

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Cyclic Regeneration

4.1.1 Propane Conversion and Coke Burning

Catalysts D₁, D₂ and D₃, having different Li/Pt weight ratios, were operated under the propane dehydrogenation reaction conditions. The reaction-regeneration procedure occurred *in-situ* in the catalyst bed and continued for 8 cycles of operations. The propane conversion profile for every cycle is shown in Figure 4.1. Time on stream in each reaction cycle is 8 hours.

The catalyst D₂ gives the highest propane conversion in all reaction cycles, both for initial and steady state conversion. The catalysts D₁ has lower reaction conversion and catalyst D₃ the lowest, respectively. All of the catalysts display a decrease in their initial conversion from the first reaction cycle through each succeeding reaction cycle in the same manner. However, the conversion of all catalysts in the later cycles run is not much different. These results can be described by the effect of chloride ion (Cl⁻). A suitable amount of chloride ion can help the redispersion of platinum. But less chloride will cause catalyst metal sintering while higher amounts of chloride will cause side reactions.

Platinum crystallites can use chloride remaining from the catalyst preparation steps to form a Pt-Cl⁻ complex during the regeneration procedure (Lieske et al., 1983). Thus the platinum will not agglomerate. However, the catalysts used in this catalysts were prepared by sequential impregnation

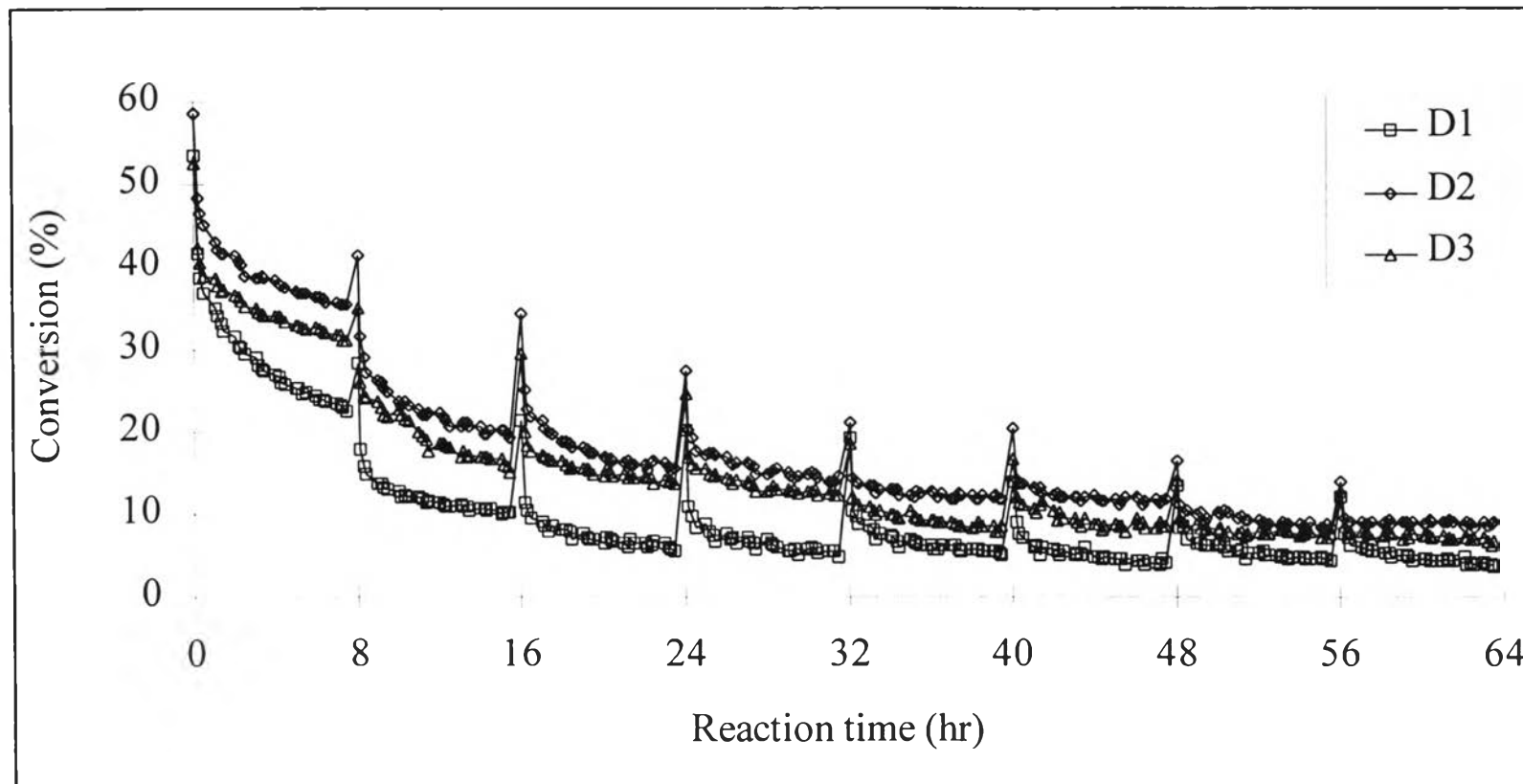


Figure 4.1 The conversion of propane for the cycle run at 600 °C.

