CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalytic Activity Measurements

The aim of this work was to study the addition of Sn for the n-octane aromatization. The aromatization of n-octane was conducted in a flow reactor at $500^{\circ}C$, constant H_2/n-octane molar ratio of 6 and at weight hour of space velocity (WHSV) of 5 h^{-1} over Pt-Sn/KL catalysts by varying Sn loading (at 0.3, 0.6 and 1.0wt%) and metal loading methods (coimpregnation and sequential impregnation). The list of catalysts prepared is shown in Table 4.1.

Table 4.1 The list of catalysts prepared

Catalyst	wt%Sn	wt%Pt	Metal Loading Methods
	Planned	Planed	
1Pt	-	1.00	Coimpregnation
1Sn	1.00	-	
0.3Sn1Pt	0.30	1.00	
0.6Sn1Pt	0.60	1.00	
1Sn1Pt	1.00	1.00	
4Sn1Pt	4.00	1.00	
0.3Sn1Pt	0.30	1.00	Sequential Impregnation (Sn before Pt)
0.6Sn1Pt	0.60	1.00	
1Sn1Pt	1.00	1.00	
1Pt0.3Sn	0.30	1.00	Sequential Impregnation (Pt before Sn)
1Pt0.6Sn	0.60	1.00	
1Pt1Sn	1.00	1.00	

4.1.1 n-Octane Aromatization

The catalysts with a different percentage of Sn loading and the methods of metals loading (sequential and coimpregnation methods) were tested for n-octane aromatization reaction and compared with Pt/KL and Sn/KL catalysts. The Pt-Sn/KL prepared by (a) coimpregnation of Pt and Sn; (b) sequential impregnation of KL catalyst, first by Sn, and then impregnation of Pt; (c) sequential impregnation, the same as (b) but in the reverse order. The activity was reported in terms of n-octane conversion, total aromatics selectivity, C8-aromatics selectivity, and EB/OX ratio.

4.1.1.1 n-Octane Conversion

The resultant evaluation of conversion is shown in Figure 4.1. As can be seen, the Pt-Sn/KL prepared by coimpregnation method show the improvement of activity on n-octane conversion. This value increases with the percentage of Sn loading. Interestingly, even 1Pt1Sn/KL gave a very high n-octane conversion but when the percentage of Sn loading was increasing from 1 to 4 it was observed that 1Pt4Sn/KL gave a very low n-octane conversion. This can refer that the large amount of added Sn (in this case 4wt%Sn loading) was tends to block or cover on active sites of Pt resulting in lower catalytic activity performance. Moreover, according to no catalytic activity from Sn/KL so it may confirm that Sn itself is catalytically <u>inactive</u>.

The metal loading methods were altered in order to investigate the effect of catalyst preparation. From the results it was observed that the metal loading via sequential impregnation method (first impregnation of Pt and then followed by Sn) gave similar behavior as obtained from coimpregnation which 1wt% Sn loading gave the highest n-octane conversion. But the results were differed in the case of reverse order (first impregnation of Sn and then followed by Pt)

The improving of activity in n-octane conversion over the Pt-Sn/KL can be explained by the ensemble effect. Because this effect occurred when Sn decreased the number of contiguous Pt atoms so multipoint adsorption of hydrocarbon molecules on the surface is hampered; thus hydrogenolysis and deactivation by coke formation can be reduced. This outcome is in agreement with

previous reports (Lee *et al.*, 1994). They conclude that the ensemble effect was an important parameter for catalytic activity in n-octane conversion.
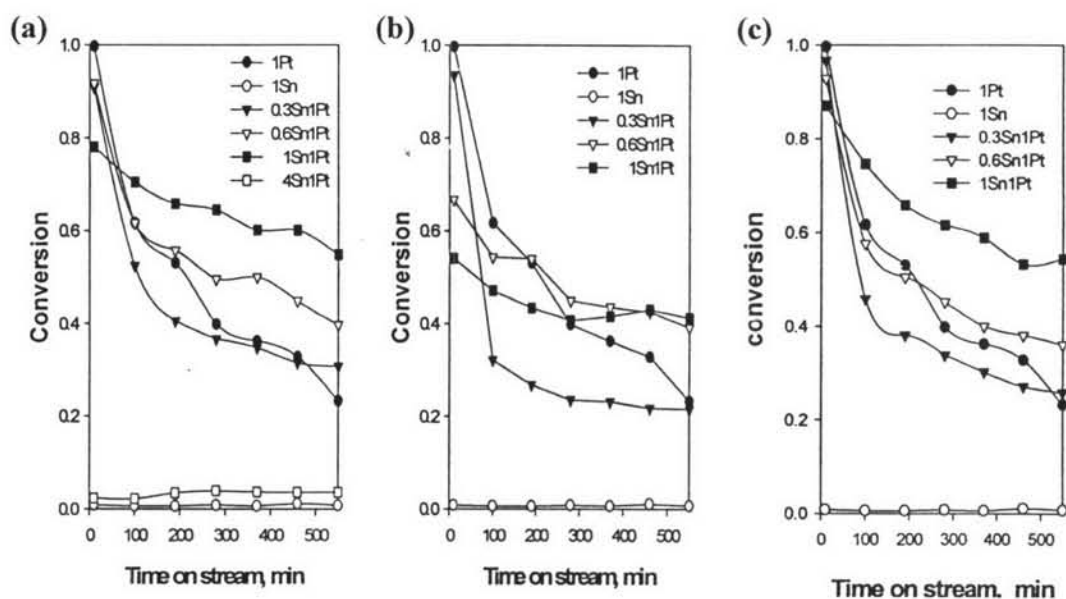

Figure 4.1 n-Octane conversion as a function of time on stream over Pt-Sn/KL catalysts prepared by (a) coimpregnation of Pt and Sn; (b) sequential impregnation of KL catalyst (Sn before Pt),and (c) sequential impregnation (Pt before Sn).

