

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Cyclic Regeneration

4.1.1 Butane Conversion and Coke Burning

Catalysts D₁, D₃ and D₅, having different Sn/Pt weight ratios, were operated in the repetitive reaction-regeneration procedure. The catalyst was left in the reactor for 8 hours during the reaction step. Then it was regenerated for an hour by flowing 1 vol% O₂ to burn off the coke deposits. This procedure occurred *in-situ* in the catalyst bed and continued for 8 cycles of operations. The butane conversion profile for every cycle is shown in Figure 4.1.

The catalyst D₅ gives the highest butane conversion in all reaction cycles, both for initial and steady state conversions. The catalyst D₃ has lower reaction conversion and the catalyst D₁ has the lowest reaction conversion, respectively. The difference in butane conversion of these catalysts can be described by the amount of active metal (Pt) sites. The increase in Sn/Pt weight ratio leads to an increase in the numbers of active sites (Charuratana, 1996). In addition, Burch et al., 1981 also found that when tin is present, the dispersion of Pt is increased. Therefore, the higher Sn/Pt weight ratio gives the higher reaction conversion.

Figures 4.2 to 4.5 show the catalyst selectivity profile during the reaction cycles of 1-butene, trans-2-butene, cis-2-butene, and 1,3-butadiene, respectively. The catalyst D₅ gives the highest selectivity in all reaction cycles, both for initial and steady state selectivity of all products. The catalyst D₃ has lower and the catalyst D₁ has the lowest, respectively. The catalyst D₅ and D₃

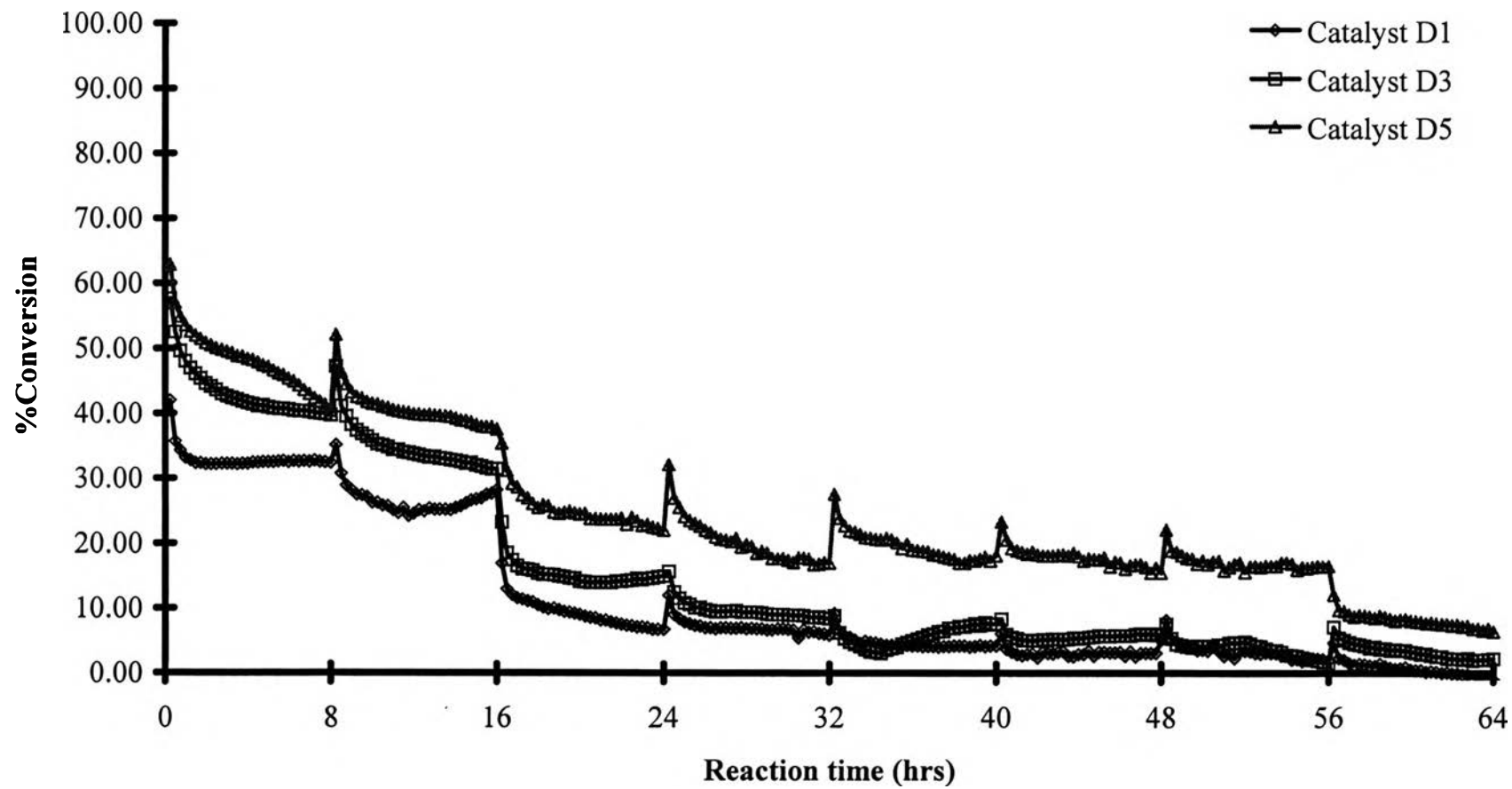


Figure 4.1 The conversion of butane for the cycle run.

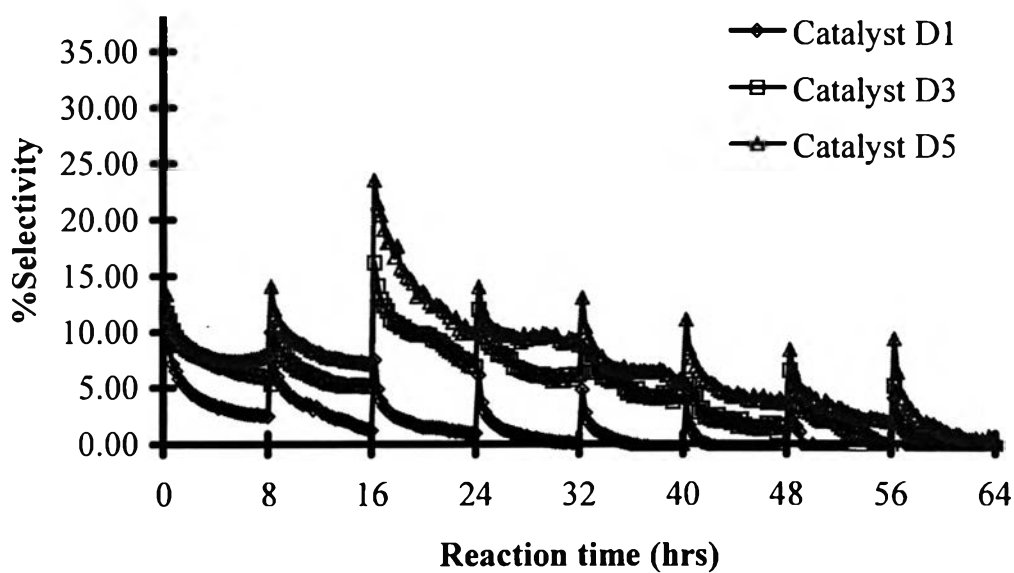


Figure 4.2 The selectivity to 1-butene for the cycle run.