(see Saimongkol, 1997) in which chloride ions may be lost during the calcination step due to a high temperature. In this case, it is likely to indicate that the decrease in activity may be due to the agglomeration of platinum or the formation of metal alloy between platinum and tin.

The residual nitrate (NO_3^-) in the catalyst can also affect the metal redispersion. It will compete with hydrogen atoms for platinum during the reduction step. Then the system will have low redispersion.

After the catalysts have been used in several cycles of the reaction-regeneration procedure, the chloride ions gradually disappear from the system due to a high operating temperature. Thus these effects are the reasons why the regeneration steps do not recover all of the initial catalyst activity.

Figure 4.2 shows the catalyst selectivity during the reaction cycles. All of the catalysts show a change in selectivity from the second reaction cycle through to the last reaction cycle. The selectivity in the later reaction cycles is not much different among the cycles. This result corresponds to the conversion results for the same reason. The increasing selectivity in the second cycle has been discussed by Saimongkol (1997).

Coke conversion was measured by CO_2 produced in the coke burning reaction shown in Figure 4.3. The decoking time for each cycle is 60 minutes and seven cycles were investigated. All of the catalysts show a decrease in their initial CO_2 signal after the first cycle through the last cycle. The rapid decrease in CO_2 signal appears in all catalysts for the first 4 decoking cycles. After that the CO_2 signal is not much different from cycle 5 to cycle 7. These results are due to the conversion as described above.

For each cycle, after the decoking procedure was carried out for 5-10 minutes, the CO_2 signals in all catalyst types went to the same CO_2 signal amplitude and trend. These results will be discussed later in section 4.2.