4.1.1.2 Total Aromatics Selectivity

Figure 4.2 illustrates the total aromatics selectivity as a function of time on stream over Pt/KL, Sn/KL, and Pt-Sn/KL catalysts. It was observed that, at the first 10 min of time on stream, Pt-Sn/KL (except 1Pt4Sn/KL) prepared by coimpregnation gave a higher total aromatics selectivity when compared with Pt/KL catalyst. 1wt% Sn loading gave the highest total aromatics selectivity when compared with the other amounts of Sn loading.

For the sequential impregnation (Pt before Sn) method, it gave a similar behavior when compared with Pt/KL. And, also 1wt% Sn loading gave the highest total aromatics selectivity. However 1wt%Sn loading by sequential impregnation (Sn before Pt) gave lower catalytic activity when compared with the

other metal loading methods. This might be because the added Sn may block or cover active sites for Pt on the KL zeolite resulting in lowering its catalytic activity.

The improving of total aromatics selectivity in the aromatization reaction over the Pt-Sn/KL can be explained by the effect of Sn. This effect Sn atoms divide the surface into smaller number of contiguous Pt atoms and that this arrangement brings about the beneficial effect on the selectivity of the catalysts (ensemble effect).
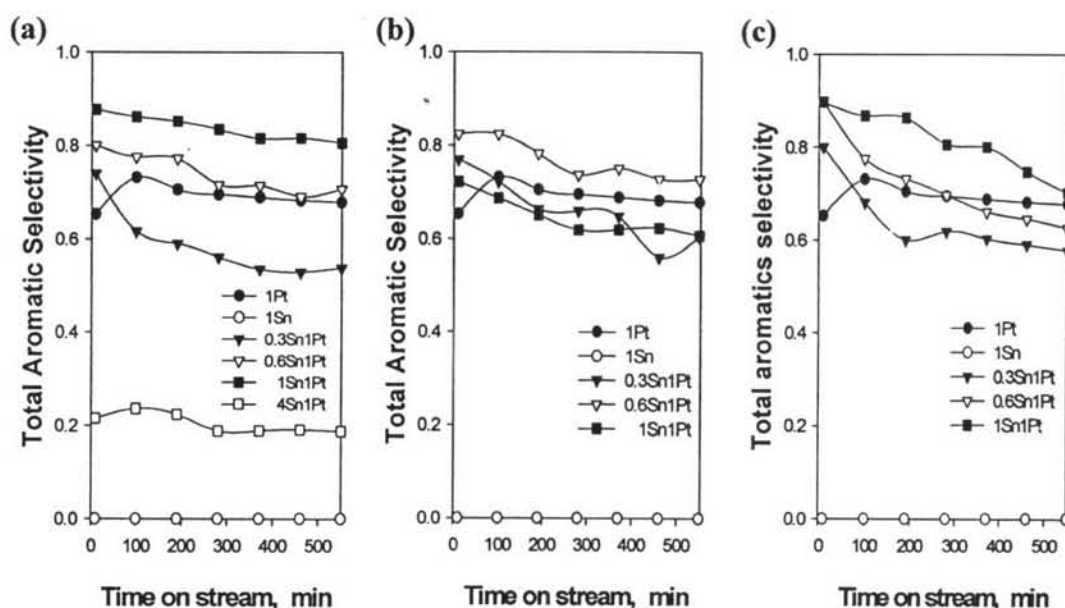

Figure 4.2 Total aromatics selectivity as a function of time on stream over Pt-Sn/KL catalysts prepared by (a) coimpregnation of Pt and Sn; (b) Pt-Sn/KL prepared by sequential impregnation of KL catalyst (Sn before Pt),and (c) sequential impregnation (Pt before Sn).

In terms of reaction products, as shown in Table 4.2, the distribution of products from all the catalysts after 550 min on stream showed that benzene and toluene instead of ethylbenzene (EB) and o-xylene (OX) as a result of direct closure of six-membered ring was found to be major aromatic compounds for Pt/KL. By the contrast, EB and OX was found to be the dominant products among the other aromatic compounds for Pt-Sn/KL (at 0.6 and 1% Sn loading). In our previous work, we observed that the hydrogenolysis become a factor to C8-

aromatics produced inside the zeolite is converted to benzene and toluene so from this result in inferred that Sn was helps to reduced the hydrogenolysis which occurred during the aromatization reaction.

Table 4.2 Product distribution over the catalysts studied at 550 min time on stream under reaction conditions 500°C, H_2/n-Octane 6:1 and WHSV 5 h^{-1}

Metal loading methods		Catalyst label*	Products Selectivity (%)						
			C1-C5	Hexene and Octene	Benzene	Toluene	Ethyl-benzene	m- and p-Xylene	o-Xylene
Coimpragnation	Pt or Sn	1Pt	19.72	12.40	19.05	27.59	13.95	1.82	5.47
		1Sn	49.38	50.62	0.00	0.00	0.00	0.00	0.00
	Pt with Sn	0.3Sn1Pt	14.25	32.00	9.10	21.95	12.84	0.00	9.85
		0.6Sn1Pt	6.42	31.09	3.76	14.84	19.32	1.31	23.25
		1Sn1Pt	1.66	34.96	0.23	7.82	21.34	0.00	33.98
Sequential Impregnation	Sn before Pt	0.3Sn1Pt	13.75	25.96	13.00	28.43	12.00	0.00	6.86
		0.6Sn1Pt	4.02	23.24	1.52	11.19	23.28	0.00	36.76
		1Sn1Pt	2.78	36.51	0.39	11.46	21.74	1.34	25.79
	Pt before Sn	1Pt0.3Sn	42.98	21.12	6.91	15.83	6.95	0.00	6.21
		1Pt0.6Sn	26.92	28.68	4.04	15.58	10.51	0.90	13.37
		1Pt1Sn	6.61	25.71	0.69	8.47	24.31	0.37	33.82

* The numerical figures before symbols represent the amount of metal added by weight percent, e.g. 0.3Sn1Pt indicates 0.3wt% Sn with 1wt% Pt incorporated in KL zeolite catalyst.