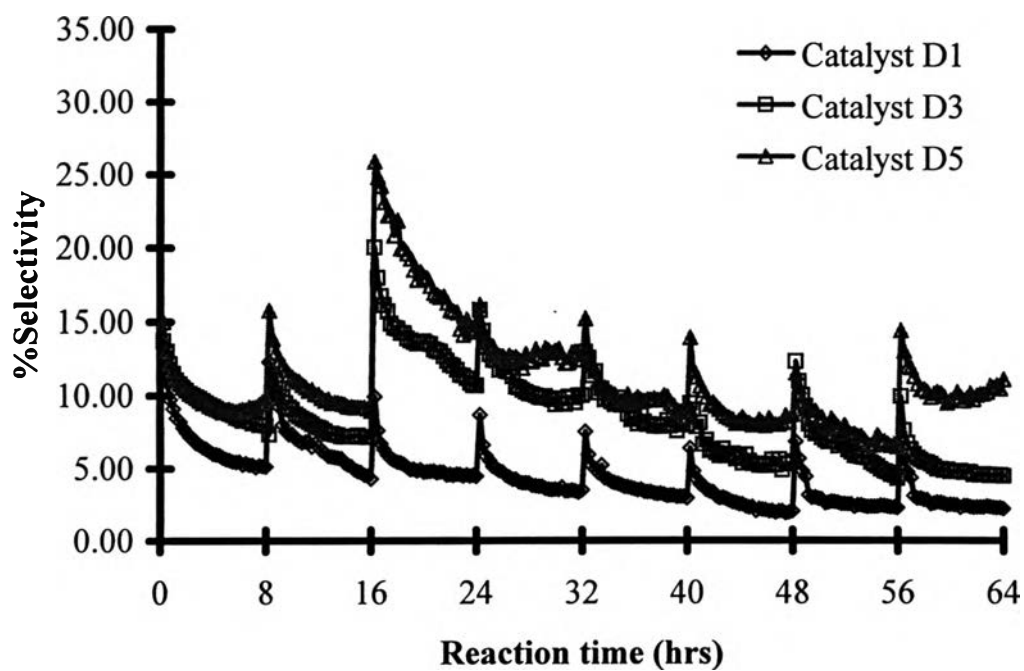


Figure 4.3 The selectivity to trans-2-butene for the cycle run.

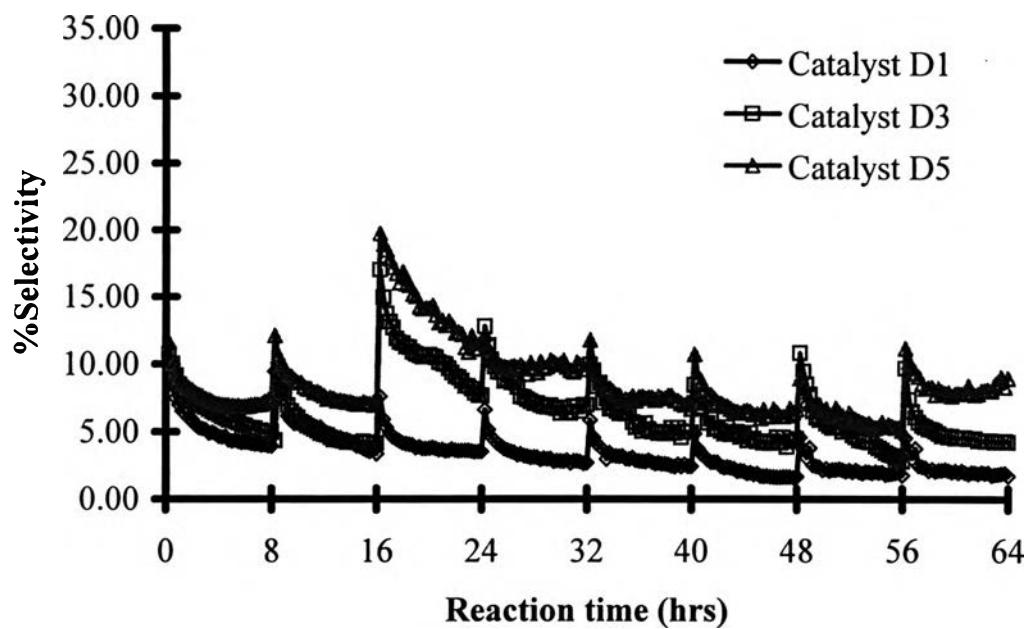


Figure 4.4 The selectivity to cis-2-butene for the cycle run.

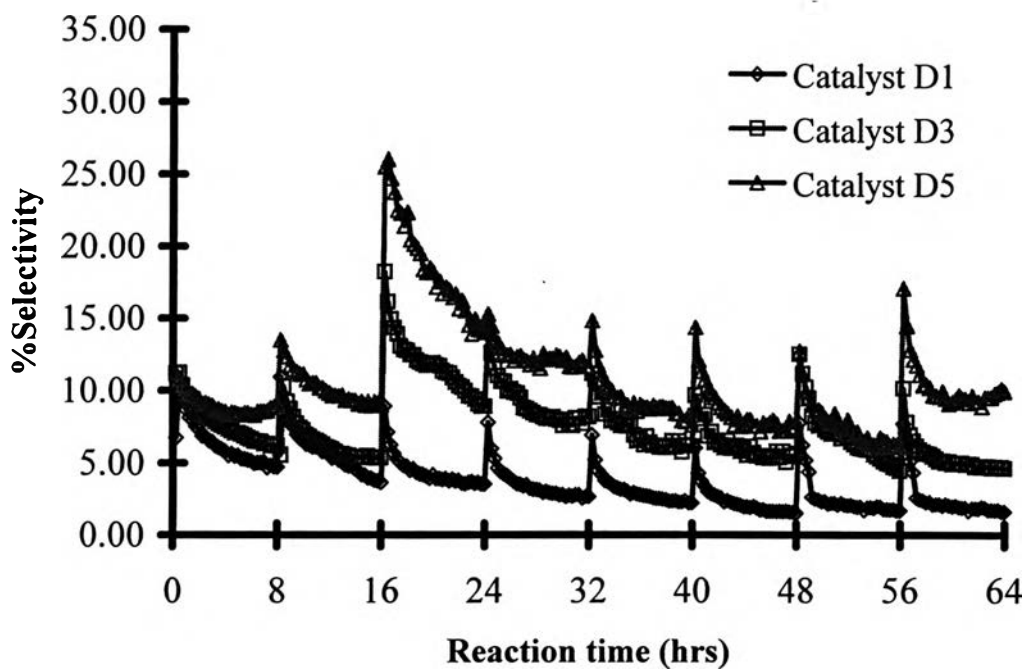


Figure 4.5 The selectivity to 1,3-butadiene for the cycle run.

