thulium as rare earth promoter was reported (Jacobs *et al.*, 1999). As the activity enhancement due to the rare earth promoter in sulfur-poisoned conditions for n-hexane aromatization, the rare earth elements may act as anchoring sites for the Pt particles, thus preventing the Pt agglomeration or they themselves act as sulfur getters protecting Pt from sulfur poisoning.

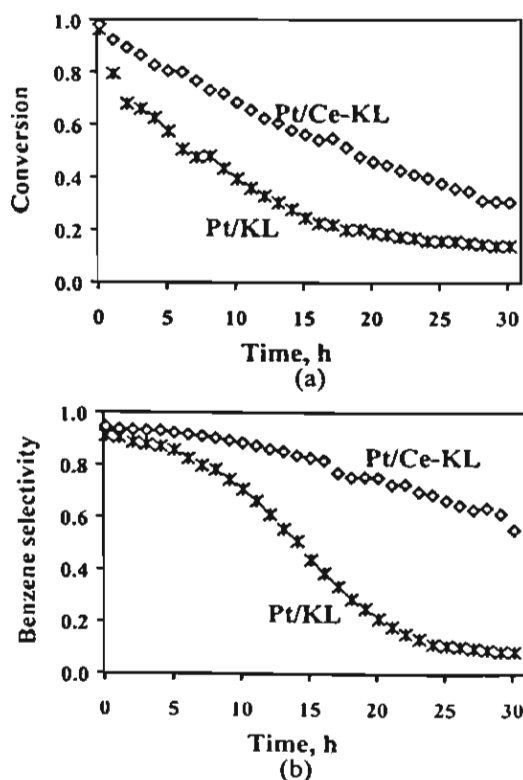


Figure 3 The variation of the (a) conversion, (b) benzene selectivity with time on stream of Pt/KL and Pt/Ce-KL prepared by VPI method under 2.5 ppm sulfur-containing feed, at 500°C, WHSV = 5 h⁻¹.

Catalytic Activity Measurement of n-Octane:

The aromatization of n-octane was investigated for 9 h at the same conditions as n-hexane aromatization. The activities of all catalysts were considered as functions of conversion and total aromatics selectivity versus time on stream.

(I) *Effect of preparation method:* In Figure 4, it can be obviously seen that the VPI catalysts give higher values of conversion, total aromatics selectivity than IWI catalysts. These results are in the same trend as the results from n-hexane aromatization that the VPI catalysts reveal the higher fraction of small Pt particles inside the channel of L-zeolite. Therefore the characteristic morphology of Pt particles produced by the VPI method also give a better catalytic performance for n-octane aromatization. When compared with C6 aromatization, C8 aromatization on Pt/KL catalysts showed much lower activity and aromatics selectivity (Figs 1 and 4). This could be due to double amounts of coke formation, which is discussed later.

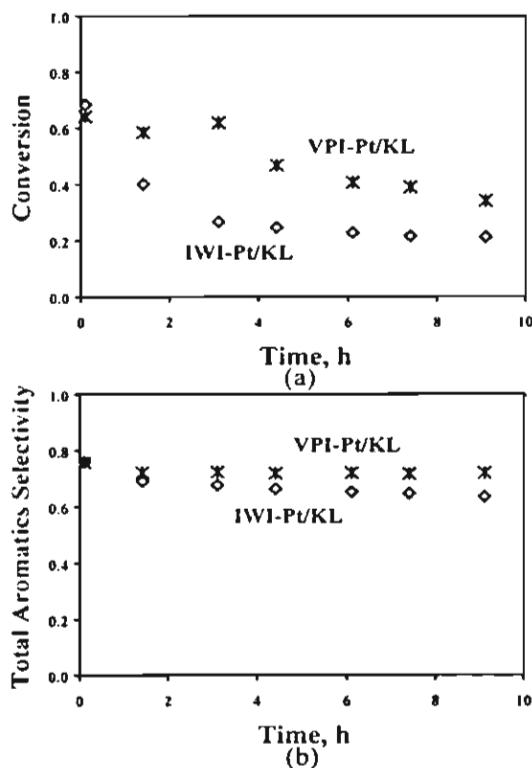


Figure 4 The variation of conversion and total aromatic selectivity with time on stream of Pt/KL catalysts prepared by IWI and VPI methods, at 500°C, WHSV = 5 h⁻¹.

(II) *Effect of sulfur in the feed:* Figure 5 shows the aromatization of n-octane on Pt/KL catalysts. When comparing with the clean conditions, the presence of 2.5 ppm sulfur in the feed caused drastic drops of conversion and total aromatic selectivity for both catalysts, especially for the VPI catalyst. As mentioned above, the deactivation of Pt/KL catalysts resulted from the Pt agglomeration that was accelerated by sulfur.

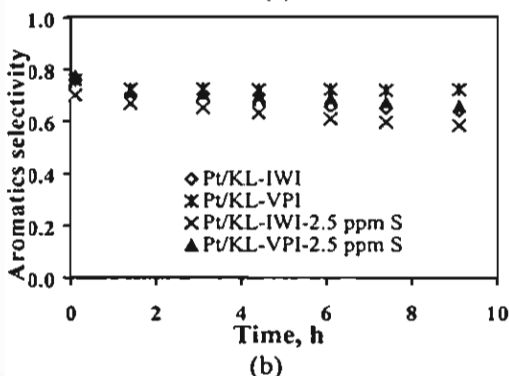
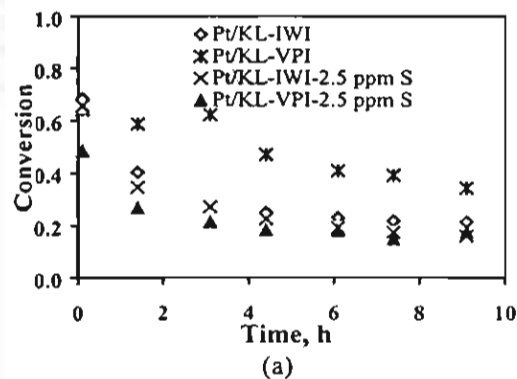


Figure 5 The variation of (a) conversion and (b) total aromatics selectivity with time on stream of Pt/KL catalysts in clean condition and in the presence of 2.5 ppm sulfur, at 500°C, WHSV = 5 h⁻¹.

(III) *Effect of rare earth promoter:* Figure 6 shows the effect of rare earth promoter in 2.5 ppm sulfur-poisoned conditions on C8 aromatization. It can be observed that the addition of rare earth promoter improves the sulfur resistance of Pt/KL catalysts, as the Ce-promoted catalyst shows higher conversion than the unpromoted, and the total aromatic selectivity of both catalysts are nearly the same. However, the improvement of the catalytic performance due to promotion of cerium in the presence of sulfur maybe seen in the longer run as the C6 aromatization results. Furthermore, the preparation method still has a strong effect even in sulfur-poisoned conditions.

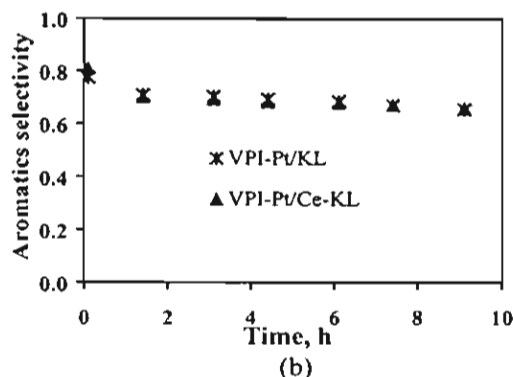
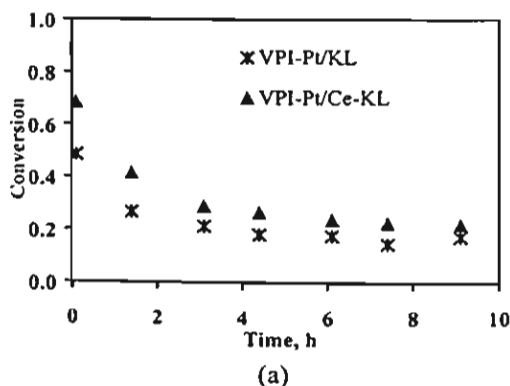


Figure 6 The variation of (a) conversion and (b) total aromatic selectivity with time on stream of Pt/KL catalysts in 2.5 ppm sulfur-poisoned condition by at 500°C, WHSV = 5 h⁻¹.

Catalyst Characterization:

Hydrogen Chemisorption Measurement: The Pt/KL catalysts prepared by different methods (IWI and VPI) and the Ce-promoted catalysts were characterized to quantify the Pt dispersion using the hydrogen chemisorption technique. The Pt dispersion of all catalysts after the reduction at 500°C is reported in Table 1. The VPI catalysts have higher Pt dispersion than IWI catalysts. This result is in good agreement with the work done by Jacobs *et al.* (2001) which demonstrated that the Pt/KL catalyst prepared by VPI is effective in dispersing Pt. The addition of Ce as promoter shows relatively lower Pt dispersion than the unpromoted Pt/KL catalysts. One possible explanation is that the anchoring of Ce might block some sites of zeolite, leading to the low Pt dispersion.

Table 1 The Pt dispersion of catalysts after reduction at 500°C

Catalyst	Pt dispersion (%)
Pt/KL-VPI	81.51
Pt/KL-IWI	78.39
Pt/Ce-KL-VPI	63.45

DRIFTS of Adsorbed CO: The fresh and spent catalysts were characterized by FTIR of adsorbed CO to determine the morphology and location of Pt clusters on the catalysts. This technique is useful for making general conclusions about the location (i.e., inside or outside the zeolite channel) and the distribution of the Pt clusters prior to disruption (Jacobs *et al.*, 2000). It has been proposed (Stakheev *et al.*, 1995) that the different regions of wavenumbers correspond to the variations of morphology of Pt clusters. Regarding the hypothesis for the low-wavenumbers, bands at 2050-1930 cm⁻¹ are assigned to Pt-carbonyl species arose from the disruption of small Pt clusters inside the L-zeolite channels. The bands between 2050 and 2075 cm⁻¹ are associated with larger Pt clusters in the near-surface region of the L-zeolite. In contrast, the bands at and above 2075 cm⁻¹ are in general assigned to larger Pt particles on the external surface of the L-zeolite. In this section, the

spectra of FTIR of adsorbed CO of the fresh and spent catalysts were examined.