4.1.1.3 C1-C2 Selectivity

The formation of C1 and C2 by all the catalysts can be used for a measure of the activity in hydrogenolysis for the metallic function of the catalyst. It should be noted that the lower C1-C2 selectivity, the lower hydrogenolysis is, thus providing a higher value for C8-aromatics selectivity. And from the results their values were low for Pt-Sn/KL and very high for Pt/KL catalyst.
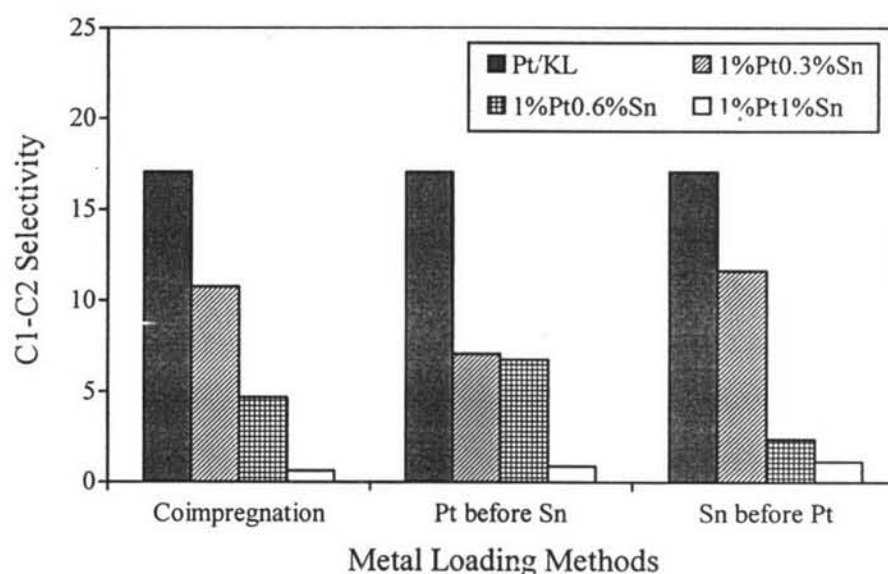

Figure 4.3 C1-C2 selectivity by Pt/KL and Pt-Sn/KL catalysts at various a metal loading methods.

4.1.1.4 C8-Aromatics Selectivity

Figure 4.4 shows the plot of C8-aromatics selectivity versus time on stream obtained on the different catalysts. Since the Pt-Sn/KL did not favor the secondary hydrogenolysis of C8-aromatics, resulting in higher C8-aromatics selectivity within a series of catalysts investigated. 1wt% Sn loading which prepared by coimpregnation and sequential impregnation (Pt before Sn) gave the highest C8-aromatics selectivity when compared with other amounts of Sn loading. The detailed product distribution analysis showed that EB and OX were the dominant products among the C8-aromatics for all the Pt-Sn/KL catalysts (at 0.6 and 1% Sn loading). Among the Pt/KL and Sn/KL resulted in lower C8-aromatics than Pt-Sn/KL.
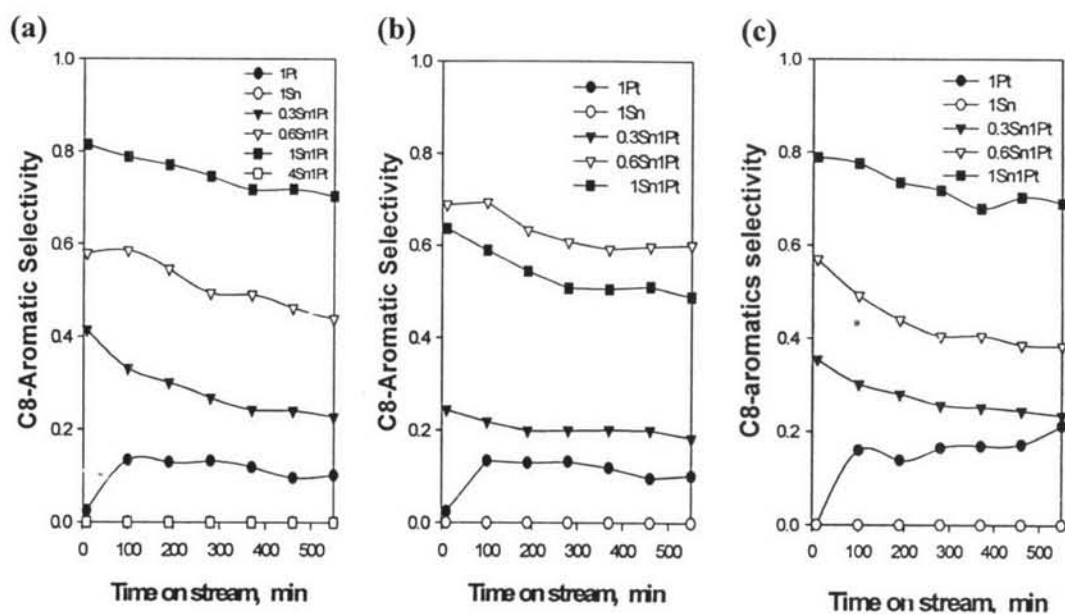
Figure 4.4 C8-aromatics selectivity as a function of time on stream over Pt-Sn/KL catalysts prepared by (a) coimpregnation of Pt and Sn; (b) sequential impregnation of KL catalyst (Sn before Pt),and (c) sequential impregnation (Pt before Sn).