show a decrease in the selectivity of all products from the third reaction cycle through the last reaction cycle while the catalyst D₁ shows a decrease from the first reaction cycle through the last reaction cycle. These results correspond to the conversion results for the same reason. An increase in selectivity of all products in the third reaction cycle has been discussed by Suthasut (1998).

The change in selectivity can be interpreted in term of a change in adsorption properties due to differences in the number of adjacent platinum atoms required for the various reaction pathways. This phenomenon is called ensemble effect (Liwu et al., 1990). When tin is present, the size of surface Pt ensembles is decreased, inhibiting the formation of highly dehydrogenated surface species that are intermediates for hydrogenolysis, isomerization, and coking reactions (Cortright et al., 1995). Since the dehydrogenation reactions can proceed on small ensembles of surface platinum atoms, the decreased size of the surface Pt ensembles caused by the addition of tin leads to high selectivity for butane dehydrogenation. Consequently, the higher the Sn/Pt weight ratio gives the higher the olefin selectivity. It furthermore follows that not only the selectivity but also the stability of the platinum function are modified by addition of tin. (Dautzenberg et al., 1980).

Figure 4.6 shows the coke conversion profile of catalyst D₁, D₃, and D₅ during the regeneration cycles. The CO₂ produced in the coke burning reaction was used for measuring this coke conversion. The decoking time for each cycle is 60 minutes and seven cycles were investigated. All of the catalysts show the highest CO₂ signal at the first decoking cycle and then decrease in their initial CO₂ signal of each cycle through the last decoking cycle. The catalyst D₁ shows the rapid decrease in CO₂ signal after the first decoking cycle while the catalyst D₃ and D₅ show the rapid decrease in CO₂ signal after the first three decoking cycles. After that the CO₂ signal is not much different. These results are due to the conversion as described above. For each cycle, after the decoking procedure was carried on for 5-10 minutes, the CO₂ signals in all

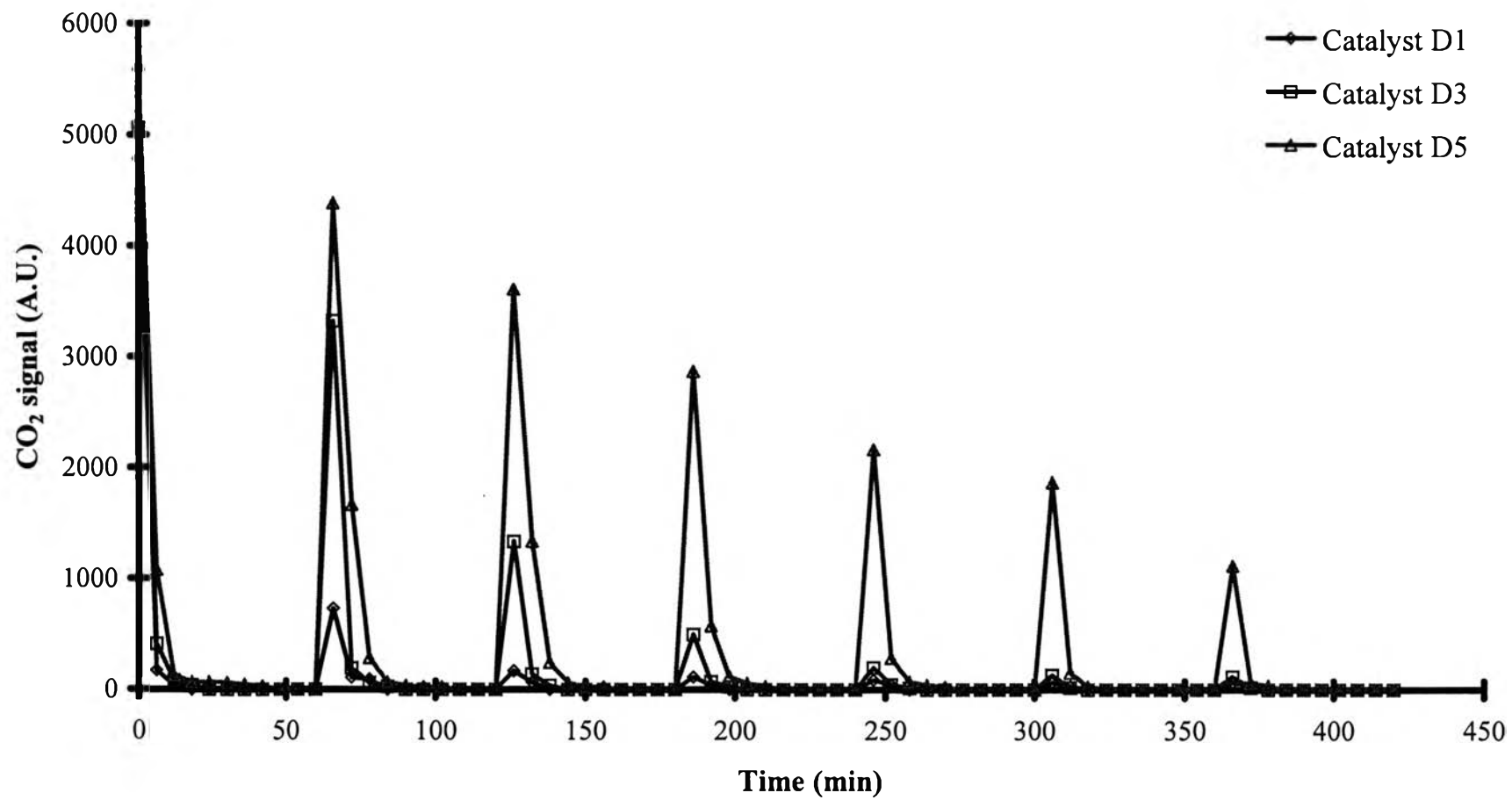


Figure 4.6 CO₂ produced during the coke burning cycles.

catalyst types went to the same CO₂ signal amplitude and trend. These results will be discussed later in section 4.2.