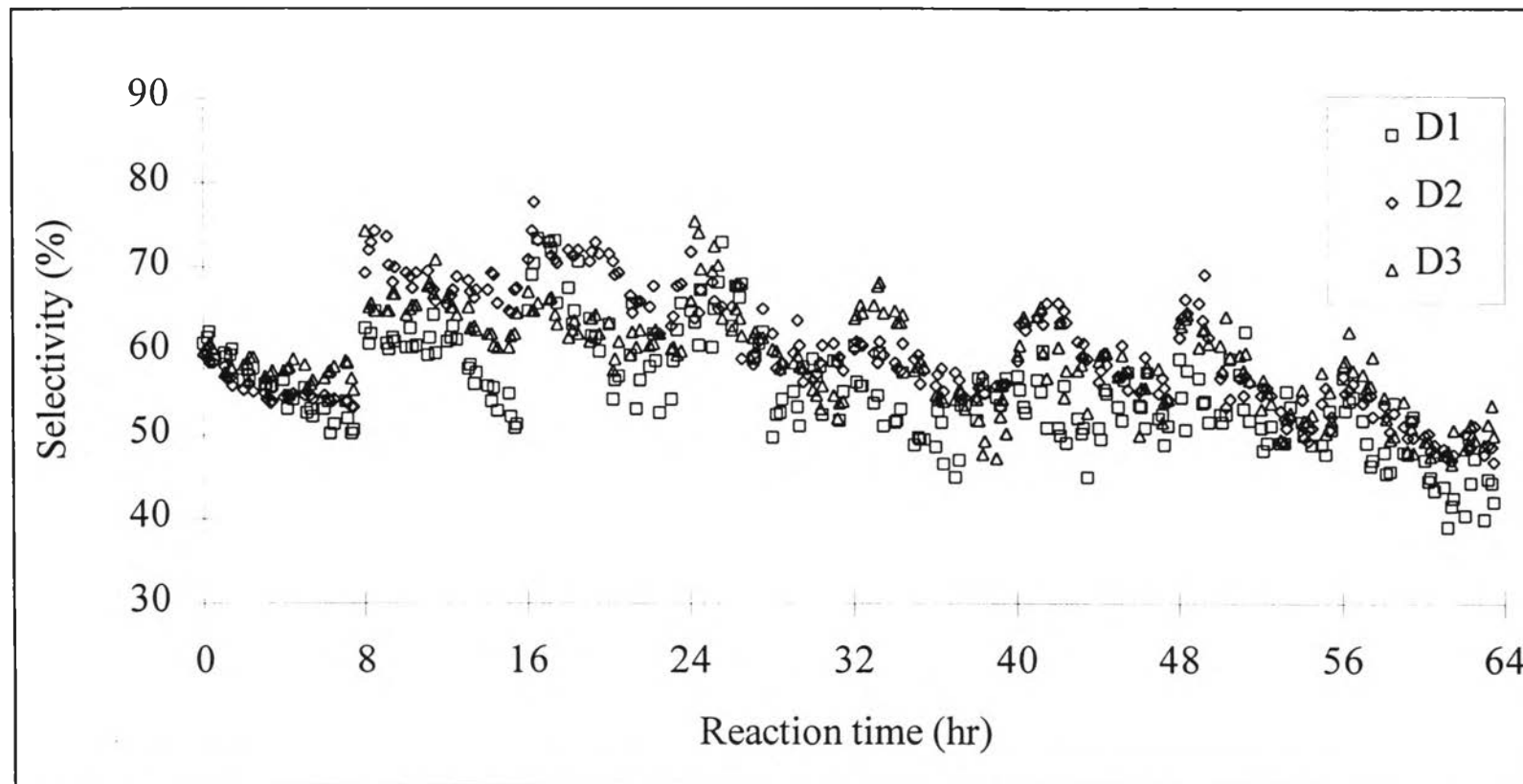


Figure 4.2 The selectivity to propylene for the cycle run at 600 °C.

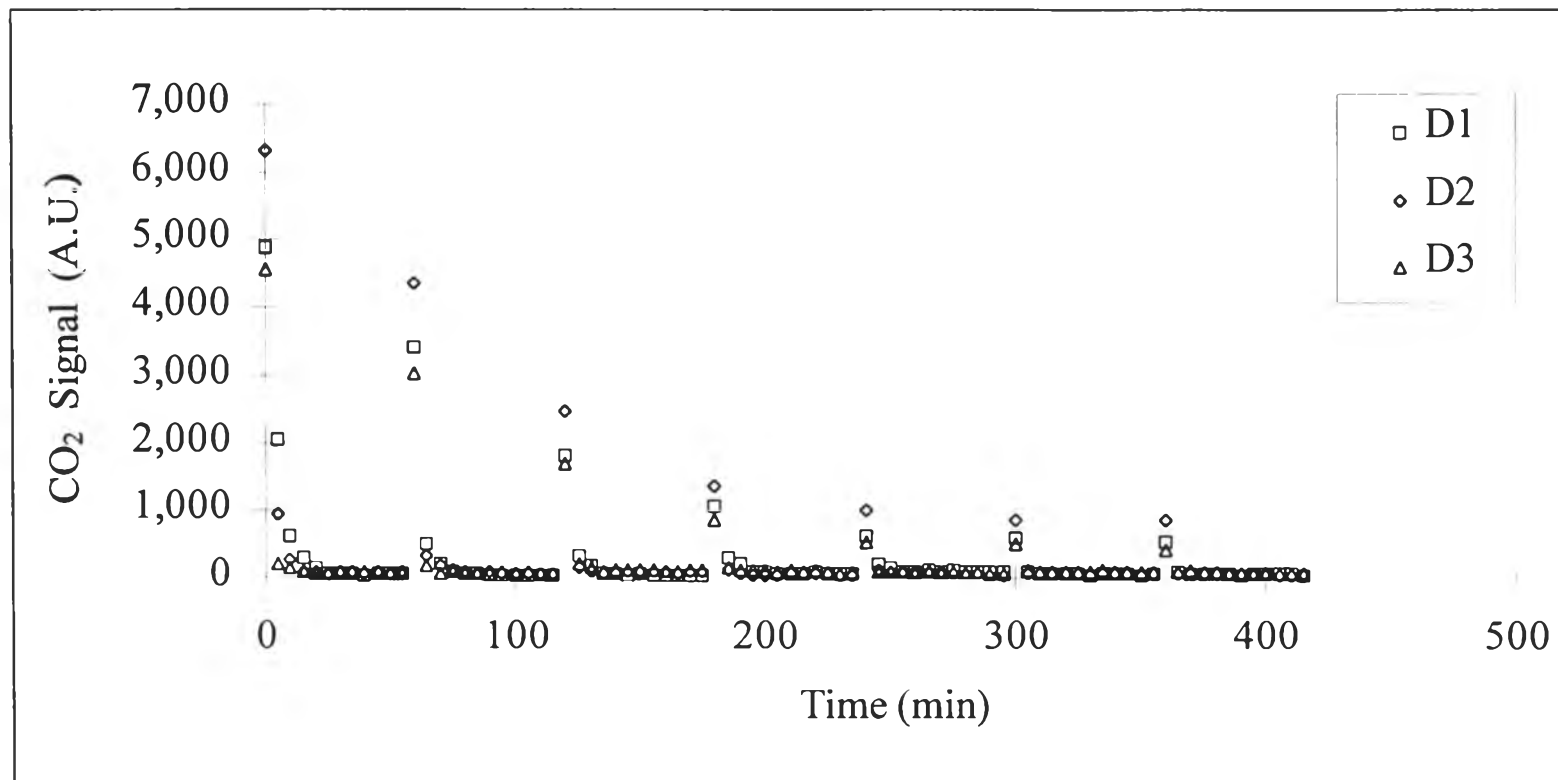


Figure 4.3 CO₂ produced during the coke burning cycles.