4.1.1.5 EB/OX ratio

In our previous study, we put forward a method of using the EB/OX ratio as an indication of mass transfer limitations inside the channels of the zeolite. As shown in Figure 4.5, the EB/OX ratio obtained from C8 feed over the Pt/KL catalyst not only is greater than one on Pt-Sn/KL (at 0.6 and 1wt% Sn loading) but it also increases as a function of time on stream. This increase may be due to an enhancement of the diffusional limitations inside the zeolite channel as coke gradually restricts the molecular transport, making it increasingly difficult for OX to leave. Very similar increases in the EB/OX ratio as function of time on stream were observed for Pt-Sn/KL catalyst at 0.3wt% Sn loading (either prepared by coimpregnation or sequential impregnation). From this result it may be replied that Sn reduced the diffusional limitations inside the zeolite channels resulted from the coke formation during the aromatization (ensemble effect). Since the catalysts had lower coke formation, C8-aromatics produced inside the zeolite diffuse out of the

system with much easier than benzene so it makes shorter resident time of OX inside the pore, and difficult to be hydrogenolyzed and lead to lower EB/OX ratio.
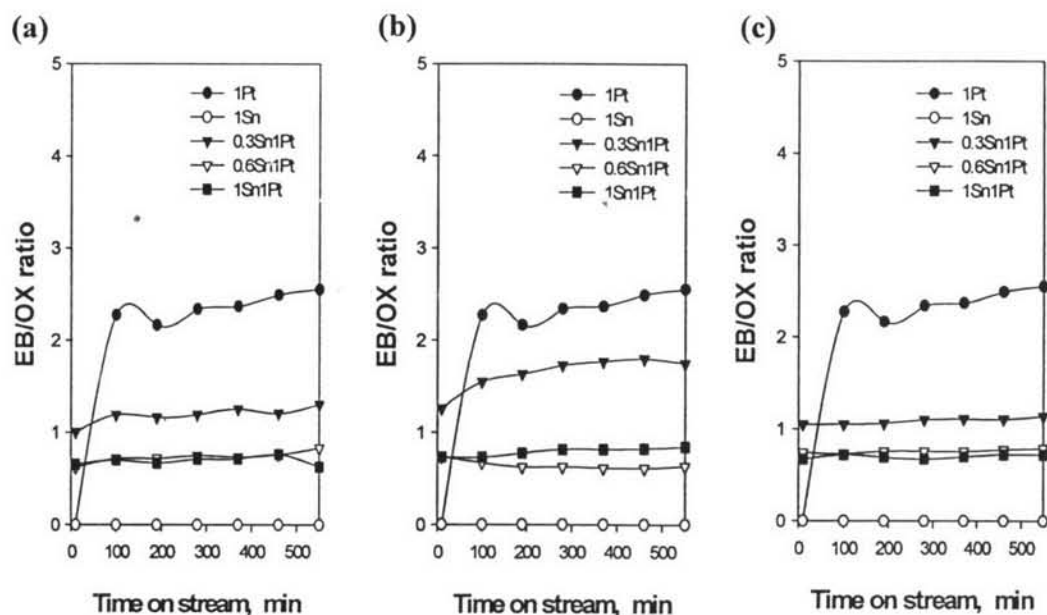

Figure 4.5 EB/OX ratio as a function of time on stream over Pt-Sn/KL catalysts prepared by (a) coimpregnation of Pt and Sn; (b) sequential impregnation of KL catalyst (Sn before Pt),and (c) sequential impregnation (Pt before Sn).

4.1.2 Catalyst Characterization

Fresh and spent samples were characterized by Atomic Adsorption Spectrometer (AAS), Fourier Transform Infrared Spectroscopy (FT-IR) with DRIFT of adsorbed CO, Hydrogen Chemisorption, Temperature Programmed Reduction (TPR), Temperature Programmed Oxidation (TPO), and Transmission Electron Microscopy (TEM).

4.1.2.1 Atomic Adsorption Spectrometer (AAS)

After KL zeolite were impregnated by Platinum (II) acetylacetonate and Tin (IV) bis(acetylacetonate) dichloride, the metal content of catalyst was determined by Atomic Adsorption Spectrometer (AAS). The results

were shown in Table 4.3 by comparing the theoretical results with the experimental results.

Table 4.3 AAS results of number of metals loading after impregnation

Catalyst	wt%Sn		wt%Pt		Metal Loading Methods
	Planned	Actual	Planned	Actual	
1Pt	-	-	1.00	1.04	Coimpregnation
1Sn	1.00	0.98	-	-	
0.3Sn1Pt	0.30	0.20	1.00	1.04	
0.6Sn1Pt	0.60	0.49	1.00	1.04	
1Sn1Pt	1.00	0.89	1.00	1.10	
4Sn1Pt	4.00	3.77	1.00	1.14	
0.3Sn1Pt	0.30	0.20	1.00	0.85	Sequential Impregnation (Sn before Pt)
0.6Sn1Pt	0.60	0.45	1.00	1.04	
1Sn1Pt	1.00	0.83	1.00	1.24	
1Pt0.3Sn	0.30	0.25	1.00	1.04	Sequential Impregnation (Pt before Sn)
1Pt0.6Sn	0.60	0.49	1.00	1.09	
1Pt1Sn	1.00	0.79	1.00	1.20	

From Table 4.3, the impregnate level of Pt and Sn were closed to the theoretical numbers. As we can see from the impregnate level of Pt it close to unity and also show the same trends in the impregnate level of Sn, which inferred to successful impregnation step.

4.1.2.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of Adsorbed CO

FTIR of adsorbed CO has been widely used to characterize Pt/KL catalysts. In most FTIR measurements of CO adsorption on Pt/KL a series of the band between 2080 and 1950 cm^{-1} have been observed. The bands of low wavenumber below 2075 cm^{-1} are related to the Pt clusters located inside the channels of the L zeolite while the bands at and above 2075 cm^{-1} are due to Pt external to the pores (Jacobs et al., 1999 and 2001). Corresponding to Zheng et al. (1996) work, CO species which adsorb on small Pt cluster presented in linear form