4.1.2 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) can play an important role in the coke characterization. It consists of exposing a sample to a flowing O₂/inert gas mixture while increasing its temperature. The amount of carbonaceous compounds oxidized being determined by quantification of the CO₂ formed (Bond et al., 1995).

Catalyst D₁, D₃, and D₅, having different Sn/Pt weight ratios, were operated under the repetitive reaction-regeneration cycles. The spent catalysts were characterized after operation of the first and the eighth reaction cycles. The carbonaceous deposits on these catalysts were analyzed by the TPO method.

Figure 4.7 and Figure 4.8 show the TPO results of the eighth cycle run and of the first cycle run, respectively. Two coke burning zones, which represent two types of carbonaceous deposits on the surface of the catalysts, were displayed in both TPO profiles in agreement with the previous works (Parera et al., 1983; Barbier et al., 1985; Liwu et al., 1990, Pieck et al., 1992 and Resasco et al., 1994). The lower burning zone, which appears in the temperature range from 300°C to 500°C, represents the burning of coke deposited on or near the metal site (Pt). The higher burning zone, which appears in the temperature range from 500°C to 700°C, is due to more refractory coke deposited on the alumina support which is more polymerized and poor in hydrogen (Pieck et al., 1992). The difference in burning temperature zone depends on the TPO conditions such as the heating rate and the concentration of the oxidant gas. The area under the TPO profile can imply the amount of coke deposited on the catalyst (Liwu et al., 1990). This area can be obtained by using the POLYMAT4 program. Table 4.1 and Table 4.2

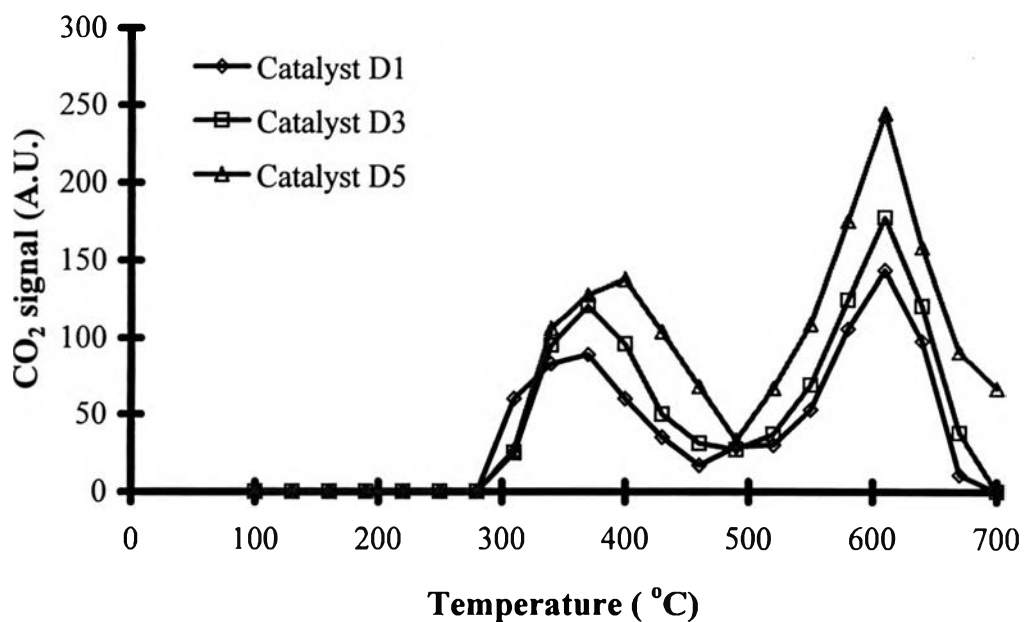


Figure 4.7 Temperature programmed oxidation profile of 8th cycle spent catalysts.

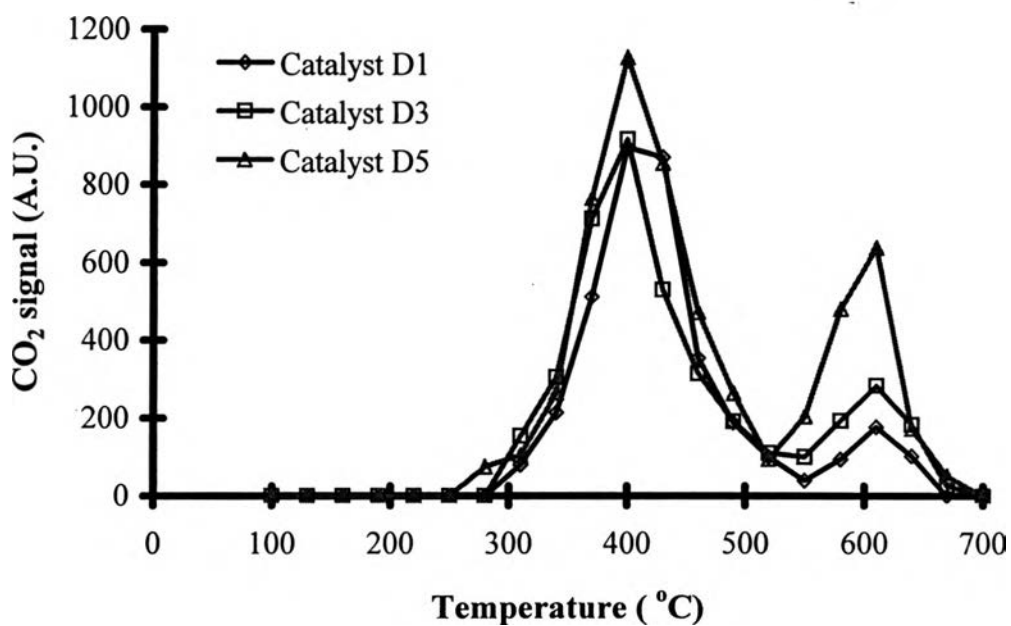


Figure 4.8 Temperature programmed oxidation profile of 1st cycle spent catalysts.