4.1.2 Temperature-Programmed Oxidation

Catalysts D₁, D₂ and D₃, having different lithium-platinum ratios, which had been used for the dehydrogenation of propane in the reactor, were characterized after operation of the first and the eighth reaction cycles. The carbon deposits on these catalysts were analyzed by Temperature programmed oxidation (TPO). The amount of carbonaceous deposits on the catalyst was determined by the quantification of CO₂ formed (Bond et al., 1995). The TPO results of the first cycle run are shown in Figure 4.4. Two coke burning zones were found which correspond to the previous work (Parera et al., 1983; Barbier et al., 1985 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 (500-700 °C) is due to more refractory coke deposited on the alumina support which is more polymerized. The difference in burning temperature zone depends on TPO conditions, e.g., the concentration of oxidant gas and heating rate. The area under the TPO profile can imply the amount of coke on the catalyst (Lin et al., 1990).

From the TPO profile, the catalyst D₁ shows the highest amount of coke on the Pt sites but gives the lowest amount of coke on the alumina support. The catalyst D₂ gives a lower amount of coke on the metal than catalyst D₁ but gives the higher amount of coke on the support while catalyst D₃ gives the lowest amount of coke on the metal but gives the highest amount of coke on the support. These results may come from the effect of Li which can induce the coke on the metal site migrate to the alumina support. The more lithium added, the less coke on the metal occurs while the more coke on the support occurs.