(I) *Effect of preparation method:* Figure 7 demonstrates the comparison of FTIR spectra of fresh Pt/KL catalysts prepared by IWI and VPI methods. The VPI catalysts show more pronounced band at low wavenumbers than IWI catalysts which represents higher fraction of small platinum clusters inside the zeolite channel in VPI catalysts. These results are in good agreement with a previous report (Jacob et al., 1999) that the VPI catalysts favor the formation of Pt carbonyls during CO adsorption which represent the small Pt clusters inside the L-zeolite rather than the IWI catalysts. These FTIR results are one of the explanations that the VPI catalysts gave better catalytic performance than those of IWI.

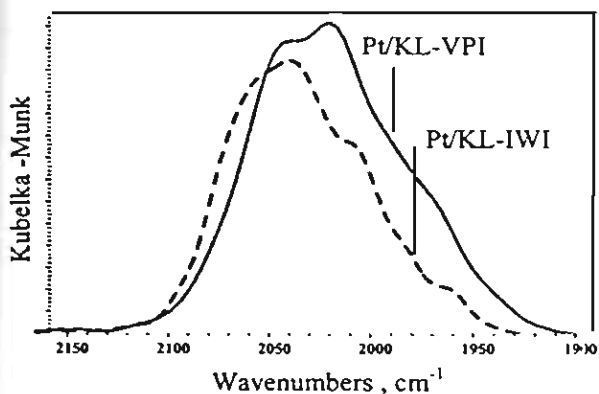


Figure 7 FTIR spectra of Pt/KL catalysts prepared by IWI and VPI methods reduced at 500°C.

(II) *Effect of sulfur in feed:* The comparison of the FTIR spectra of fresh and spent (with sulfur) Pt/KL catalysts at 500°C as seen in Figure 8, clearly shows the drop in intensity after exposed to the reaction with the sulfur containing feed due to Pt agglomeration. However, the addition of Ce caused higher intensity or lower Pt agglomeration when compared with the unpromoted catalyst. As for catalytic activity results of the aromatization of n-C6 and n-C8, both conversion and aromatics selectivity remarkably dropped due to sulfur poisoning. A previous study (Jacobs et al., 2000) indicated that sulfur can cause Pt agglomeration or sulfur strongly competitively adsorbed on Pt metal surface. Both cases cause reduction in quantity of CO adsorbed on Pt surface, hence lower in spectrum intensities.

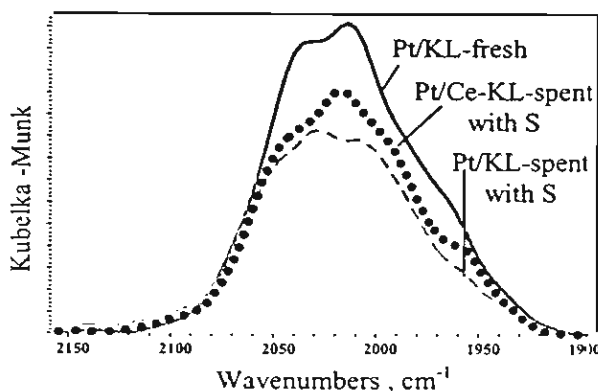


Figure 8 FTIR spectra of Pt/KL_VPI catalysts freshly reduced and after spent in 2.5 ppm sulfur, reduced at 500°C.

Temperature Programmed Oxidation (TPO): The spent catalysts were carried out with TPO measurements to examine the amount and nature of the coke deposit on the different catalysts during the course of reactions. Table 2 summarizes the amount of carbon formation in the n-C6 and n-C8 aromatization reaction of the spent Pt/KL catalysts after 9 h on stream with clean and 2.5 ppm sulfur conditions. It can be seen that the aromatization of n-C8 generates approximately double amount of carbon more than the n-C6 aromatization reaction at both sulfur-free and sulfur-poisoned conditions. This maybe because the higher carbon atoms of C8 are easier to form coke. It could be the chief reason of very low activity of C8 aromatization in comparison with that of C6 reaction at the same conditions.

Table 2 Amount of carbon formation on the Pt/KL catalysts in the n-C6 and n-C8 aromatization reactions, as determined by TPO.

Aromatization	% C after 9-h run	
	clean condition	2.5 ppm S condition
n-C6	1.02	1.03
n-C8	2.26	2.40

In the presence of sulfur, the TPO profiles were shifted to higher temperatures for both the C6 and C8 reactions as shown in Figure 9. The shift of TPO profiles by sulfur poisoning was discussed in a previous work (Jacob et al., 2000) given that when Pt particle was poisoned by sulfur, the ability of Pt to catalyze oxidation at low temperatures was less pronounced.

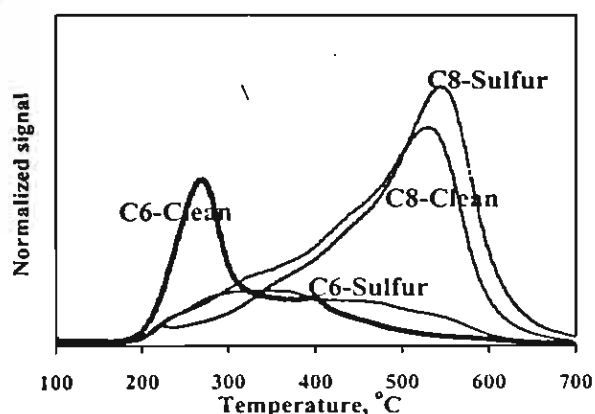


Figure 9 TPO profiles for the Pt/KL-VPI catalysts after clean run and after spent in 2.5 ppm sulfur for both the aromatization of n-C6 and n-C8.

Kinetics of iso-Butane Sorption: To support the idea that the cokes formed plug the pore of L-zeolite leading to very low activity and selectivity in C8 aromatization, the kinetics of iso-butane sorption were studied. The amount of iso-butane adsorbed on KL, spent Pt/KL-VPI catalysts with C6 and C8 and diffusive parameter (D/r_o^2) for each material are given in Table 3. The data show the maximum adsorption of iso-butane for the blank KL. The adsorption was lower for the Pt/KL-C6 and significantly lower for the Pt/KL-C8. The results indicate greater coke plugging in Pt/KL-C8 than that in Pt/KL-C6. The diffusivities were reported in terms of D/r_o^2 . It is observed that the clean KL shows the highest D/r_o^2 while the Pt/KL-C6 presents an intermediate case close to Pt/KL-C8. That means though the Pt/KL-C8 has relatively higher coke formation (lower iso-butane sorption) than those of Pt/KL-C6, the similar value of D/r_o^2 indicate the same degrees of iso-butane mobility.

Table 3 Adsorption and diffusive parameters of KL-zeolite and coked catalysts

Catalyst	Iso-butane adsorption, mol/g.cat	$D/r_o^2, s^{-1}$
KL-zeolite	4.63E-04	1.84E-03
Pt/KL-C6	3.21E-04	1.31E-03
Pt/KL- C8	1.64E-04	1.25E-03

Conclusions

The results indicated that the VPI catalysts exhibited better catalytic performance than the IWI catalysts for both C6 and C8 aromatization. The characterization results (H_2 chemisorption, FTIR of adsorbed CO) showed that the Pt/KL prepared by VPI method contained higher Pt dispersion which well dispersed inside the channels of L-zeolite than the IWI catalysts. Therefore, the methods of preparation have a strong effect on Pt/KL catalysts to obtain the high performance in different conditions. The aromatization

of C8 on Pt/KL showed much lower activity than the aromatization of C6 due to coke formation. The addition of Ce as rare earth promoter improves the catalytic performance in the presence of sulfur for both C6 and C8 reactions.

Acknowledgements

This research was supported by the Petroleum and Petrochemical College of Chulalongkorn University, the Thailand Research Fund, and School of Chemical Engineering and Materials Science, University of Oklahoma, USA.

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2002 Spring National Meeting



• paper 119e • Hugh D Guthrie*,
NETL/DOE, Morgantown, WV, Charles W
Byrer, National Energy Technology Laboratory,
Morgantown, WV

**[120] WEDNESDAY, MAR 13; 8:30 AM
ROOM: CAMBRIDGE**

LNG-IV-RESEARCH & DEVELOPMENT

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ChevronTexaco Corp., Bellaire, TX

Yoshitsugi Kikkawa, Vice-Chair
Chiyoda Corp., Tsurumiku, Yokohama, Japan

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**Qualification of a Transfer System for
LNG Between Two Floating Vessels in
Harsh Environment • 8:30 AM • paper
120a • Eide Jorgen*, Framo Engineering A/S,
Sandst, Norway**

**Higher Efficiencies and Lower Emissions
for a Base Load LNG Plant, Are You
Ready for That? • 9:00 AM • paper 120b
• Nelson B Peterson*, Dave Messersmith, Bechtel
Corporation, Houston, TX, Bill Woodard, Kent
Anderson, Phillips, Houston, TX**

**Exducer Turbines, the Third
Generation of LNG Expanders • 9:30
AM • paper 120c • Everett H. Hylton*, Hans
Kimmel, Ebara International Corporation,
Sparks, NV**

**Thermoacoustic Natural Gas
Liquefaction • 10:00 AM • paper 120d •
David Gardner, Gregory W. Swift, Scott
Backhaus, Los Alamos National Laboratory, Los
Alamos, NM, John J Wollan*, Praxair, Denver,
CO**

**Condensation of Hydrocarbons in
Micro-fin Tubes • 10:30 AM • paper
120e • Bengt Olav Neeraas*, SINTEF Energy
Research AS, Trondheim, Norway**