Table 4.1 The percentage of coke on the metal and the support of TPO profile of 8th cycle spent catalysts obtained from the POLYMAT4 program

Temperature range (°C)	Area under the TPO profile		
	Catalyst D ₁	Catalyst D ₃	Catalyst D ₅
300-500	10846.3	12910.8	17580.9
500-700	13690.0	17512.2	26805.7
Total area	24536.3	30423.0	44386.6

Position	Percentage of coke on each site		
	Catalyst D ₁	Catalyst D ₃	Catalyst D ₅
Metal	44.21	42.44	39.61
Support	55.49	57.56	60.39
Total	100	100	100

Table 4.2 The percentage of coke on the metal and the support of TPO profile of 1st cycle spent catalysts obtained from the POLYMAT4 program

Temperature range (°C)	Area under the TPO profile		
	Catalyst D ₁	Catalyst D ₃	Catalyst D ₅
300-500	90521.7	91084.2	112681.0
500-700	18009.4	29459.7	52939.1
Total area	108531.1	120543.9	165620.1

Position	Percentage of coke on each site		
	Catalyst D ₁	Catalyst D ₃	Catalyst D ₅
Metal	83.41	75.56	68.04
Support	16.59	24.44	31.96
Total	100	100	100

represent the area under the TPO profile and the percentage of coke on the metal and the support of TPO profile of the eighth and the first cycle spent catalysts, respectively.

From Figure 4.7, which represents the TPO profile of the eighth cycle run, shows that the catalyst D₁ has the lowest amount of coke on the catalyst both on the metal (Pt) and alumina sites. The catalyst D₃ gives a higher amount of coke on the metal and on the support while the catalyst D₅ gives the highest. This result is due to the higher conversion of the higher Sn/Pt weight ratio. However, Table 4.1 shows that the catalyst D₅ displays the highest percentage of the amount of coke on the alumina support. The catalyst D₃ gives the lower percentage of the amount of coke on the support than the catalyst D₅ while the catalyst D₁ gives the lowest. These results may come from the effect of promoter (Sn) which can induce the coke on the metal site to migrate to the alumina support. The more tin added, the more percentage of coke on the support occurs. The amount of coke on the metal in each catalyst is lower than the amount of coke on the support. This phenomenon can be explained by a proposed drain off mechanism (Lieske et al., 1987). It is suggested that the coke precursors, polymer olefinic, and aromatic species are adsorbed less strongly on the tin containing samples due to an ensemble effect of tin. Consequently they are more mobile and can more easily migrate to the alumina where they are finally deposited as coke. Moreover it is known that tin promotes the activity and especially the stability of Pt/Al₂O₃ reforming catalysts although coke production is not reduced (Dautzenberg et al., 1980). This drain off effect guarantees that a larger portion of active Pt sites will remain free from blocking coke precursors and provides higher activity for the trimetallic samples.

Figure 4.8, which shows the TPO profile of the first cycle run, can also verify the effect of tin on the migration of coke which corresponds to the TPO profile of the eighth cycle run. Again, the catalyst D₅ gives the highest amount of coke on the metal and on the support while the catalyst D₃ gives

lower and the catalyst D₁ gives the lowest, respectively. However, Table 4.2 shows that the catalyst D₅ displays the highest percentage of the amount of coke on the alumina support while the catalyst D₃ gives the lower and catalyst D₁ gives the lowest, respectively. These results behave in the same manner as the TPO results of the eighth cycle run except that the amount of coke on the metal in each catalyst is lower than the amount of coke on the support in this cycle. The comparison between TPO profile of the eighth and the first cycle spent catalysts is shown in Figure 4.9. It can also be observed that the amount of coke both on the metal and the support of each catalyst of the first cycle run is greater than that of the eighth cycle run. This result may be due to the high conversion on the first cycle run because the catalyst is still fresh. The carbonaceous deposits are formed very rapidly on the Pt sites. As a result, more coke deposits are formed on the metal sites than can be transported away to the alumina support (Lieske et al., 1987).

The TPO results of the first and the eighth cycle run show that the total amount of coke on the catalyst D₅ is higher than that of the catalyst D₃ and the catalyst D₁, respectively. These results correspond to the previous results in section 4.1.1 that give the same trend in the amount of CO₂ produced from each of the catalysts.

4.2 Coke Partial Regeneration

Catalyst D₁ to D₅, which were operated for 8 hours in the butane dehydrogenation reaction, were characterized after processing for different decoking periods. The means of Elemental analysis, Simultaneous thermal analysis (STA), and Fourier transform infrared spectroscopy (FTIR) were used to investigate the partially regenerated catalyst.