and appeared at 1900-2150 cm^{-1}. The spectra of Pt/KL and Pt-Sn/KL, which prepared by coimpregnation and sequential impregnation (Pt before Sn), are shown in Figure 4.6 and 4.7, respectively. These results inferred that all catalysts (prepared by both methods) gave a similar shape of spectra having a small metal clusters. From these results also indicating internal external and pore mouth location of Pt clusters.
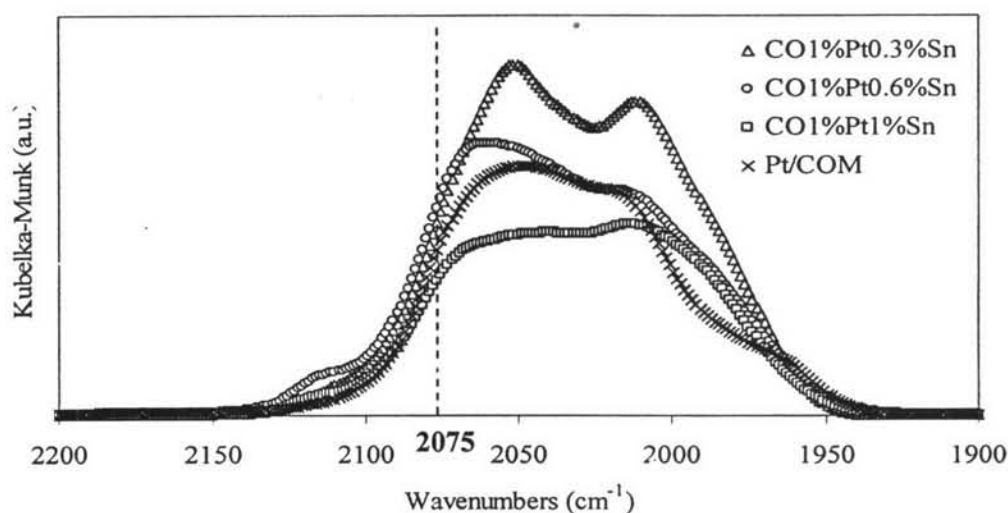

Figure 4.6 DRIFT spectra of CO adsorbed on Pt-Sn/KL catalysts, at 0.3, 0.6 and 1% Sn loading synthesized by coimpregnation method.
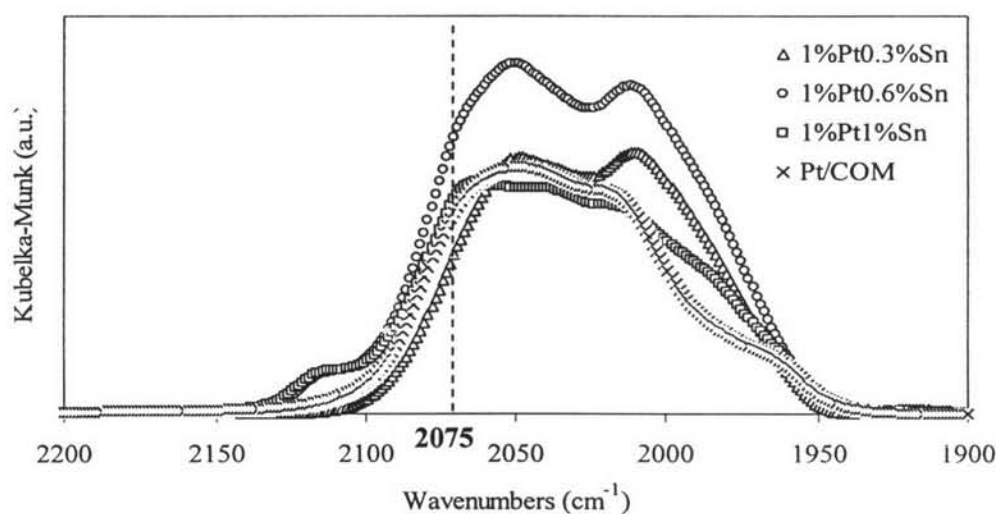
Figure 4.7 DRIFT spectra of CO adsorbed on Pt-Sn/KL catalysts, at 0.3, 0.6 and 1% Sn loading synthesized by sequential impregnation (Pt before Sn) method.

4.1.2.3 Transmission Electron Microscopy (TEM) Analysis

According to the catalytic activity measurements we observed that the 1Pt1Sn/KL catalyst which prepared by coimpregnation method showed the highest catalytic performance when compared with the others so we used the transmission electron microscopy (TEM) analysis to investigated the metal dispersions, morphology ,and location of the metal clusters on the catalyst. Also, the mono- or bimetallic nature of the metal particles was confirmed by energy dispersive X-ray (EDX) analysis. From TEM studied of the 1Pt1Sn/KL catalysts (coimpregnation) showed the presence highly dispersed PtSn particles (10 nm size) inside the channel of KL zeolite and the some of them located in the surface region of catalyst (Figure 4.8). This outcome is in agreement with the results from the FTIR of adsorbed CO. From the results shown that the 1Pt1Sn/KL catalysts (coimpregnation) gave a shape of spectra having a small metal clusters and most of them located inside the channel. In Figure 4.9 representative EDX analyses of individual Pt and PtSn particles are shown.
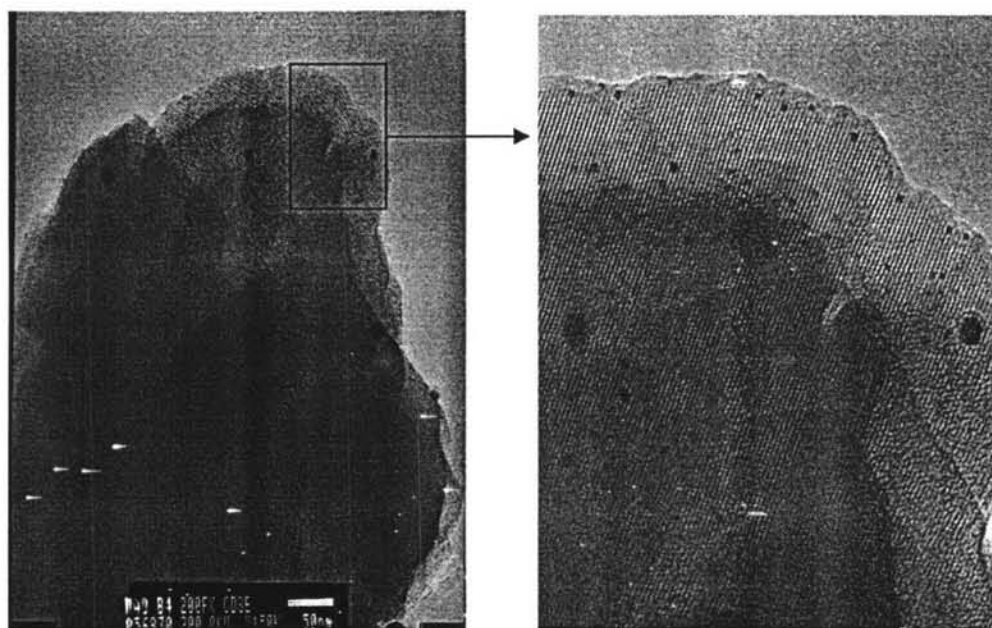