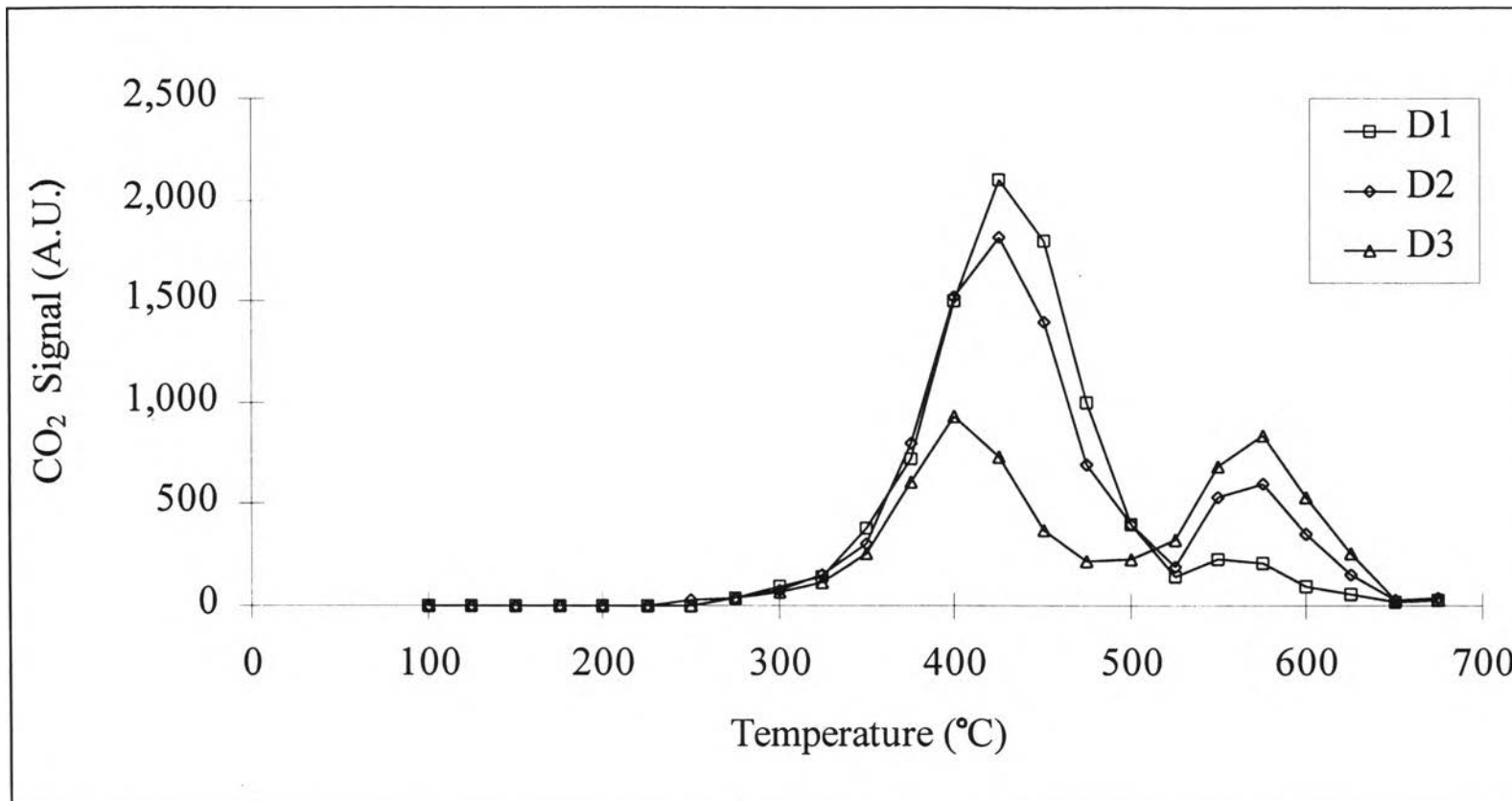


Figure 4.4 Temperature-programmed oxidation profile of 1st cycle spent catalysts.

The amount of coke on the metal in each catalyst is higher than the amount of coke on the support. This result may be due to the high conversion on the first cycle run because the catalyst is still fresh. Therefore, the rate of reaction is much faster than the rate of migration of coke from the metal site to the support.

The total amount of coke in catalyst D₁ is more than that of catalyst D₃ but less than that of catalyst D₂. This result also corresponds to the amount of CO₂ produced in the first cycle run.

The TPO profile of the eighth cycle run in Figure 4.5 can also verify the effect of lithium on the migration of coke which corresponds to the TPO profile of the first cycle run. The catalyst D₁ gives the highest amount of coke on the metal while the catalyst D₂ has less and catalyst D₃ gives the lowest amount of coke on the metal. On the other hand, the catalyst D₃ gives the highest amount of coke on the support while the catalyst D₁ gives the lowest amount of coke on the support. These results are the same as described above.

However, the amount of coke in each catalyst is not much different after 8 cycles. These results correspond to the previous results in section 4.1.1 which give almost the same amount of CO₂ produced from each of the catalysts in the late coke burning cycle.

4.2 Coke Partial Regeneration

Catalysts D₁ to D₅, which were operated in the propane dehydrogenation reaction, were regenerated in different decoking periods. The partially regenerated catalysts were characterized by Elemental analyzer, Simultaneous thermal analysis (STA) and Fourier transform infrared (FTIR) spectroscopy.