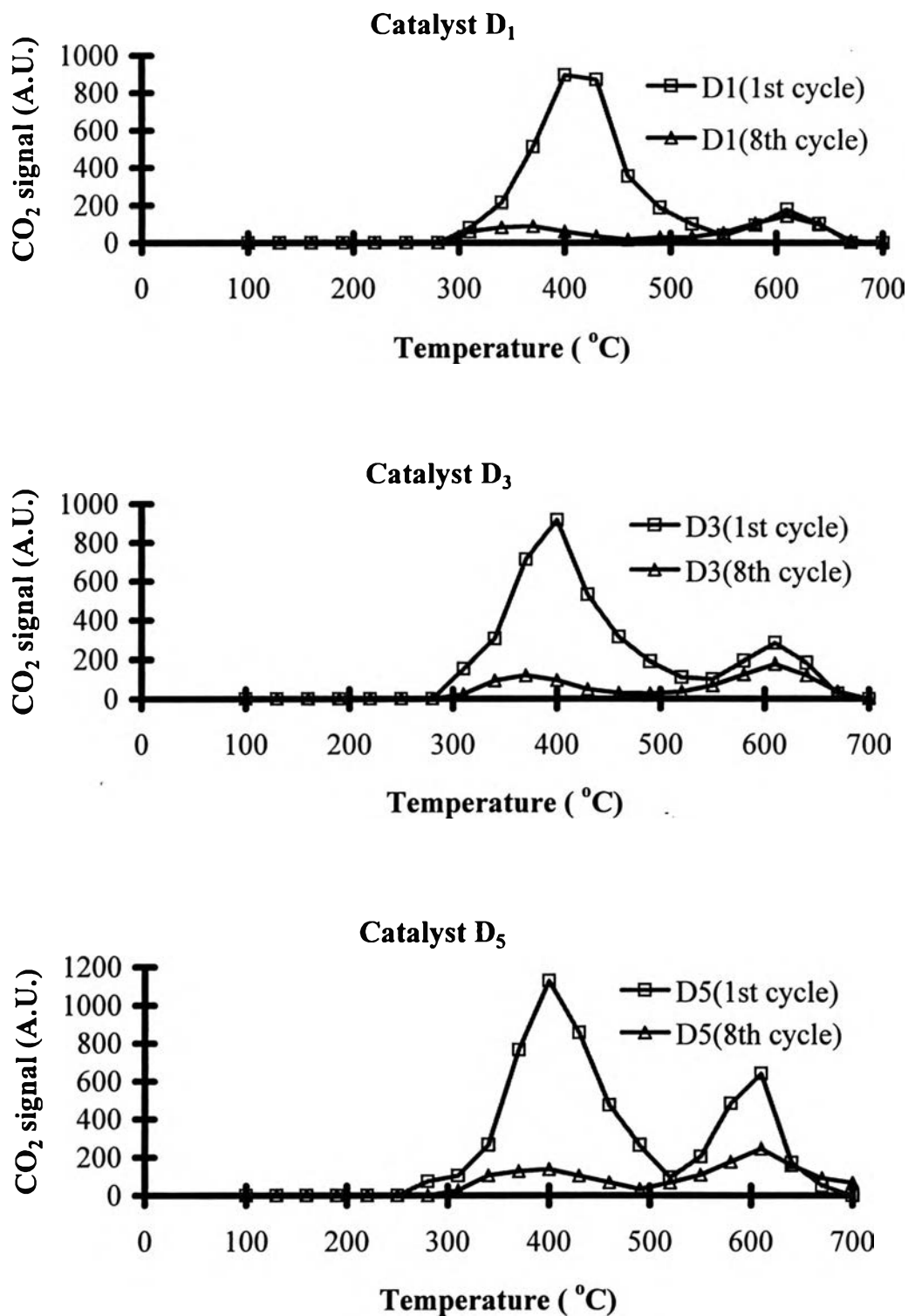


Figure 4.9 Comparison between the TPO profile of 1st and 8th cycles of catalyst D₁, D₃, and D₅.

Figure 4.10 shows the weight percentage of carbon remaining on the spent and partially regenerated catalysts obtained from the elemental analysis. The spent catalyst D₅ has the highest carbon weight percentage while catalysts D₄, D₃, D₂, and D₁ have less carbon, respectively. The initial decoking rate is very high in the first 5 minutes of regeneration time. After 5 minutes of regeneration time, the decoking rate in all type of catalysts gradually decreases through the end of the regeneration time. The higher the Sn/Pt weight ratio gives the higher decoking rates. These results may be due to the initial coke formed.

The amount of carbonaceous deposits on the spent and partially regenerated catalysts were also tested by simultaneous thermal analyzer. There were three weight loss zones in the thermobalance diagram. The first weight loss zone which appeared at a temperature below 150°C represents the loss of moisture in the catalyst pores. According to the TPO discussion in section 4.1, the second weight loss zone (300-500°C) and the third weight loss zone (500-700°C) represent the weight loss due to the combustion of coke deposits on the metal and alumina sites, respectively.

Table 4.3 shows the coke remaining on the metal and on the support after partial regeneration. The total amount of coke on the catalyst can be determined from the total coke removed from both the metal and the support. This total amount of coke can be shown in Figure 4.11. The coked catalyst that has the higher Sn/Pt weight ratio gives the higher amount of coke. These results are the same as estimated from the elemental analyzer. The catalyst D₅ shows the highest amount of coke both on the metal and on the support while the catalysts D₄, D₃, D₂, and D₁ show the lower, respectively. These results also agree with the TPO discussion in section 4.1.2.

All types of catalysts show that the coke is rapidly removed during the first 5 minutes of regeneration time. The coke deposited on the metal is mostly removed in this period, while the coke deposited on the support continues to

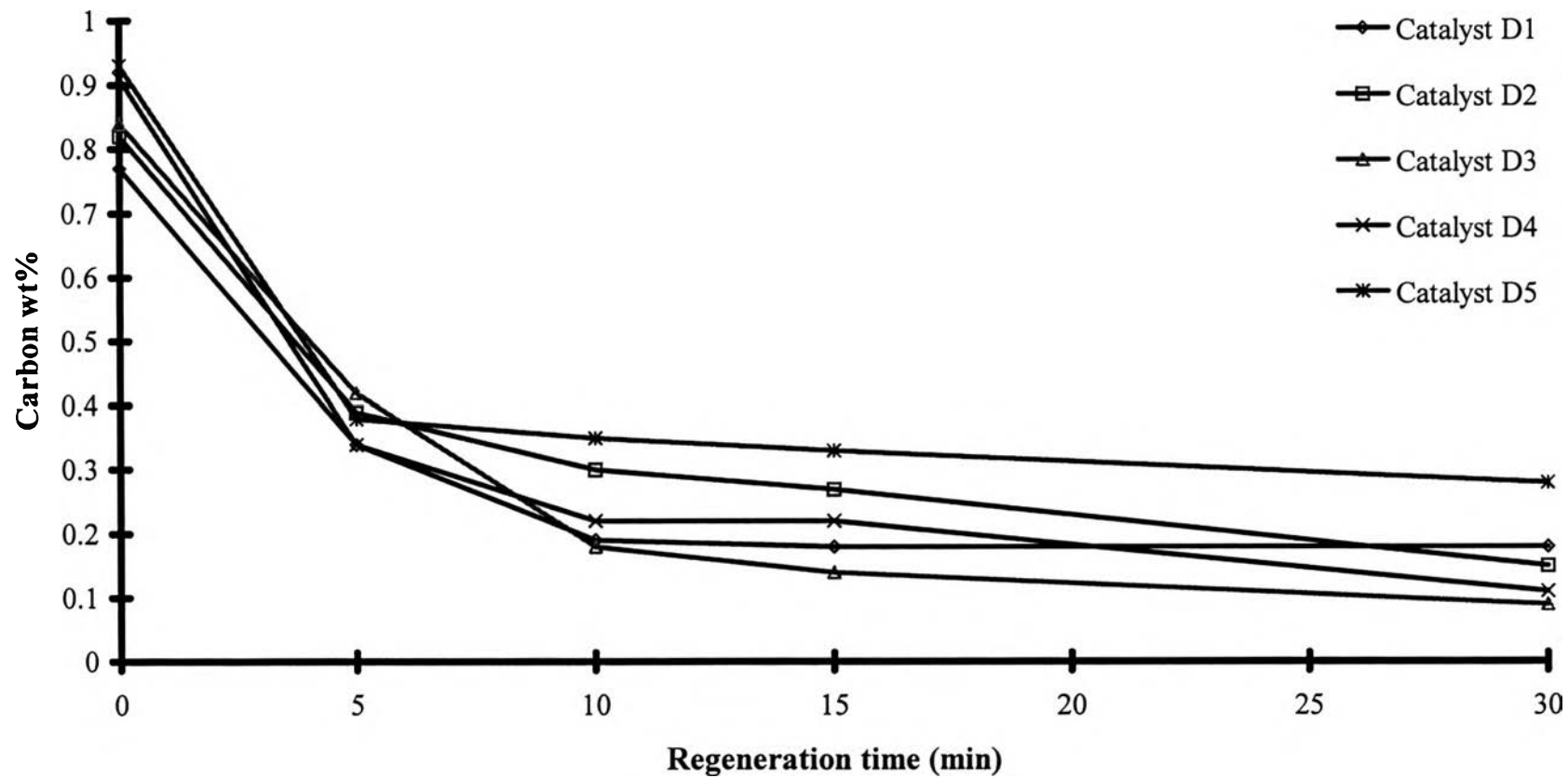


Figure 4.10 Carbon remaining on partially regenerated catalyst samples of 1st cycle.