Figure 4.8 Bright field TEM image of 1Pt1Sn/KL catalyst. PtSn particle is present.
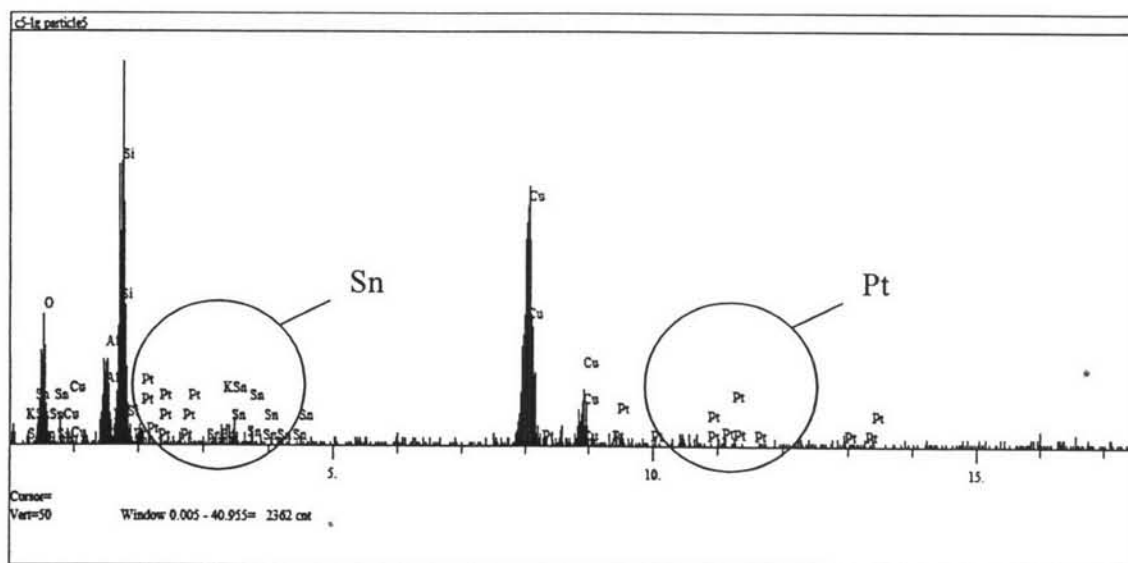
Figure 4.9 EDX pattern of representative PtSn particles of the 1Pt1Sn/KL catalyst which prepared by coimpregnation method.

4.1.2.4 Temperature Programmed Reduction (TPR)

Temperature Programmed Reduction was performed to determines the number of reducible species present in the catalyst and reveals the temperature at which the reduction occurs.

The TPR profiles of spent Pt/KL and Pt-Sn/KL, at 0.3, 0.6 and 1wt% Sn loading catalyst by varying metal loading methods, are shown in Figures 4.10 – 4.12. Pt/KL shows a peak centered at about 230°C attributed to the reduction of surface oxychlorated platinum species (Garetto et $al.$, 1995), and another peak centered at about 510 °C ascribed to platinum species in strong interaction with the support to Pt/KL species. Pt-Sn/KL at 0.3 and 0.6 wt% Sn loading which prepared by coimpregnation and sequential impregnation presents two peaks, the first at 250°C can be attributed to the reduction of platinum oxide and of some Sn oxide in its vicinity or previously alloyed, and another peak around 500°C corresponding to Sn oxide reduction (Stagg et $a.l$, 1996). It can be observed a shift it in the platinum reduction peak form 230 to 250 °C that can be assigned to a Pt-Sn interaction. For Pt-Sn/KL catalyst at 1% Sn loading which prepared by coimpregnation and sequential impregnation (Pt before Sn) methods gave only one reduction peak around 280°C, but

for 1Pt1Sn/KL catalyst which prepared by sequential impregnation (Sn before Pt) method presents two peaks, the first at 300 °C and another peak around 425 °C. From these results, it gave an evidence of the formation of Pt-Sn alloy in the 1Pt1Sn/KL catalysts which prepared by coimpregnation and sequential impregnation (Pt before Sn) methods.
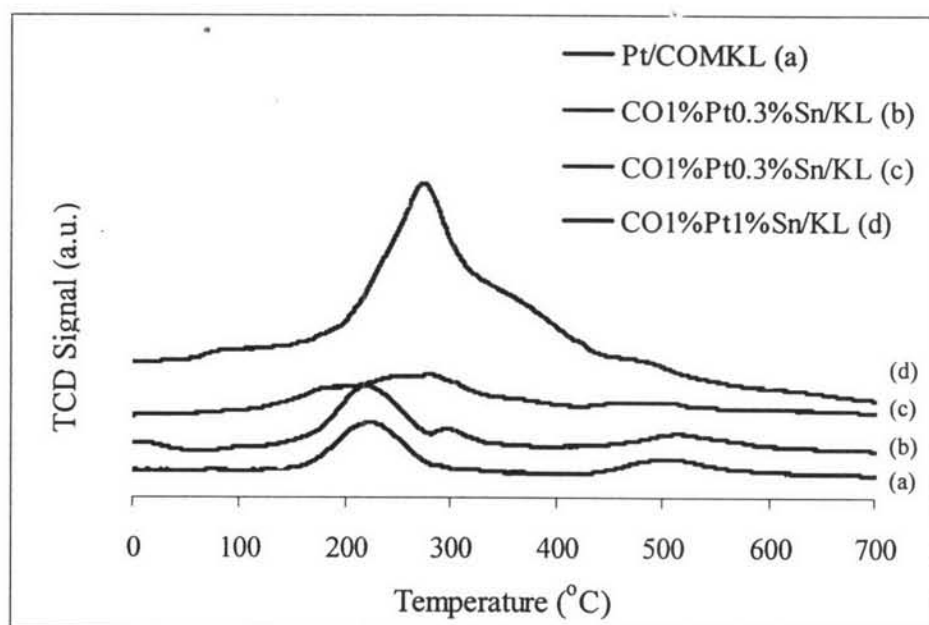