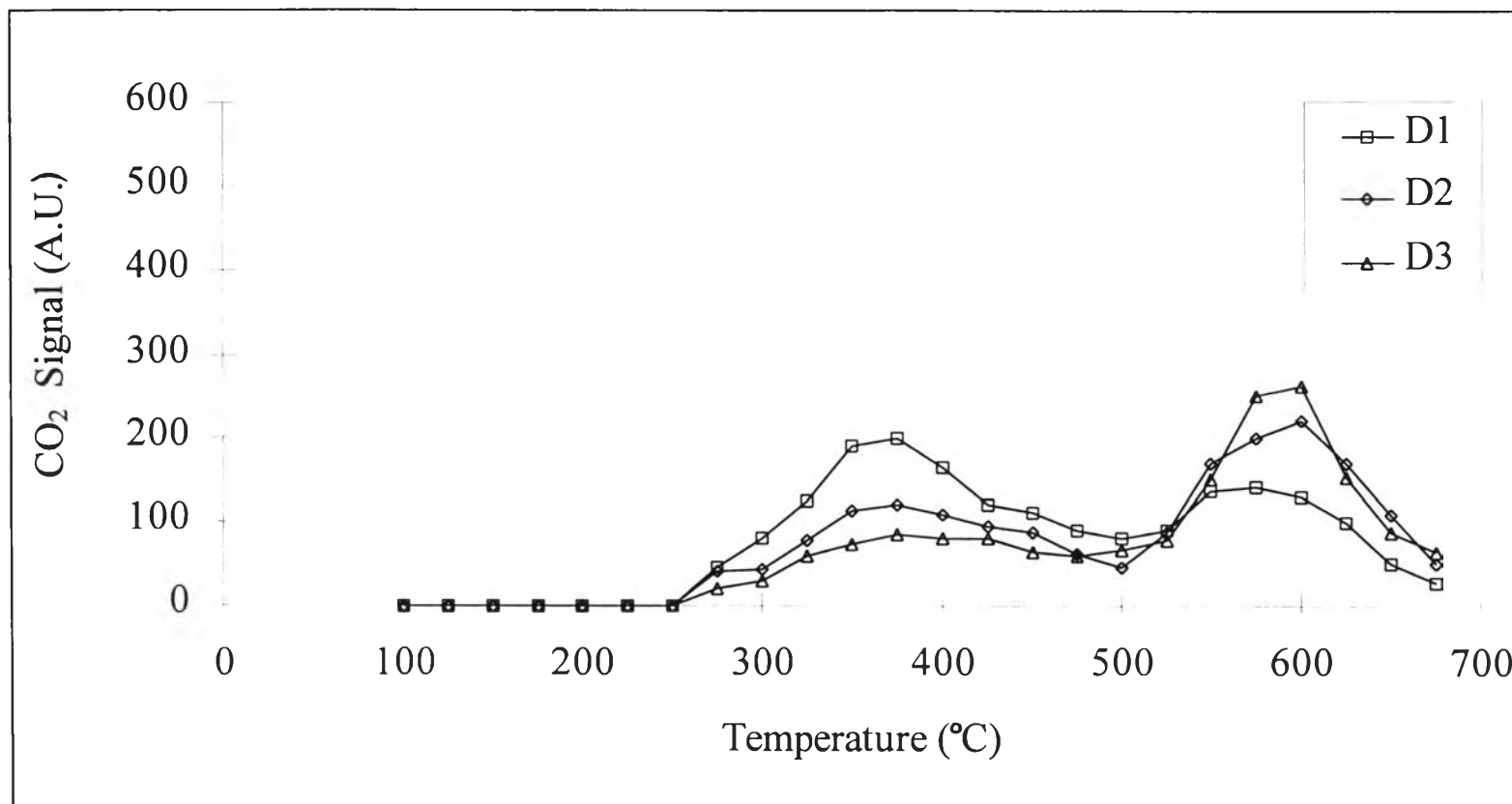


Figure 4.5 Temperature-programmed oxidation profile of 8th cycle spent catalysts.

The weight percentage of carbon remaining on the spent and partially regenerated catalysts is shown in Figure 4.6. The spent catalyst D₂ has the highest carbon weight percentage while catalysts D₁, D₃, D₄ and D₅ have less carbon respectively. The initial decoking rate is quite high for the first 5 minute period of regeneration time. After 5 minutes, the decoking rates for all of the catalysts gradually decrease through the end of regeneration time. The higher Li/Pt ratios will give the lower decoking rates. These results may be due to the initial coke formed.

Simultaneous thermal analysis was also used to investigate the amount of carbonaceous deposits on the spent and partially regenerated catalysts. There were 3 weight-loss zones in the thermobalance diagram. The first zone which appeared at a temperature of below 150 °C represents the loss of moisture in the catalyst pores. The second weight loss zone (300-500 °C) and the third weight loss zone (500-700 °C) show the weight loss due to the combustion of coke deposits on the metal sites and alumina support, respectively, which also correspond to the TPO profile. The coke remaining on the metal and the support after partial regeneration is shown in Table 4.1.

The total amount of coke can be determined from the total coke removed from both metal and support. The catalyst D₂ shows the highest total amount of coke while the catalyst D₁, D₃, D₄ and D₅ show lower total amount of coke, respectively. These results are the same as estimated from the elemental analyzer data.

The catalyst D₁ shows the highest amount of coke on the metal but shows the lowest amount of coke on the support. The catalysts D₂, D₃, D₄ and D₅ show lower amount of coke on the metal but higher amount of coke on the support, respectively. These results also agree with the TPO discussion in section 4.1.2.