Table 4.3 The coke (investigated by STA) on metal site and alumina support of spent catalyst and partially regenerated catalyst for 5 minutes (Par5), 10 minutes (Par10), 15 minutes (Par15), and 30 minutes (Par30)

Catalyst	Position	Percentage of weight loss (%)				
		Coked	Par5	Par10	Par15	Par30
D ₁	Metal	1.06	0.46	0.11	0	0
	Support	0.40	0.28	0.04	0	0
D ₂	Metal	1.07	0.50	0.15	0	0
	Support	0.41	0.25	0.09	0	0
D ₃	Metal	1.14	0.47	0.17	0	0
	Support	0.52	0.40	0.13	0	0
D ₄	Metal	1.17	0.43	0.22	0	0
	Support	0.53	0.34	0.19	0	0
D ₅	Metal	1.24	0.45	0.25	0	0
	Support	0.59	0.36	0.20	0	0

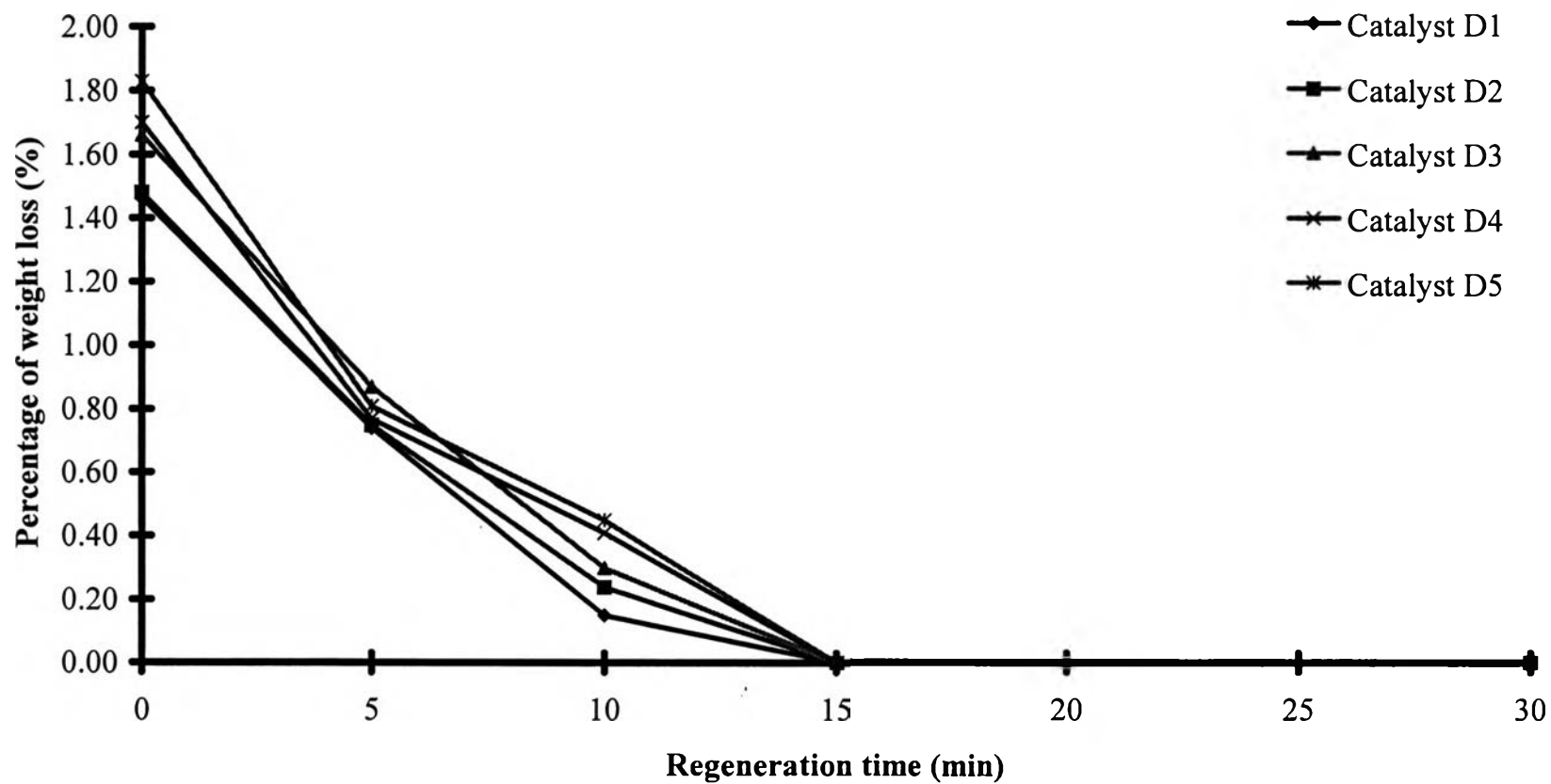


Figure 4.11 The total amount of coke on partially regenerated catalyst samples of 1st cycle obtained from STA.

decrease over a longer period of time. However, after the catalysts were regenerated for 15 minutes, all of the coke on the catalysts was completely removed. Unlike the result obtained from the elemental analyzer, there is some coke remaining on the catalyst after being regenerated for 15 minutes. This remaining coke may come from the high burning temperature that is 950°C whereas the temperature in the simultaneous thermal analyzer is only 700°C. Therefore, the amount of coke that is measured from the elemental analyzer is greater than that from the simultaneous thermal analyzer. The coke on the support of catalyst D₁ can be burnt faster than those of catalysts D₂, D₃, D₄, and D₅, respectively. These results may be due to the effect of promoter (Sn). The coke deposits on the alumina support required the O₂ dissociated adsorption on the metal site which diffused to the alumina to complete the combustion reaction. The metal alloy that occurs on the high promoter (Sn) loading leads to the inhibition of the dissociated O₂ on the platinum atom (Charuratana, 1996).

Fourier transform infrared spectroscopy has often been used to characterize the nature of the coke deposits (Royo et al., 1994). The general view of the 1000-1800 cm⁻¹ regions of the infrared spectra of the original coke and of that from the partially regenerated samples of catalysts D₁, D₃, and D₅ are shown in Figure 4.12.