**Methods of Earthquake-proof Safety
Design for Plant Structure and Cost
Reduction of a Pipe Rack in LNG
Plants • 11:00 AM • paper 120f • Shigemi
Ochiai*, Jonquil Consulting Inc., Tokyo, Japan,
Makita Takenori, Hasegawa Tatsuya, Anzai
Hajime, Nihonkai LNG Co. Ltd., Yoshida
Keijiro, Nakamura Tomomichi, Mitsubishi
Heavy Industries, Ltd., Hyogo Prefecture, Japan**

**[121] WEDNESDAY, MAR 13, 2:00 PM
ROOM: CAMBRIDGE**

LNG-V-SAFETY & SIMULATION

Chen-Hwa Chiu, Chair
ChevronTexaco Corp., Bellaire, TX

Hans Kimmel, Vice-Chair
Ebara International Corporation, Sparks, NV

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**Documenting Code Compliance for
LNG Facilities • 2:00 PM • paper 121a •
Harry H West*, Dale C Zinn, Michael E.
Stofford, Shawnee Engineers, Houston, TX**

**CNG Module Gas Dynamics • 2:30 PM
• paper 121b • Jan V Wagner, Fluor Canada
Ltd., Calgary, Canada, Satish L. Gandhi*,
Flour Daniel, Sugar Land, TX**

**Hazop and IPF Guidelines for
Variable Speed Liquid Expanders •
3:00 PM • paper 121c • Joel V. Madison*,
Ebara International Corporation, Sparks, NV**

**Unique Phenomena in Liquefied Gas
Fluid Machinery • 3:30 PM • paper
121d • Hans Kimmel, Ebara International
Corporation, Sparks, NV, Dave Luget*,
M.W. Kellogg Limited, Greenford,
Middlesex, UK**

**Safe Commissioning of an Ethylene
Pipeline System • 4:00 PM • paper 121e
• Hugh D. Kaiser*, IDS Engineering, Houston, TX**

**Production of LNG using Dual
Independent Expander Refrigeration
Cycles • 4:30 PM • paper 121f • Jorge H
Foglietta*, ABB Lummus Global Randall
Division, Houston, TX**

**[122] MONDAY, MAR 11, 8:00 AM
ROOM: CHEQUERS**

AROMATICS PRODUCTION

Paul Eve, Chair
Global Aromatics, BP

James A Johnson, Vice-Chair
UOP

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**Aromatization of n-Hexane and n-
Octane over Pt/KL and Pt/SiO₂
Catalysts • 8:00 AM • paper 122a •
Somchai Osuwan, Chulalongkorn University,
Patumwan, Thailand, Daniel E Resasco, The
University of Oklahoma, Norman, OK, Walter E
Alvarez, University of Oklahoma, Norman, OK,
Siriporn Jongpatiwut*, Chulalongkorn University,
Yannawa, Sathorn, Thailand, Paneeya
Sackamduang, The Petroleum and Petrochemical
College, Chulalongkorn University, Patumwan,
Thailand, Thirasak Rirksomboon, Chulalongkorn
University, Patumwan, Thailand**

**ParamaX: A Single-source Solution
for BTX Complexes • 8:30 AM • paper
122b • C Dupraz*, J Rault, Axens, Rueil-
Malmaison, France**

**Real Time Optimization of Para-
Xylene Unit: Application and the Uses
of Rt-Opt Model • 9:00 AM • paper
122c • John E Myers*, BP Chemicals,
Naperville, IL, Peter J Hanratty, Aspen
Technology, Houston, TX**

**Debottlenecking of Existing Aromatic
Production Loop: The Hybrid Eluxyl
Process Offers An Attractive Alternative**

**Solution • 9:30 AM • paper 122d • G
Hotier*, Axens, Rueil-Malmaison, France**

**Designer Catalysts and Processes for
Para-Xylene Production: The P_xMaxSM
Technology for Selective Toluene
Upgrading • 10:00 AM • paper 122e •
David I Stern*, ExxonMobil, Baytown, TX**

**First Stage Hydrotreating of Pyrolysis
Gasoline • 10:30 AM • paper 122f •
Mark P Kaminsky*, Equistar Chemical, Alvin, TX**

**[123] MONDAY, MAR 11, 1:00 PM
ROOM: CHEQUERS**

AROMATICS PROCESSING

Jose Santiesteban, Chair
ExxonMobil Research and Engineering
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**Specialty Aromatic Chemicals from
Naphthalene and Biphenyl by Shape-
Selective Catalysis • 1:05 PM • paper
123a • Chunshon Song*, Pennsylvania State
University, University Park, PA**

**UOP's New Xylene Isomerization
Catalyst • 1:30 PM • paper 123b •
Thomas Ebner*, Patrick Silady, Kevin O'Neil
UOP LLC, Des Plaines, IL**

**Improved Economics from New
Generation of Xylene Isomerization
Catalyst • 1:55 PM • paper 123c • E
Kochler*, Sud-Chemie AG, Munchen,
Germany, H Takeda, Sud-Chemie Catalysts
Japan, Munchen, Germany, J Osbourne, Sud-
Chemie Inc, Munchen, Germany, P Roeger, G
Burgfels, Sud-Chemie AG, Munchen, Germany**

**UOP's New Tatoray Catalyst for
Maximum Yields & Product Quality •
2:20 PM • paper 123d • Antoine Negiz*,
Jason NOE, Tom Stoodt, Chee Hong Tan, UOP
LLC, Des Plaines, IL**

**XyMax: ExxonMobil's State-of-the-
Art Xylenes Isomerization Technology
• 2:45 PM • paper 123e • Gary D Mohr*,
ExxonMobil, Baytown, TX**

**Operational Experience with GT-BTX
Aromatics Recovery Technology • 3:10
PM • paper 123f • Joseph C Gentry*, C S
Kumar*, GTC Technology Corp., Houston, TX**

**[124] TUESDAY, MAR 12, 8:00 AM
—ROOM: CHEQUERS**

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UOP LLC, Des Plaines, IL

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AROMATIZATION OF n-HEXANE AND n-OCTANE OVER Pt/KL AND Pt/SiO₂ CATALYSTS

Siriporn Jongpatiwut*, Paneeya Sackamduang*, Thirasak Rirksomboon*,
Somchai Osuwan*, Walter E. Alvarez**, and Daniel E. Resasco**

* The Petroleum and Petrochemical College,
Chulalongkorn University, Bangkok, Thailand

** School of Chemical Engineering and Materials Science,
The University of Oklahoma, Norman, OK 73019

Key words: Pt/KL, Pt/SiO₂, n-hexane aromatization, n-octane aromatization, FTIR of adsorbed CO, TPO, iso-butane sorption

Prepared for presentation at the 2002 Spring Meeting, New Orleans, LA, March 10-14

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Chulalongkorn University and The University of Oklahoma

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Abstract

Pt/KL catalysts have been known for two decades that they exhibited an exceptionally high activity and selectivity for n-hexane aromatization. In this work, Pt/KL and Pt/SiO₂ catalysts were tested for aromatizations of n-hexane and n-octane at 500°C. Pt/KL catalysts were prepared by two methods; incipient wetness impregnation (IWI) and vapor phase impregnation (VPI) while Pt/SiO₂ catalyst was prepared only by the IWI method. The results indicated that for both n-hexane and n-octane aromatization, the Pt/KL catalysts, especially the one prepared by VPI, exhibited higher catalytic activity and aromatic selectivity than Pt/SiO₂. The aromatization of n-octane resulted in much lower activity over both Pt/SiO₂ and Pt/KL catalysts when compared to the aromatization of n-hexane. However, total aromatic selectivity over Pt/SiO₂ was much more pronounced for n-octane than n-hexane reaction. The main aromatic products obtained from n-octane reaction over Pt/SiO₂ were ethylbenzene and o-xylene, which are predicted by directly six-membered ring closure. On the other hand, the main products observed over Pt/KL were benzene and toluene. Reaction pathways for the production of benzene and toluene from n-octane over Pt/KL were investigated by varying the reaction temperature and WHSV. In addition, reactions of suspicious intermediates, which are ethylbenzene, o-xylene, toluene, and n-heptane over Pt/KL were also studied. The fresh and spent catalysts were analyzed by a number of techniques. DRIFTS of adsorbed CO and hydrogen chemisorption results indicated that the Pt/KL prepared by VPI had a higher fraction of small platinum clusters inside the zeolite channel than that prepared by IWI. TPO analysis and iso-butane sorption study revealed that the drastic drop in conversion of n-octane was due to the large amount of coke deposit during the course of reaction, resulting in catalyst pore blocking.

Introduction

The aromatization of n-alkanes is an important reaction with respect to its industrial application and fundamental viewpoints. In 1969, Davis and Venuto [1] investigated aromatic products obtained from 10 different C8-C9 paraffin carbon skeleton structures over nonacidic Pt-Al₂O₃-K catalyst. In all cases, the aromatic products were those predicted by a direct six-membered ring closure (ethylbenzene and o-xylene). Davis [2] further studied the adding of tin in Pt-Al₂O₃-K. He carried out that the aromatic distribution changed to favor o-xylene when tin was added to the Pt catalyst. In 1976, Davis et al. [3] observed that the percent loading of Pt influenced the distribution of aromatic products. In 1994 Meriaudeau et al. [4] compared the aromatization of n-octane on Pt/SiO₂ and Pt/silicalite. Unexpectedly, the catalytic performance of Pt supported on microporous silicalite catalyst was less than that of Pt supported on nonmicroporous silica. They suggested that the reaction on Pt/silicalite is limited by diffusion of the reactant and the products lead to less conversion and aromatics selectivity.

Bernard et al. (1980) [5] revealed that platinum supported on basic L-zeolite catalysts resulted in exceptionally high conversion and selectivity for n-hexane aromatization. The Pt/KL catalysts differ from conventional, bifunctional catalyst, because they exhibit the metallic function. In fact, Lane et al. (1991) [6] clearly showed that Pt/KL catalysts benefits from the absence of acid-catalyzed hydrocracking resulting in higher liquid yields. There have been many literatures reported on aromatization of n-hexane by Pt/KL. Some of the researches attempted to figure out its mechanism [7, 8]. Some [9, 10, 11] tried to improve the catalysts by varying pretreatment and preparation method. However, there is no literature reported the aromatization of longer chain alkane e.g. n-octane on the Pt/KL. In this contribution, we therefore decided to study activity and product distribution of n-hexane and n-octane aromatization reaction over basic Pt/KL and Pt/SiO₂ catalysts.