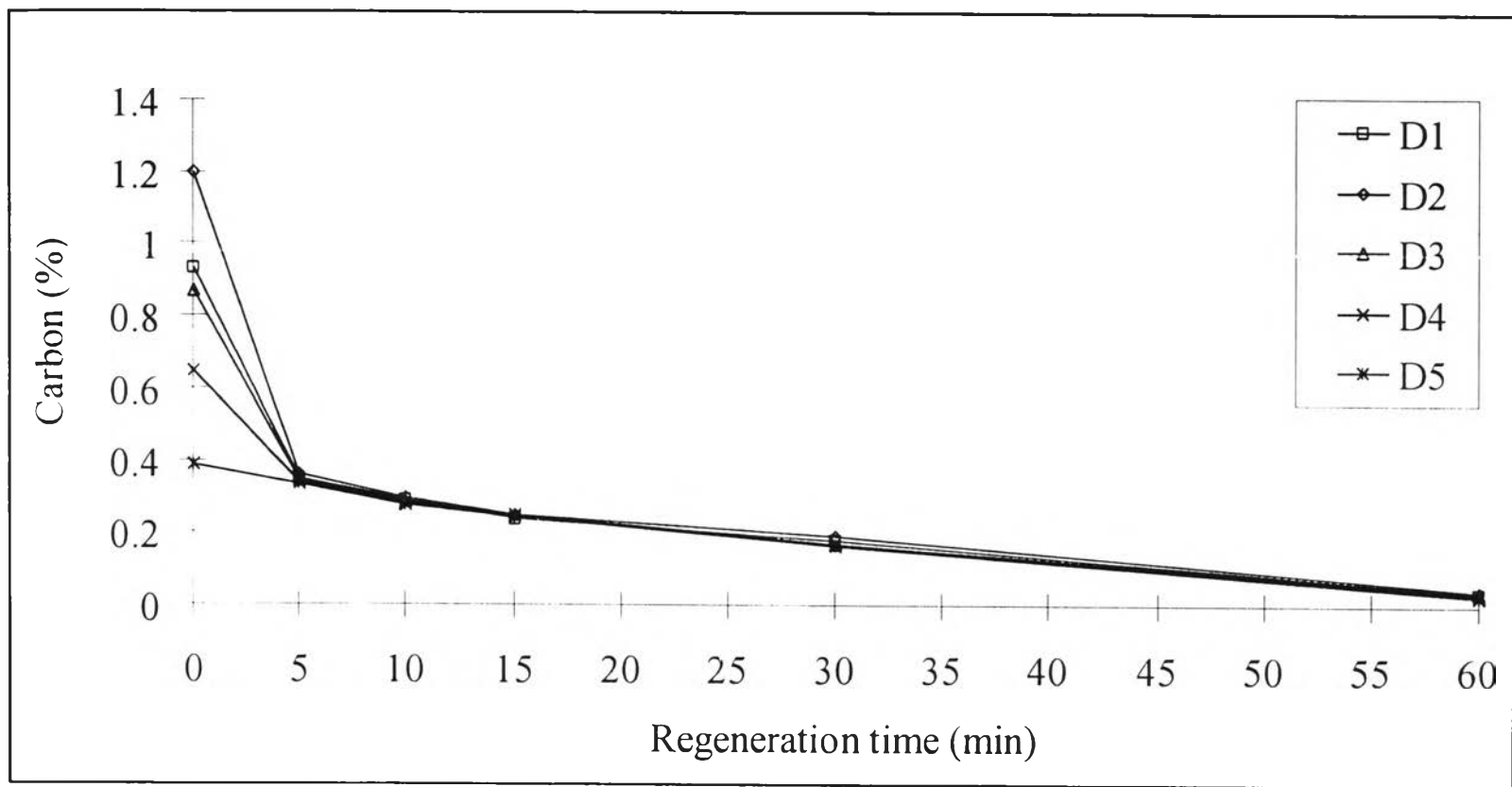


Figure 4.6 Carbon remaining on partially regenerated catalyst samples of 1st cycle.

Table 4.1 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	wt%				
		Initial coke	Par5	Par10	Par15	Par30
D1	Metal	1.5	0.5	0.4	0.3	0.2
	Support	0.3	0.2	0.2	0.1	0.1
D2	Metal	1.4	0.5	0.4	0.3	0.2
	Support	0.5	0.3	0.2	0.2	0.1
D3	Metal	0.9	0.4	0.3	0.2	0.1
	Support	0.5	0.3	0.2	0.2	0.1
D4	Metal	0.5	0.4	0.3	0.2	0.2
	Support	0.6	0.3	0.2	0.1	0.1
D5	Metal	0.3	0.3	0.2	0.1	0.1
	Support	0.6	0.3	0.2	0.2	0.1

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 continue to decrease over a longer period of time.

From both catalyst characterizations, the role of the promoter (Li) in decoking can be established. The high burning temperature (500 °C) causes the coke burning process to behave like a non selective burning (Pieck et al., 1992). The amount of coke removed on both sites 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 that was still burning on the alumina supports. The different lithium loadings cause different decoking rates. When the metal (Pt) is surrounded by a significant amount of tin and lithium with the electronic interaction, the catalyst with the higher lithium loading may block the O₂ diffusion path due to its geometric function. Therefore, the high lithium loading will give a slow decoking rate.

Infrared spectroscopy has often been used to characterize the nature of the coke deposits (Royo et al., 1994). Figure 4.7 shows IR (1200-1800 cm⁻¹) spectra of the original coke and of that from the partially burned samples of catalysts D₁, D₂ and D₃.

By using the instrument computer, the same intensity is given to the peak at 1580-1680 cm⁻¹ in all the spectra in order to take it as a reference to compensate differences in coke concentration and thickness of the KBr disks. The absorption band appearing between 1580-1680 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 at about 1400 cm⁻¹ represents the C-H bond stretching in C-(CH₃)₂ or C-(CH₃)₃ groups (Pieck et al., 1992).