Using the equipment computer, the same intensity to the peak at 1580-1680 cm⁻¹ in all the spectra was given in order to take it as a reference to compensate differences in coke concentration and thickness of the disks. The absorption band appearing between 1580 and 1680 cm⁻¹ in all samples can be ascribed to the stretching of the C=C bond belonging to olefins, aromatic rings, and polyaromatics. The peak between 1450 and 1475 cm⁻¹ can be ascribed to the C-H bond stretching in C-(CH₃)₂ or C-(CH₃)₃ groups. The adsorption peak at about 1100 cm⁻¹ is due to the C-OH functional group (Pieck et al., 1992).

All of the catalyst types show the decrease in both aromatic and aliphatic bands when increasing the regeneration time. However, the FTIR spectra show

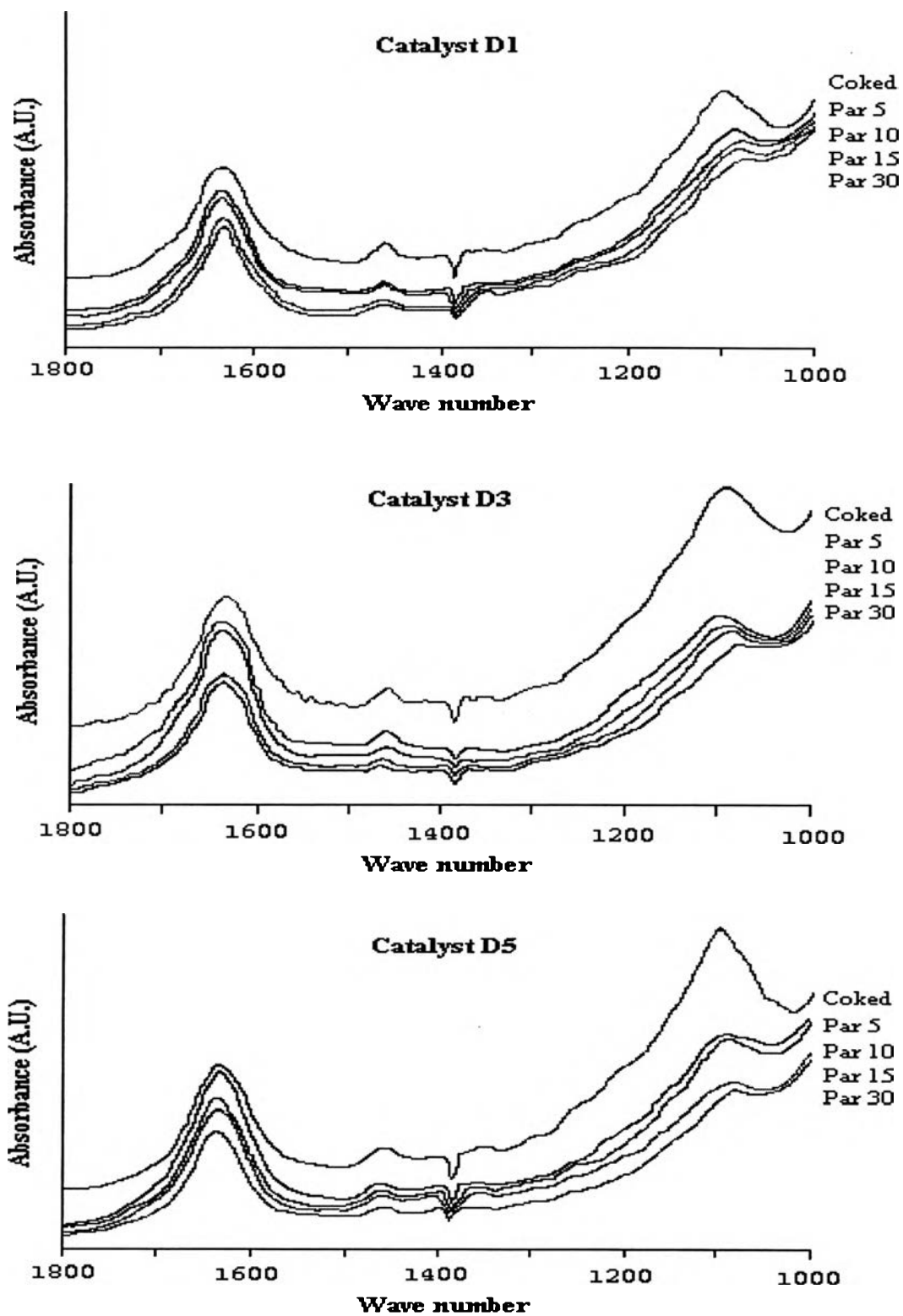


Figure 4.12 FTIR spectra of coke and partially regenerated catalyst for 5 minutes (Par5), 10 minutes (Par10), 15 minutes (Par15), and 30 minutes (Par30).

that the aromatic band slightly decreases although the catalyst was regenerated for 30 minutes whereas the aliphatic band almost disappears. This can indicate that the structure of the residual coke is the stretching of the C=C bond type belonging to olefins, aromatic rings, and polyaromatic. The coke, which is removed from the catalyst, is the stretching of the C-H bond and the C-OH bond. In a comparison of the absorption spectra of all samples, it can be seen that the catalyst D₃ shows the highest change in both functional groups from spent catalyst in the first 5 minutes of partially regenerated catalyst and catalysts D₅ and D₁ show less and the least changes, respectively. But slower change occurs in the last 15 minutes of the partial regeneration procedure. After 15 minutes of regeneration time, all catalyst types show the slowest change in both aromatic and aliphatic carbon stretching. These FTIR results can confirm the previous analyses about the decoking rates.

The intermediate groups, which is the C=O functional group, was not found by FTIR. This may be due to the high coke burning temperature (500°C) that can change this intermediate group to the complete combustion product (Pieck et al., 1992).

From catalyst characterization, the role of promoter (Sn) in decoking procedure was established. The elemental analyzer and the simultaneous thermal analyzer (STA) show that the decoking rate is fast in the first 5 minutes of regeneration time. The high burning temperature (500°C) causes the coke burning process to behave as nonselective burning and all coke components are burnt from the external layers to the inner part that can be explained by the shrinking core model (Pieck et al., 1992). The amount of coke removed on the metal and on the support represents the total coke burning rate. However, coke deposits on the metal still burn in the catalyzed condition, Pt-O form (Basso et al., 1991), and give a fast decoking rate. After the coke deposited on the metal sites was completely burned off, the decoking rate only comes from the coke which was still burning on the alumina supports. The different amount of

promoter (Sn) loading cause the different decoking rates. The metal (Pt) is always surrounded by the significant amount of promoters (Sn) with the electronic interaction. The higher tin loading catalyst may block the O₂ diffusion path due to its geometric function.