Figure 4.10 TPR profiles for the Pt-Sn/KL catalysts, at 0.3, 0.6 and 1% Sn loading synthesized by coimpregnation method, compared with the Pt/KL catalyst.
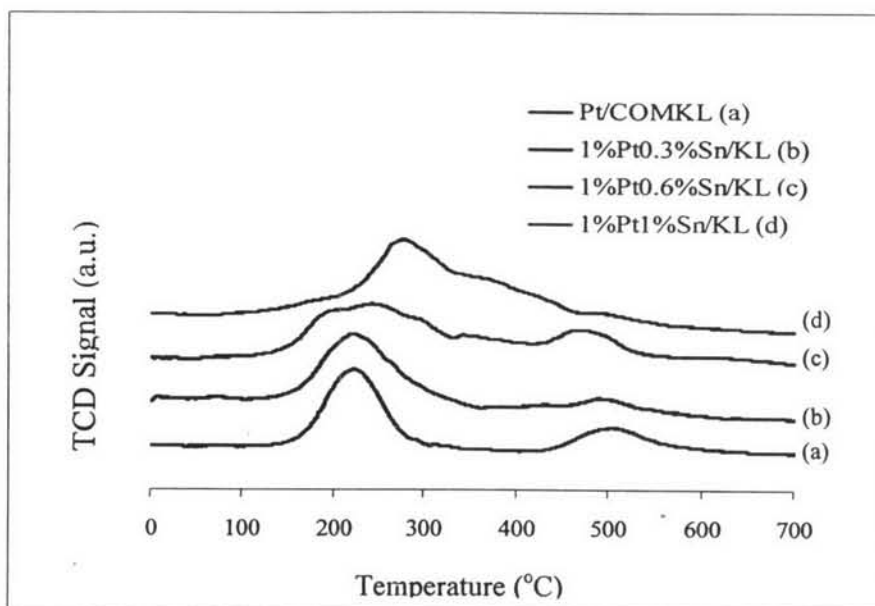
Figure 4.11 TPR profiles for the Pt-Sn/KL catalysts, at 0.3, 0.6 and 1% Sn loading synthesized by sequential impregnation method, first by Pt then impregnation of Sn, compared with the Pt/KL catalyst.
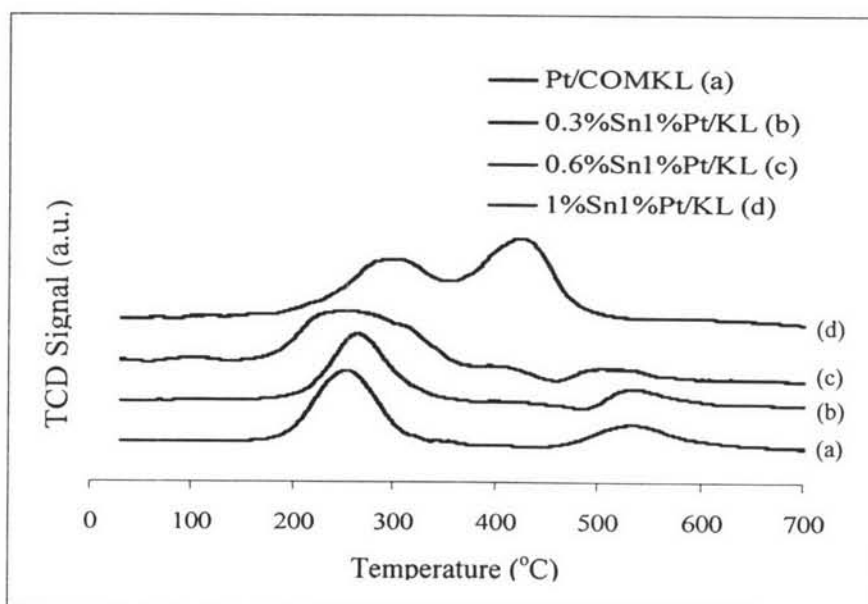

Figure 4.12 TPR profiles for the Pt-Sn/KL catalysts, at 0.3 ,0.6 and 1% Sn loading synthesized by sequential impregnation method, first by Sn then impregnation of Pt, compared with the Pt/KL catalyst.

4.1.2.5 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation was performed to investigate amount of coke formation that occurred in each catalyst after 550 min on stream for n-octane aromatization.