Experimental

1. Catalyst Preparation

Pt/KL catalysts were prepared with 1wt% loading of platinum (Pt) by two methods; incipient wetness (IWI) and vapor phase impregnation (VPI) whereas Pt/SiO₂ catalyst was only prepared by IWI method. The K-LTL-zeolite (Lot#1041, BET area = 292 m²/g, SiO₂/Al₂O₃ ratio = 6) was produced by Tosoh Corp. The precipitated silica Hi-Sil[®] 233 (CAS# 7631-86-9, BET area = 140 m²/g) was provided by PPG Siam Silica Co., Ltd. Prior to addition of the platinum metal, the supports were dried in an oven at 110°C overnight and calcined at 400°C in a dry airflow of 100 cm³/min.g for 5 h.

In IWI method, tetraamineplatinum (II) nitrate (Merck) was weighed and dissolved in deionized water (0.69 cm³/g support) and then impregnated in the dried support by slowly drops of solution under dried nitrogen atmosphere. Next, the mixture was dried in an oven at 110°C overnight. The cool mixture was loaded into a glass tube and calcined at 350°C in a dried air flow of 100 cm³/min.g for 2 h and left cool to room temperature. The resultant catalyst (Pt/KL-IWI or Pt/SiO₂) was stored in a desiccator. The Pt/KL-VPI catalyst was prepared by physically mixing weighed platinum (II) acetylacetonate (Alfa Aesar)

and the dried support under nitrogen atmosphere. The mixture was then loaded into the reactor tube under helium flow of 2 cm³/min.g. The mixture temperature was slowly ramped to 40°C and held there for 3 h, and ramped again to 60°C and held again for 1 h. After that, further ramped to 100°C, at which temperature the mixture was held for 1 h to sublime the Pt (AcAc)₂. After sublimation, the mixture was ramped to 130°C and held for 15 minutes to ensure that all of Pt(AcAc)₂ was sublimed. The reactor was allowed to cool to room temperature. After that it was ramped to 350°C in flow of air for 2 h and calcined at that temperature to decompose the platinum precursor. Finally, the Pt/KL prepared by VPI method was stored in a desiccator.

2. Catalytic Activity Measurement

The catalytic activity studies were conducted at atmospheric pressure in a 0.5-inch glass tube with an internal K-type thermocouple for temperature measurement. The reactor was a single pass and continuous-flow type. 200 mg of catalysts was used in each run. Prior to reaction, the temperature was slowly ramped in flowing H₂ at 100 cm³/min.g for 2 h up to 500°C and *in-situ* reduced at that temperature for 1 h. n-Hexane (or n-octane) was added by infusion with a syringe pump. In all experiments, the hydrogen to n-hexane (or n-octane) molar ratios was kept at 6. The products were analyzed in a Shimadzu GC-17A equipped with a capillary column HP-PLOT/Al₂O₃ "S" Deactivated. GC column temperature was programmed to obtain adequate products separation. The temperature was first kept constant at 40°C for 10 min then it was linearly ramped to 195°C by a rate of 5°C/min and held at this temperature for 30 min. To identify m- and p-xylene, the analysis of liquid product was performed using a capillary column ATTM-1000. The activity data are reported in terms of total n-hexane or n-octane conversion and product selectivity, which is defined as weight of each individual product per weight of n-hexane or n-octane converted.

3. Catalyst Characterization

3.1 Hydrogen Chemisorption: The amount of adsorbed hydrogen on all fresh catalysts was performed in a static volumetric adsorption Pyrex system, equipped with a high capacity, high vacuum pump that provided vacuum on the order of 10⁻⁹ torr. Prior to each experiment, 400 mg of dried fresh catalyst was reduced *in-situ* at 500°C for 1 h under flowing of H₂, cooled down to 300°C, evacuated to at least 10⁻⁷ torr at 300°C for 20 min, then cooled down to room temperature under vacuum. The adsorption isotherm was schemed by several adsorption points ranging from 0 to 100 torr.

3.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of Adsorbed CO: The fresh and spent Pt/KL and Pt/RE-KL catalysts were characterized by DRIFTS Bio-Rad FTS-40 spectrometer equipped with a MCT detector using CO as a probe. Experiment was performed in a diffuse reflectance cell from Harrick Scientific, type HVC-DR2, with ZnSe windows. For each IR spectrum, it was taken at a resolution of 8 cm⁻¹ and 128 scans. Prior to each spectrum, the sample was *in-situ* reduced in a flow of H₂ at 300°C for 1 h, purged in He for 30 min at room temperature, and collected the background. Then, the catalyst was exposed to a flow of 3%CO in He for 30 min, purged in He for 30 min, and then collected the adsorbed CO spectrum.

3.3 Temperature Programmed Oxidation (TPO): Temperature programmed oxidation technique was employed to analyze amount and characteristic of coke deposits on spent catalysts. TPO of the spent catalysts was performed in a continuous flow of 2% O₂/He while the temperature was linearly increased (heating rate of 12°C/min). The oxidation was conducted in a ¼" quartz fixed-bed reactor. The spent catalyst was dried at 110°C overnight before weighing. 30 mg of the dried sample was supported on a bed of quartz glass wool. The catalyst was flushed by 2% O₂ in He for 30 min before the TPO was performed. The CO₂ produced by the oxidation of coke species was further converted to methane by 15%Ni/Al₂O₃ at 400°C. The methane was analyzed by a FID detector. The amount of coke was calibrated by using 50 µl pulses of pure CO₂.

3.4 Kinetics of iso-Butane Sorption: Kinetic studies were performed to investigate the characteristics of iso-butane diffusivity into fresh and coked catalysts. The experiment was conducted in a Pyrex volumetric system equipped with a 0-100 torr MKS Baratron precision gauge. Prior to each adsorption run, 200 mg of sample was activated by heating in vacuum (10⁻⁶ torr) at 350°C for 2 h then the temperature of the adsorbent bed was set to 100°C. The Pyrex system was also kept constant at 100°C by heating tape equipped with a temperature controller. 37 cm³ of iso-butane at 100 torr and 100°C was expanded to the reactor (total volume = 54 cm³). The pressure change was dynamically monitored by a connected computer. D/r₀² was calculated by using the following equation [12].

$$\frac{M_t}{M_\infty} = \frac{1+K}{K} \frac{6}{r_0} \left(\frac{Dt}{\pi} \right)^{1/2}$$

Where M_t/M_∞ is the fraction approach to equilibrium, K is the ratio of amount of sorbate in the gas phase to the amount in the sorbent in equilibrium, D is the diffusivity (cm²/sec), t is time (sec), and r₀ is the particle radius (cm).

Results and discussion

1. Catalytic activity measurement

The Pt/KL-VPI, Pt/KL-IWI, and Pt/SiO₂ catalysts were tested for the aromatizations of n-hexane and n-octane. The evolutions of the conversion and total aromatics selectivity are shown in Figures 1a and 1b. Among Pt/KL catalysts, Pt/KL-VPI exhibited higher conversion, benzene selectivity, and stability than Pt/KL-IWI for n-hexane aromatization. In the same trend, the VPI-catalyst showed higher n-octane conversion and aromatics selectivity than IWI-catalyst in the first 12 h on stream. However, it is clearly observed that the rate of deactivation was much more pronounced on the reaction of n-octane than that of n-hexane. Pt/SiO₂ showed much lower conversion than Pt/KL at the same conditions however the conversion of n-octane was lower than that of n-hexane. Interestingly, the aromatics selectivity of n-octane over the Pt/SiO₂ was considerably higher than that of n-hexane. This phenomenon might be because the longer chain of n-octane molecule is easier to encircle an aromatic ring over nonmicroporous Pt/SiO₂. However, the ring enclosure over Pt/KL was also forced by the unidimensional pore of L-zeolite, resulting in high aromatization performance even with n-hexane.

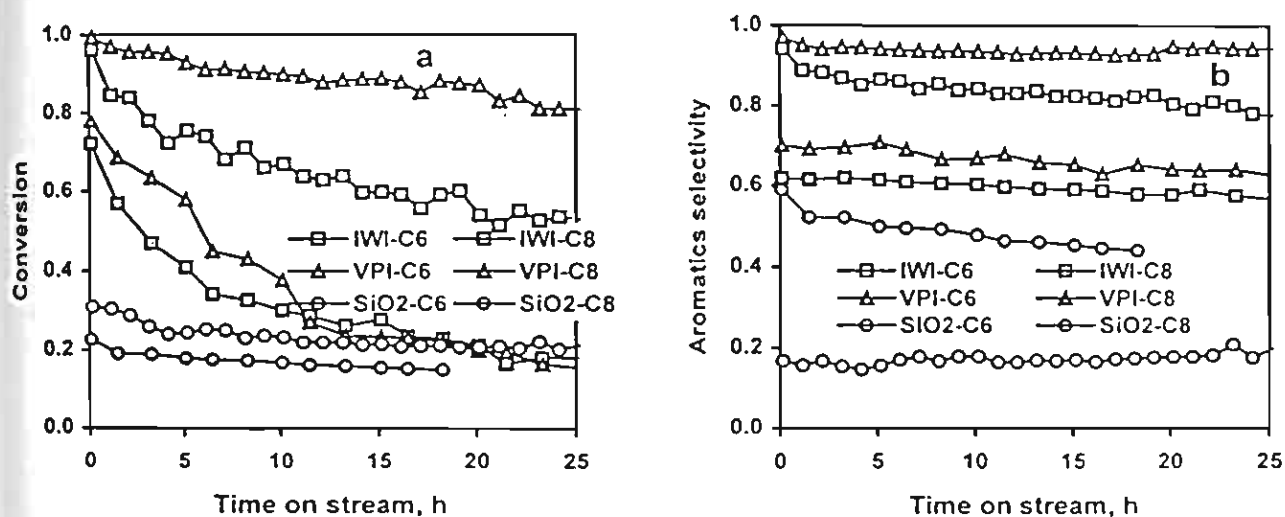


Figure 1 n-Hexane and n-octane conversion (a) and aromatics selectivity (b) vs. time on stream over Pt/KL-VPI, Pt/KL-IWI, and Pt/SiO₂ catalysts. Reaction conditions: 500°C, H₂/n-C₆ (n-C₈) molar ratio 6:1, WHSV 5 h⁻¹.