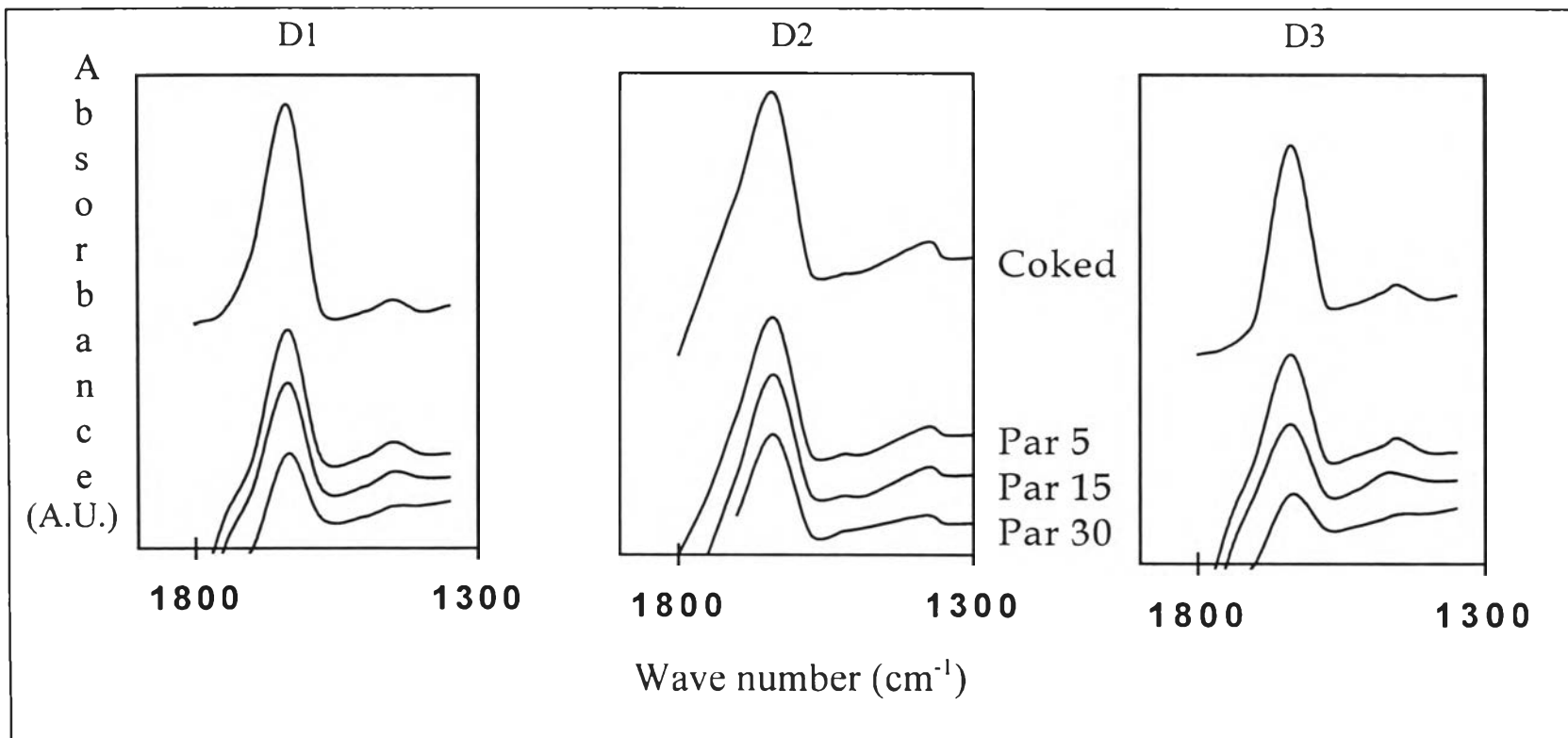


Figure 4.7 FTIR spectra of coke and partially regenerated catalyst for 5 minutes (Par5), 15 minutes (Par15) and 30 minutes (Par30).

All catalyst types show decreases in both aromatic and aliphatic bands, as regeneration proceeds. The catalyst D₂ displays the highest adsorption band in the original coke. This result may be due to a higher amount of coke. The catalysts D₁ and D₃ have lower peaks, respectively, in this order. Thus the catalyst D₂ shows the largest change in both functional groups from spent catalyst and catalysts D₁ and D₃ show less and the lowest changes, respectively. However, all catalysts show the rapid changes in both functional groups from the original coke catalyst in the first 5 minutes of partial regeneration. Slower changes occur in the last 15 minutes of the partial regeneration procedure as expected. The FTIR results confirm the previous analyses about the decoking rates.

The intermediate groups, which are C=O and C-OH functional groups, were not found by IR. These groups were lost with the complete combustion products due to the high coke burning temperatures (Pieck et al., 1992).