The TPO profiles of spent Pt/KL and Pt-Sn/KL, at 0.3, 0.6 and 1% Sn loading catalyst by varying metal loading methods, are shown in Figures 4.13 – 4.15. The spent Pt-Sn/KL catalysts showed a dominant peak at lower temperatures (425-450°C) when compared with the Pt/KL catalysts which showed a dominant peak at 465°C. It was indicated that coke which formed on Pt-Sn/KL was easily to oxidized than that on Pt/KL. Furthermore, it was found that the amount of coke deposit on Pt-Sn/KL (first, Sn then impregnation of Pt) was smaller than Pt-Sn/KL which prepared by coimpregnation and sequential impregnation (first, Pt then impregnation of Sn). These results can be implied that the first catalyst preparation method had the higher stability to coke formation when compared with the other methods.
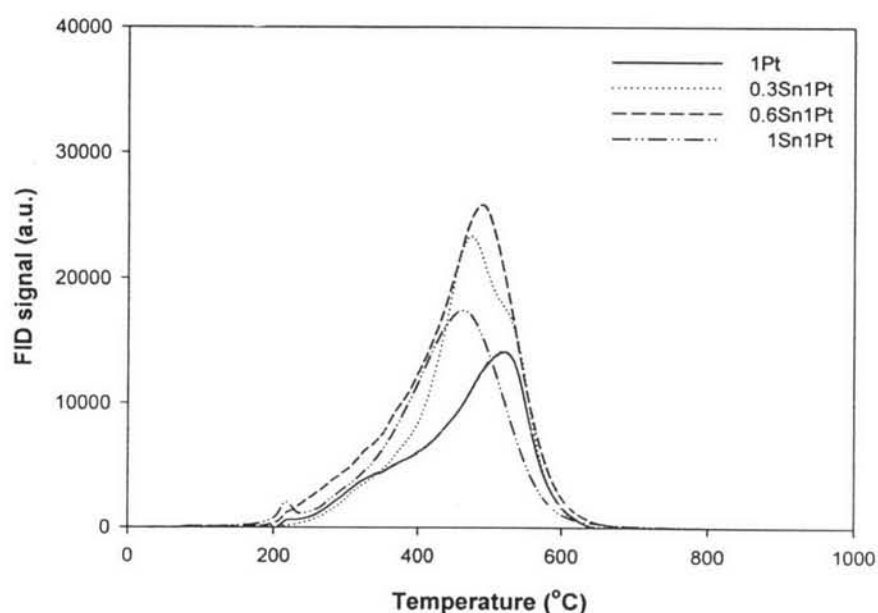

Figure 4.13 TPO profiles for the Pt-Sn/KL catalysts, at 0.3, 0.6 and 1% Sn loading synthesized by coimpregnation method, compared with the Pt/KL catalyst after spent on n-octane aromatization for 550 min on stream.
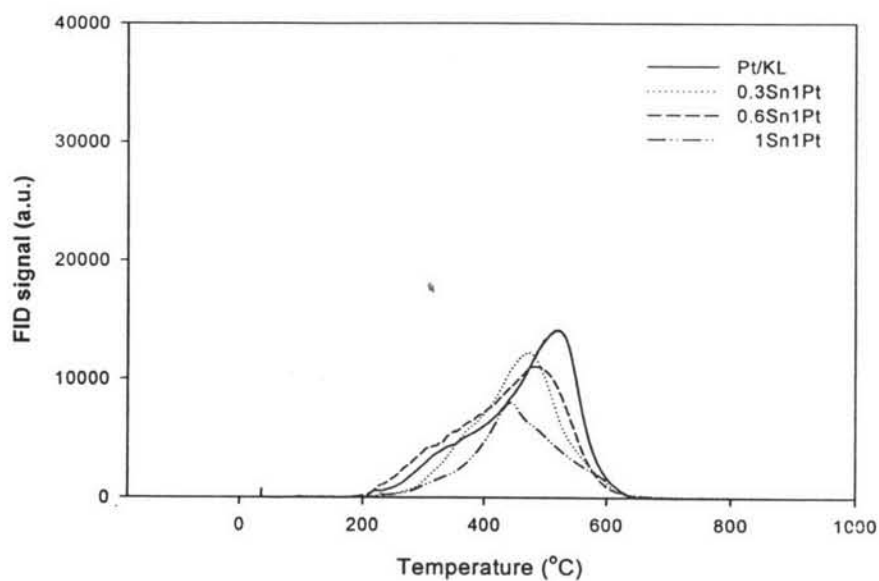
Figure 4.14 TPO profiles for the Pt-Sn/KL catalysts, at 0.3 ,0.6 and 1% Sn loading synthesized by sequential impregnation method, first by Sn then impregnation of Pt, after spent on n-octane aromatization for 550 min on stream.
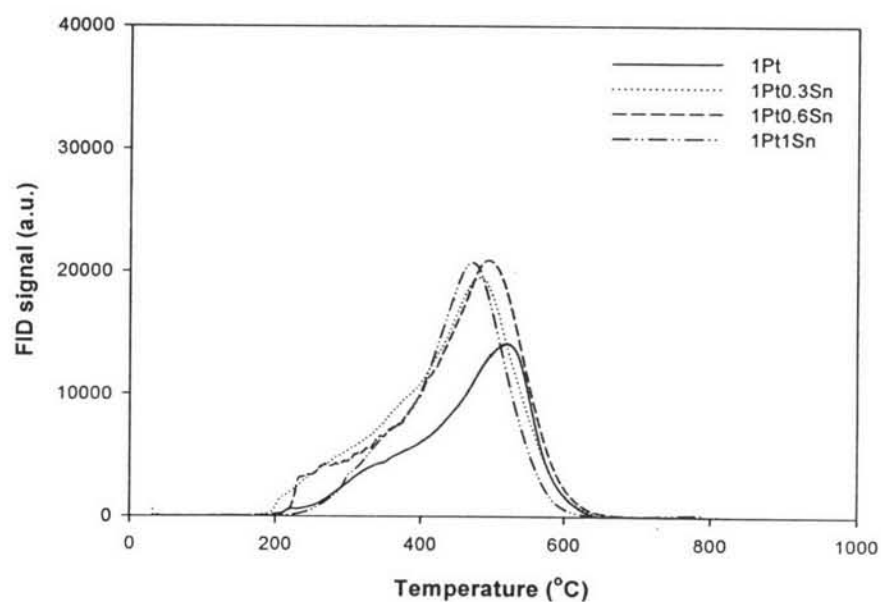

Figure 4.15 TPO profiles for the Pt-Sn/KL catalysts, at 0.3, 0.6 and 1% Sn loading synthesized by sequential impregnation method, first by Pt then impregnation of Sn, after spent on n-octane aromatization for 550 min on stream.