Table 1 summarizes the product distribution obtained after 10 h on stream on the Pt/SiO₂, Pt/KL-IWI, and Pt/KL-VPI catalysts for n-hexane and n-octane aromatizations. In case of n-hexane, the Pt/KL especially the one prepared by VPI exhibited substantial conversion and benzene selectivity while the Pt/SiO₂ gave much poorer ability to produce aromatics in which its main product was dehydrogenated hexenes. For n-octane, despite higher aromatics selectivity over Pt/KL, most aromatics gained were benzene and toluene while the dominant products obtained from Pt/SiO₂ were ethylbenzene and o-xylene which were expected from a directly one-six membered ring closure. The directly one-six membered ring closure was observed by Davis [1] for various C₈-C₉ paraffin reactions over Pt/Al₂O₃-K. There was no benzene obtained from the reaction over Pt/SiO₂. Like n-hexane, n-octane reaction over Pt/SiO₂ showed a great amount of dehydrogenated products when compared to Pt/KL.

Figure 2a shows conversion and aromatics selectivity as a function of temperature. It was found that the higher temperature the higher conversion. As for selectivity, at below 400°C all aromatics increased with temperature but above 400°C toluene, benzene, methane, and ethane increased whereas C₈-aromatics decreased with increasing temperature. Two possible pathways for the production of benzene and toluene from n-octane are illustrated in Schemes 1a and 1b. To figure out the reaction pathway, ethylbenzene, toluene, o-xylene, and n-heptane were investigated on the activity and product selectivity over Pt/KL-VPI catalyst at the same condition. The conversion and product distributions are listed in Table 2. The results showed that the reaction of ethylbenzene over Pt/KL caused only terminal cracking leading to overwhelming benzene and toluene. In common with ethylbenzene, o-xylene reaction resulted in the abundance of benzene and toluene. Moreover the little amount of m-xylene and p-xylene was observed. In parallel with ethylbenzene and o-xylene, toluene reaction indicated that the terminal cracking generated benzene. The reaction results indicated very stable of aromatic ring over Pt/KL catalysts. The reaction of n-heptane also produced toluene and benzene, however, the conversion was only 36.41% (see Table 2. In fact, there was no n-heptane eluted from the n-octane reaction. Therefore the reaction pathway in Scheme 1b should not be possible.

The most probable mechanism at reaction temperature of 500°C is that the C8-aromatics were first directly formed then further cracked to toluene or benzene. Some of o-xylene was isomerized to m- and p-xylene. By varying weight hourly space velocity (WHSV) at a constant reaction temperature (500°C), the conversion and product selectivity are shown in Figure 2b. The conversion decreased with an increase in WHSV. In agreement with varying reaction temperatures, at somewhat long contact time (WHSV=1 h⁻¹), the C8-aromatics formed were further cracked to toluene and benzene. As WHSV increased, C8-aromatics were increased while hexenes, heptenes, and octenes were also increased (not shown). At this point, we believe that the Pt/KL catalyst favor for terminal adsorption, leading to cracking and dehydrocyclization. Moreover, octenes, heptenes, and hexenes might be considered as intermediates for production of aromatics.

Table 1 Product distributions of n-hexane and n-octane aromatizations over Pt/KL-VPI catalyst, after 10 h on stream. Reaction conditions: 500°C, H₂/n-C6 (or n-C8) molar ratio 6:1, WHSV 5 h⁻¹.

Property	C6 Aromatization			C8 Aromatization		
	Pt/SiO ₂	Pt/KL-IWI	Pt/KL-VPI	Pt/SiO ₂	Pt/KL-IWI	Pt/KL-VPI
Conversion	18.84	71.05	90.55	16.80	30.08	37.71
Products selectivity						
C1-C5	8.76	22.35	12.17	7.10	34.02	29.41
Hexenes	78.73	5.94	0.68	3.50	1.17	0.69
Benzene	15.08	85.55	93.60	0.00	27.36	27.66
Toluene	-	-	-	0.90	22.79	28.25
Heptenes	-	-	-	34.78	2.62	0.60
Octenes	-	-	-	5.41	1.42	1.89
Ethylbenzene	-	-	-	21.54	5.90	6.53
m-Xylene	-	-	-	1.16	1.12	1.18
p-Xylene	-	-	-	0.39	0.26	0.19
o-Xylene	-	-	-	24.79	2.80	2.97

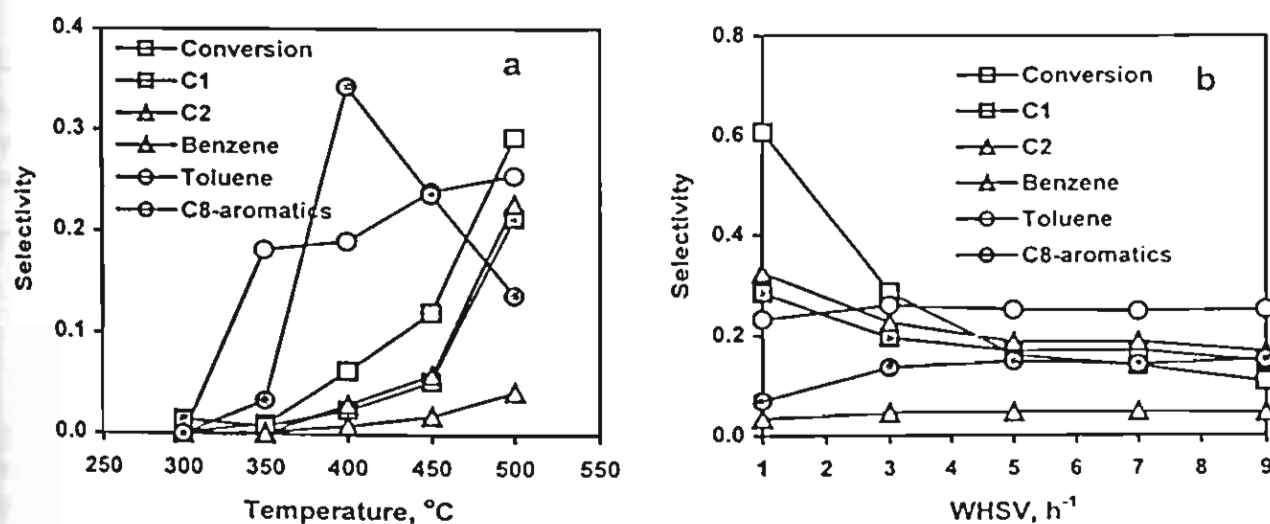
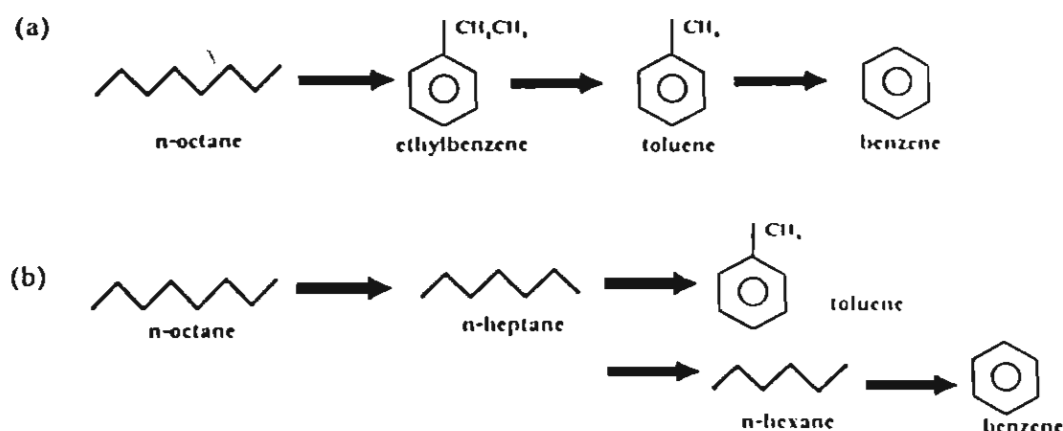


Figure 2 (a) n-Octane conversion and product selectivity vs. reaction temperature. Reaction conditions: H₂/n-C8 molar ratio 6:1, WHSV 5 h⁻¹ (b) n-Octane conversion and product selectivity vs. WHSV. Reaction conditions: H₂/n-C8 molar ratio 6:1, 500°C.



Scheme 1 Two possible pathways for the production of benzene from n-octane reaction

Table 2 Product distributions of n-octane, ethylbenzene, o-xylene, toluene, and n-heptane over Pt/KL-VPI catalysts. Reaction conditions: 500°C, H₂/reactant molar ratio 6:1, WHSV 5 h⁻¹.

Property	Reactant				
	n-Octane	Ethylbenzene	o-Xylene	Toluene	n-Heptane
Conversion	37.71	71.46	16.68	64.93	36.41
Products selectivity					
C1-C5	29.41	20.12	11.83	15.36	27.81
Hexenes	0.69	0.00	0.00	0.00	7.45
Benzene	27.66	46.54	6.43	84.32	28.51
Toluene	28.25	32.90	78.92	-	33.13
Heptenes	0.60	0.00	0.00	0.00	2.29
Octenes	1.89	0.00	0.15	0.00	0.00
Ethylbenzene	6.53	-	0.15	0.00	0.00
m- and p-Xylene	1.37	0.00	1.77	0.00	0.00
o-Xylene	2.97	0.19	-	0.00	0.00

2. Catalyst Characterization

2.1 Hydrogen Chemisorption: Table 3 shows H/Pt on Pt/KL-VPI and Pt/KL-IWI catalysts after reduction at 500°C. The results are consistent with our previous work [13] that is the VPI catalyst showed higher Pt dispersion than that of IWI catalyst. In parallel with reaction, it was found that the higher Pt dispersion, the higher catalytic performance.

Table 3 Hydrogen chemisorption data on fresh (reduced) catalysts.

Catalyst	H/Pt
Pt/KL-IWI	0.559
Pt/KL-VPI	0.906

2.2 DRIFTS of adsorbed CO: The Pt/KL catalysts were characterized by a DRIFTS of adsorbed CO in the range 2150-1900 cm⁻¹ to determine the morphology and location of Pt clusters. As described in previous studies [13, 14], a band below 2000 cm⁻¹ has been ascribed to the formation of Pt carbonyls stabilized inside the L-zeolite channels. Since these carbonyls can only be formed from very small Pt clusters, the presence of this band indicates a very high degree of dispersion. The bands between 2050-2000 cm⁻¹ were related to CO adsorbed on particles near the pore mouth. In contrast, when the catalyst contains Pt particles located outside the channels of the zeolite, a clear shoulder is evident at 2070 cm⁻¹.

As shown in Figure 3, after reduction at 500°C it was found that both of Pt/KL catalysts prepared by VPI and IWI have most of Pt particles inside the channel. However, a band at 1970 cm⁻¹ was clearly observed on the spectrum of the Pt/KL catalyst prepared by VPI (VPI-catalyst) while the band was less pronounced on the spectrum of the Pt/KL catalyst prepared by IWI

method (IWI-catalyst). This indicated that the VPI-catalyst had greater fraction of small Pt clusters located inside the zeolite channel than IWI-catalyst.

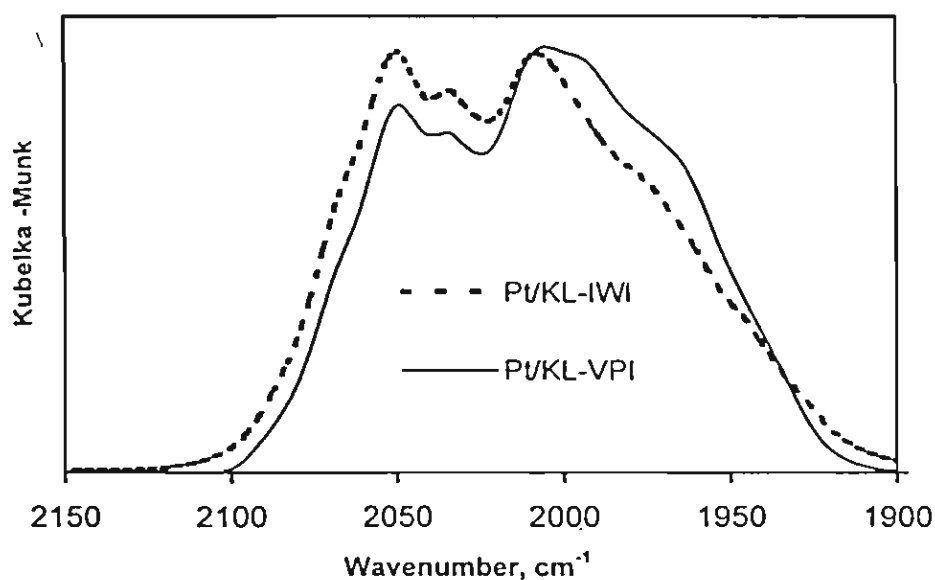


Figure 3 DRIFTS of CO adsorbed on Pt/KL-VPI and Pt/KL-IWI catalysts reduced in-situ at 500°C. The reduced catalysts were exposed to a flow of 3%CO in He for 30 min at room temperature and purged in He for 30 min.

2.3 TPO of Coke Deposit: The spent catalysts were determined coke deposits by using TPO technique. TPO profiles of coke formed in n-hexane and n-octane aromatization reactions of Pt/KL are shown in Figure 4. The results indicated much more coke deposit on Pt/KL spent with n-octane (Pt/KL-C8) when compare to Pt/KL spent with n-hexane (Pt/KL-C6). The substantial coke deposit could be the main cause of the poor activity of n-octane reaction. The TPO profile of coke from n-octane reaction is more pronounced at high temperature (500°C), which may be because of coke plugging in the zeolite pore leading to inhibition of Pt-catalyzed oxidation at low temperature.

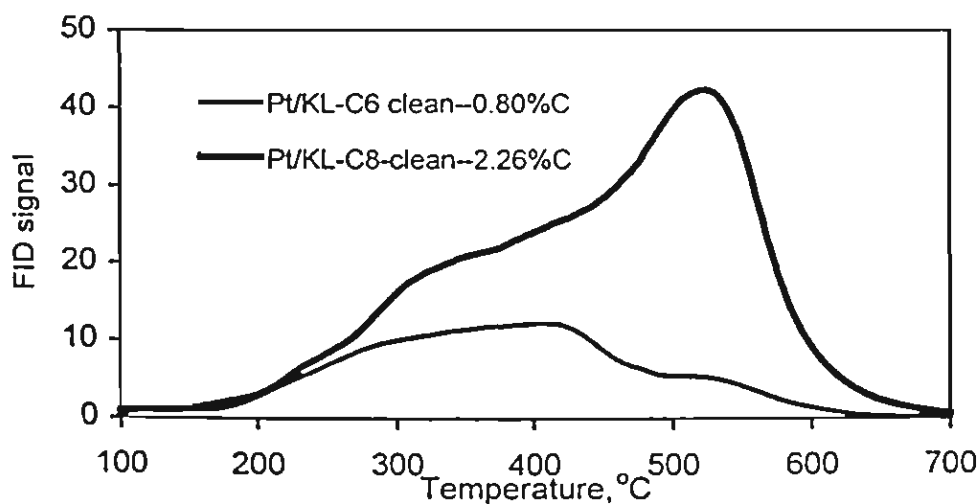


Figure 4 TPO profiles of coke formed during n-hexane and n-octane aromatizations over Pt/KL catalysts after 30 h on stream.

2.4 Kinetics of iso-Butane Sorption: To support the idea that the coke deposit during the reaction causes pore blocking of L-zeolite, the kinetics of iso-butane sorption was tested. The fraction approach to equilibrium of iso-butane sorption versus time of clean KL, Pt/KL-C6, and Pt/KL-C8 are illustrated in Figure 5. After emitting, iso-butane suddenly diffused into pore of zeolites with continuous decreasing in rate of diffusion. The curves showed the maximum adsorption of iso-butane in blank KL. The Pt/KL catalysts, especially the one spent with n-octane, exhibited lower iso-butane adsorption than the blank KL zeolite. The results can be inferred that the reaction over Pt/KL of n-octane leads to greater coke blocking than the reaction of

n-hexane. The slopes at initial adsorption can be determined the amount of iso-butane adsorbed and diffusive parameter (D/r_o^2) for each material as shown in Table 4.

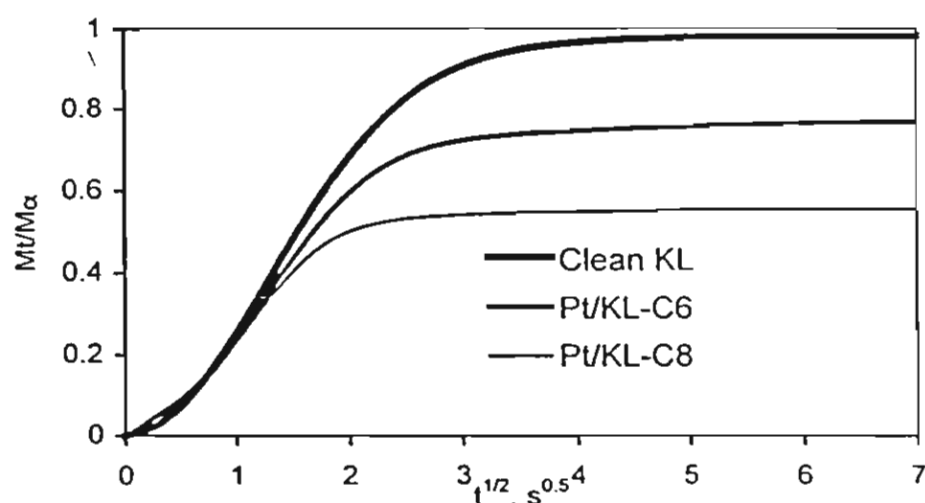


Figure 5 iso-Butane sorption isotherms in KL-zeolite and Pt/KL catalysts after reaction with n-hexane and n-octane feed. The adsorption was operated at 100°C.

The diffusivities were also calculated in terms of D/r_o^2 . It was observed that the clean KL showed the highest D/r_o^2 , while the Pt/KL-C6 represented an intermediate case close to Pt/KL-C8. Even though the Pt/KL-C8 showed higher coke formation and lower iso-butane sorption than those of Pt/KL-C6, the vicinity of D/r_o^2 indicated the same degree of coke covering in each pore.

Table 4 Diffusive parameters for iso-butane adsorption on KL zeolite and spent Pt/KL catalysts. The adsorption was operated at 100°C.

Catalyst	Iso-butane adsorption, mol/g.cat	$D/r_o^2, s^{-1}$
Calcined KL	4.63E-04	1.84E-03
Pt/KL-C6	3.21E-04	1.31E-03
Pt/KL-C8	1.64E-04	1.25E-03

Conclusions

Pt/KL exhibited higher conversion and aromatic selectivity than Pt/SiO₂ catalyst for both n-hexane and n-octane aromatization. For n-octane, the aromatic products from reaction over Pt/SiO₂ are ethylbenzene and o-xylene, which were predicted by a directly six-membered ring closure. On the other hand, the aromatic products gained over Pt/KL are mainly toluene and benzene which were derived from C8-aromatics. Among Pt/KL catalysts, the one prepared by VPI has higher Pt dispersion located inside the zeolite channel, resulting in higher conversion and selectivity than IWI-catalyst. When compared to n-hexane, n-octane aromatization over Pt/KL exhibited faster deactivation due to pore blockage of coke formation.

Acknowledgements

This work was supported by The Thailand Research Fund under the Royal Golden Jubilee Ph.D. project. Part of the experimental work was supported by the Oklahoma Center for the Advancement of Science and Technology (OCAST).

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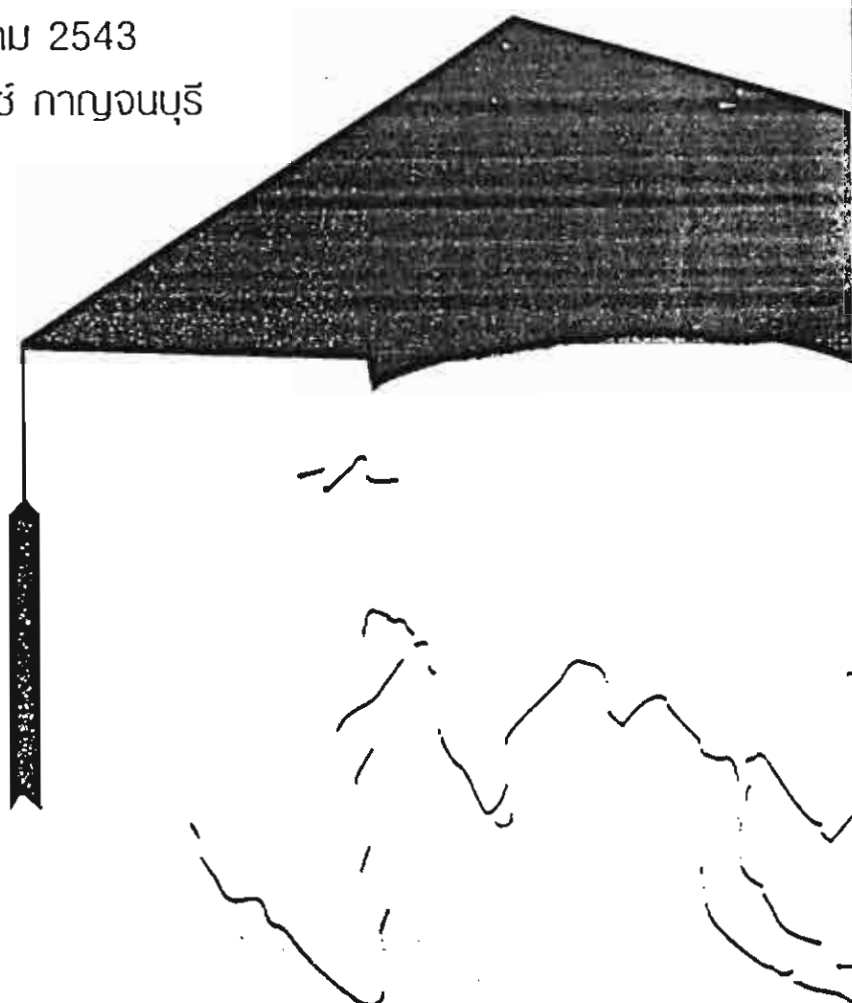
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S5-O4

Increased Sulfur Tolerance of Pt/KL Catalysts Containing Rare Earth Promoters for n-Hexane Aromatization

Siriporn Jongpatiwut^a, Banchong Lertrojanochoosit^a, Thitiporn Thongsrikate^a, Thirasak Rirksomboon^a, Somchai Osuwan^a and Daniel E. Resasco^b

^a The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

^b School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, Oklahoma, 73017, USA.

Objective

To increase sulfur tolerance of Pt/KL catalysts.

Methods

Different Pt/KL (platinum supported on the potassium form of zeolite L) and Pt/KL containing rare earth (RE) catalysts were prepared by two techniques, incipient wetness impregnation (IWI) and vapor phase impregnation (VPI). Two rare earth elements (Ce and Yb) were used. The catalysts prepared were tested for the activity and the selectivity of n-hexane aromatization to benzene. The effects of reaction temperature and weight hourly space velocity (WHSV) were also investigated. The future work is to study the effects of sulfur and water containing feed and catalyst regeneration on the catalyst prepared. Characterization by Fourier Transform Infrared spectroscopy (FTIR) will be accomplished to explain the quantity and morphology of platinum clusters inside the channels of the zeolite.

Results

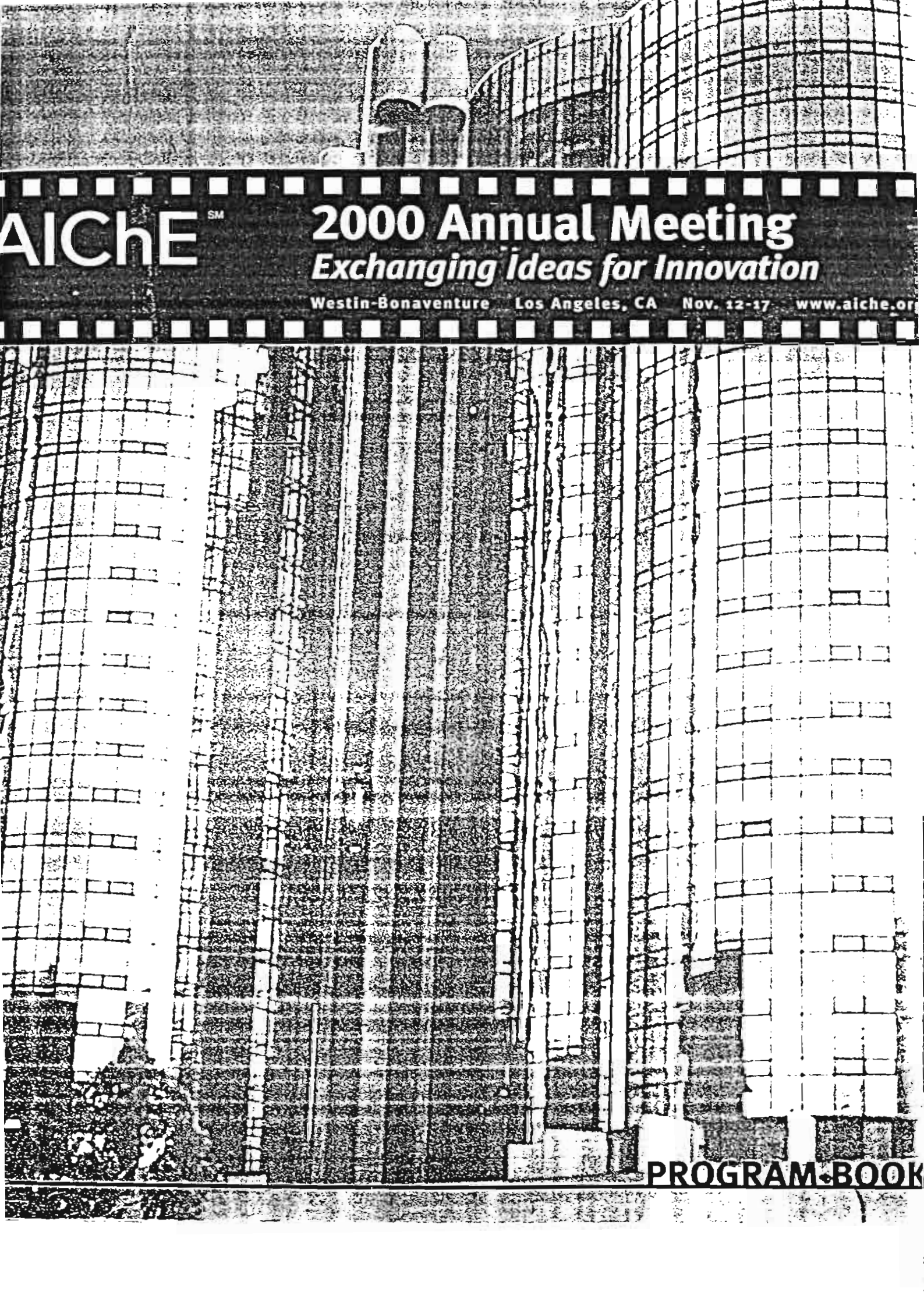
The catalysts prepared by VPI technique exhibited much higher activity and selectivity than those of IWI. The FTIR result of the VPI catalysts showed the majority of Pt particles were inside the zeolite pore. The selectivities of the VPI catalysts were fairly high at 400°C. By varying WHSV, the selectivities were still high even at very low conversion. It was found that under sulfur-free conditions, the promotion of rare earth showed a slight difference on the activity and selectivity of the reaction. The effect of sulfur containing feed will be further investigated.

Conclusion

This work showed that the morphology of Pt prepared by VPI technique could improve the performance of the catalyst. The VPI catalysts exhibited high selectivity even at low temperature or low conversion. The addition of rare earth promoters showed an insignificant effect on the activity of the reaction under sulfur-free conditions however it is expected to improve the activity of the Pt/KL catalysts under sulfur poisoned conditions.

Selected References

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PROGRAM BOOK

BP Amoco, Naperville, IL, Randall Q. Snurr, Harold H. Kung*, Northwestern University, Evanston, IL

Hydride Transfer in Alkylation of isobutane with n-butene over Molecular Sieves • 9:30:00 AM • paper 352e • Johannes A. Lercher*, Andreas Feller, Gautam Nivanthi, Stefan Gaab, Technical University of Munich, München, Germany

The Liquid-Phase Beckmann Rearrangement of Oxime over HBEA Catalyst: A Typical Case of Active Solvent Participation • 9:45:00 AM • paper 352f • Young-Min Chung, Hyun-Ku Rhee*, Seoul National University, Seoul, Korea

Reaction Pathways of the Coupling of Thiophene Desulfurization and Propane Dehydrogenation on Cation-Modified H-ZSM5 • 10:07:00 AM • paper 352g • Sara Y. Yu*, Wei Li, Enrique Iglesia, University of California, Berkeley, Berkeley, CA

Increased Sulfur Tolerance of Pt/KI Catalysts Containing Rare Earth Promoters for n-Hexane Aromatization • 10:22:00 AM • paper 352h • Banchong Lertrojanchosut, Thitiporn Thongsrikate, Siriporn Jongpatiwut*, Thirasak Rirksomboon, Somchai Osuwan, Petroleum and Petrochemical College, Bangkok, Thailand, Daniel E. Resasco, University of Oklahoma, Norman, OK

Study of Coking Behavior of Pt/H-Zeolite Catalysts using Cyclopentane Hydroconversion • 10:37:00 AM • paper 352i • Srikant Gopal*, Panagiotis Smirniotis, University of Cincinnati, Cincinnati, OH

Osmium Clusters in NaX Zeolite: Characterization by 129Xe NMR, EXAFS, and IR Spectroscopies • 10:52:00 AM • paper 352j • Bruce C. Gates, Bryan A. Enderle*, University of California, Davis, Davis, CA, Andrea Labouriau, Los Alamos National Laboratory, Los Alamos, NM

Integrating Adsorption Separation and Reaction on the Catalyst Level in Partial Oxidation Reactions in Titanium Zeolites • 11:07:00 AM • paper 352k • Gino V. Baron*, Gunther Langhendries, Werner Verdict, VUB, Brussel, Belgium, Dirk E. De Vos, Frederik Van Laar, Pierre A. Jacobs, KULeuven, Heverlee, Belgium

[353] Thursday, Nov. 16, 8:30 AM
Room: Concourse Ballroom Salon 1

CATALYTIC MEMBRANES AND MEMBRANE REACTORS

Theodore T. Tsotsis, *Chair*
University of Southern California
Los Angeles, CA
Shamsuddin Ilias, *Vice-Chair*
North Carolina A&T State University
Greensboro, NC

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Hydrogen Selective Ceramic Membranes: Application to the Transformation of

Greenhouse Gases • 8:30:00 AM • paper 353a • Ted S. Oyama*, Anil Prabhu, DooHwan Lee, Lixiong Zhang, Virginia Polytechnic Institute & State University, Blacksburg, VA

Pervaporation-Enhanced, Lipase Catalyzed Synthesis of Geranyl Acetate in n-Hexane • 8:50:00 AM • paper 353b • Karsten Bartling, Fachhochschule Giessen-Friedberg, Giessen, Germany, Peter Pfromm, Institute of Paper Science and Technology, Atlanta, GA, Peter Czerniak, Fachhochschule Giessen-Friedberg, Giessen, Germany, Mary E. Rezac*, Georgia Institute of Technology, Atlanta, GA

Coal Gas Reforming in a Palladium Membrane Reactor • 9:10:00 AM • paper 353c • Stephen N. Paglieri*, Stephen A. Birdsell, Los Alamos National Laboratory, Los Alamos, NM

Reaction and Transport in Catalytic Nanoporous Carbon Membranes • 9:30:00 AM • paper 353d • Michael S. Strano*, Henry C. Foley, University of Delaware, Newark, DE

Ceramic Membrane Reactor for Oxygen Separation and Conversion of Methane to Synthesis Gas • 9:50:00 AM • paper 353e • James T. Ritchie*, Dan Luss, M. D. Nersisyan, J. T. Richardson, University of Houston, Houston, TX

Methanol Oxidative Dehydrogenation in a Catalytic Packed-Bed Membrane Reactor: Selectivity to Formaldehyde and Membrane Effect on Reactor Stability • 10:10:00 AM • paper 353f • Arvind Varma, Notre Dame University, Notre Dame, IN, Victor E. Diakov*, David Lafarga, University of Notre Dame, Notre Dame, IN

The Effect of Surface Modifications of Perovskite Membranes for the Oxidative Coupling of Methane • 10:30:00 AM • paper 353g • William J. Thomson*, Matt Fountain, Washington State University, Pullman, WA

Design Criteria and Kinetic-Transport Models for Non-Oxidative Conversion of Methane with Continuous Removal of H₂ • 10:50:00 AM • paper 353h • Lin Li*, Richard W. Borry, Enrique Iglesia, University of California, Berkeley, Berkeley, CA

Water Gas Shift Kinetics under Membrane Reactor Conditions • 11:10:00 AM • paper 353i • Carl R. Lund*, Donghao Ma, SUNY-Buffalo, Buffalo, NY

[354] Thursday, Nov. 16, 8:30 AM
Room: Concourse Ballroom Salon 3

REACTIONS IN BENIGN SOLVENTS

Phillip E. Savage, *Chair*
University of Michigan
Ann Arbor, MI
Joan F. Brennecke, *Vice-Chair*
University of Notre Dame
Notre Dame, IN

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Polyglycol-Water Solutions as Benign Solvents • 8:30:00 AM • paper 354a • Neil F.

Leininger*, Donald J. Kirwan, John L. Gainer, University of Virginia, Charlottesville, VA

Activated Carbon from Macadamia Nut Shell by Air Oxidation in Boiling Water • 8:50:00 AM • paper 354b • Michael J. Antal*, Man S. Tam, University of Hawaii, Honolulu, HI

Acid Catalysis in High-Temperature Water: Kinetics and Mechanisms of Cyclohexanol Dehydration • 9:10:00 AM • paper 354c • Naoko Akiya*, Phillip E. Savage, University of Michigan, Ann Arbor, MI

Solvent Effects on Chemical Reactions in Nearcritical Water • 9:30:00 AM • paper 354d • Jie Lu*, James S. Brown, David Bush, Charles L. Liotta, Georgia Institute of Technology, Atlanta, GA, Charles A. Eckert, Georgia Institute of Technology, Atlanta, GA

Investigation of Catalytic Surface Mechanism during Hydroformylation in scCO₂ • 9:50:00 AM • paper 354e • Andrew R. Tadd*, Greg A. Snyder, Martin A. Abraham, University of Toledo, Toledo, OH

CO₂-Alcohol Systems for Novel in situ Acid Generation • 10:10:00 AM • paper 354f • Christy W. Culp*, Kevin N. West, Jonathan P. McCarney, Georgia Institute of Technology, Atlanta, GA, Kristen N. Griffith, Griffith, Atlanta, GA, Charles L. Liotta, David Bush, Georgia Institute of Technology, Atlanta, GA, Charles A. Eckert, Georgia Institute of Technology, Atlanta, GA

1-Butene/Isobutane Alkylation over unsupported and SiO₂-supported Nafion in Liquid and Supercritical Reaction Phases • 10:30:00 AM • paper 354g • Carmo Pereira, E.I. duPont de Nemours & Co., Wilmington, DE, Bala Subramaniam, Christopher J. Lyon*, University of Kansas, Lawrence, KS

Activity of Perfluoropolyether-Modified NAD(H) in Fluorous Solvents and Carbon Dioxide • 10:50:00 AM • paper 354h • Janice L. Panza*, Alan J. Russell, Eric J. Beckman, University of Pittsburgh, Pittsburgh, PA

Catalysis with Environmentally Benign Solvents at Elevated Temperature and Pressure • 11:10:00 AM • paper 354i • Kristen N. Griffith, Griffith, Atlanta, GA, James S. Brown*, Jason P. Hallett, Roger Glaser, Charles L. Liotta, Georgia Institute of Technology, Atlanta, GA, Charles A. Eckert, Georgia Institute of Technology, Atlanta, GA

[355] Thursday, Nov. 16, 2:00 PM
Room: Concourse Ballroom Salon 1

FUNDAMENTALS OF CARBON CATALYSIS

Fabio H. Ribeiro, *Chair*
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Worcester, MA
Raman Venkatesh, *Vice-Chair*
Calgon Carbon Corp
Pittsburgh, PA

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Carbon-Supported Pd and Cu Catalysts • 2:05:00 PM • paper 355a • Albert Vannice*, N. Krishnakutty, A. Dandekar, Pennsylvania State University, University Park, PA

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Final Program & Abstracts of Papers
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Saturday, March 3, 2001

11

PROMOTION OF PT/KL CATALYSTS WITH RARE EARTH OXIDES FOR THE AROMATIZATION OF C6 AND C8 FEEDS. **S. Jongpatiwut**, P. Sackamduang, T. Rirksomboon, S. Osuwan, W. E. Alvarez, D. E. Resasco, University of Oklahoma, 100 East Boyd St., Norman OK 73019, and PPC, Chulalongkorn University, Bangkok, Thailand

Pt/KL zeolites containing rare earth oxides (Ce and Yb) were prepared by vapor phase (VPI) and incipient wetness impregnation (IWI). The catalysts were tested for the activity and the selectivity of n-hexane and n-octane aromatization with clean and sulfur containing feeds. The differences between aromatization of C6 and C8 will be discussed. The VPI method resulted in much higher activity and selectivity than those prepared by IWI. The effects of promoters strongly varied according to the type of feed and the presence of sulfur. The addition of Ce had its maximum beneficial effect in the presence of sulfur with C6 feed, but not with C8 feeds. The loss of activity of the different samples by exposure to water has also been investigated by a detailed structural characterization with EXAFS and FTIR.

12

INNOVATIVE LABORATORY EXERCISES FOR THE INSTRUMENTAL ANALYSIS LABORATORY. **Thomas M. Harris**, Department of Chemistry and Biochemistry, University of Tulsa, 600 S. College Ave., Tulsa, OK 74104

Over the past decade the University of Tulsa has undertaken a major upgrade of the Instrumental Analysis Laboratory experience for its chemistry, biochemistry and chemical engineering majors. This upgrade has included the acquisition of analytical instrumentation and significant changes in the curriculum. With respect to the latter, it was desired to have each of the laboratory exercises involve "real world" samples. Each exercise also involves the use of more than one instrument to quantify the analyte, or some other means of ascertaining the quality of the data. At the present time the students perform five laboratory exercises, each two weeks in length. Details of each of these exercises will be presented.

