

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The cyclic regeneration

4.1.1 Propane conversion and Coke burning

Catalyst D₃, D₄ and D₅, having different tin -- platinum weight ratios, were operated under propane dehydrogenation reaction. The Reaction - Regeneration procedure occurred *in-situ* in the catalyst bed and continued for 8 cycles of operations. The propane conversion profile in every cycle is shown in Figure 4.1. Time on stream in each reaction cycle is 8 hr.

Catalyst D₄ gives the highest propane conversion in all reaction cycle, both for initial and steady state conversions. Catalysts D₃ and D₅ have lower reaction conversion and the lowest reaction conversion respectively. The difference in propane conversion can be explained by the amount of active metal (Pt) sites. The increase in Sn/Pt weight ratio leads to an increase the numbers of active sites (Siripoln, 1995). Sn in dehydrogenation catalyst stabilizes the metal Pt and acts as electron donating or electron inductive promoter in oxidized form (Sn²⁺) (Burch et al., 1981). The catalyst D₃, Sn/Pt weight ratio 1.5, and D₄, Sn/Pt weight ratio 2.0, also act in the same fashion. But the initial propane conversion decreases when the Sn/Pt weight ratio goes to 2.5. At the high Sn/Pt weight ratio, it is possible that the state of Sn in the system change from oxidized state to Sn⁰ and form metal alloy with Pt⁰ (Li et al., 1990). When metal alloy is formed, the dehydrogenation activity decreases substantially from the Pt⁰-Sn²⁺ state (Yarusov et al., 1992) due to the

difference between lattice parameters in Pt crystallites and Pt-Sn alloy particles or alloy surfaces covered by Sn at the high reaction temperature (Verbeek H. and Sachtler W.M.H., 1976). However, the catalyst D₄ has propane conversion closely to catalyst D₃ in the late reaction cycle.

All of the catalysts display a decrease in its initial conversion after the 2nd reaction cycle through the last reaction cycle but still keep the same conversion order. In this study, Pt crystallite can use only the remaining Cl⁻ from the catalyst preparation steps to form a Pt-Cl⁻ complex (Lieske et al., 1983) during the regeneration procedure. When the catalysts were used for several times in cyclic reaction-regeneration procedure, Cl⁻ gradually disappears from the system due to the high operation temperature. Then the later regeneration steps cannot recover all of the initial active sites because of the lack of Cl⁻. The increase in initial conversion from the 1st reaction cycle to the 2nd cycle has been discussed by Kamolwan, 1996.

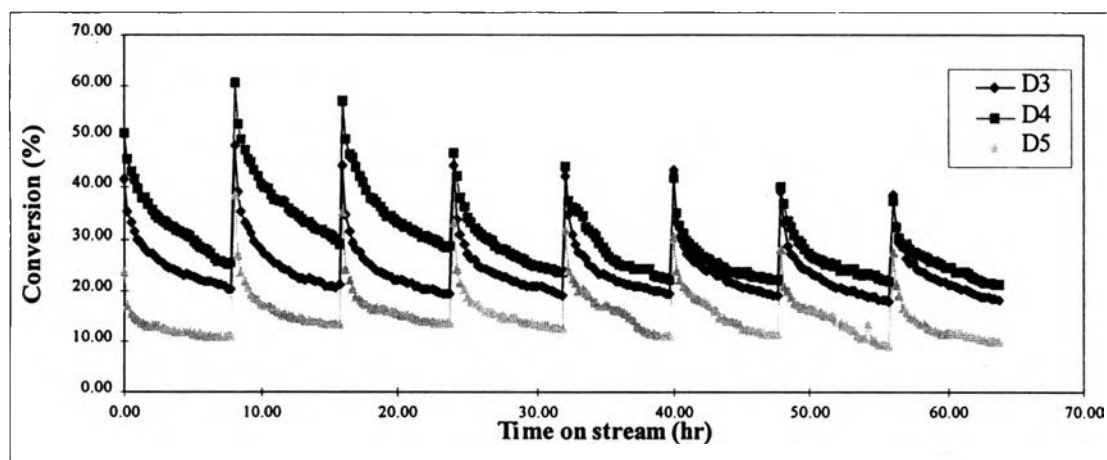


Figure 4.1 Propane conversion of catalyst D₃, D₄ and D₅ in reaction cycle (1st-8th).

Figure 4.2 shows the catalyst selectivity during the reaction cycles (1st, 2nd and 8th). Catalyst D₃ and D₄ show significant changes in selectivity when the numbers of cycles increase. The selectivity of both catalysts decrease

from the 2nd reaction cycle to lower values than catalyst D₅ in the last cycle of operation. The catalyst D₅ has insignificant changes in propylene selectivity. According to Yarusov et al., 1992 the dehydrogenation selectivity of the metal alloy is still high. Probably, the Pt-Sn alloy formed in a stable state such that operating conditions have no effect on the catalyst D₅. The reduced in number of Pt active sites sequentially increases the effective Sn/Pt atomic ratio. This ratio change to the higher values and may be lead to a value more than the optimum value (Sn/Pt weight ratio of 2) in the last cycle operation.

Coke conversion was measured by CO₂ produced in the coke burning reaction shown in Figure 4.3. Decoking time is 60 minutes, seven cycles were investigated. Catalyst D₃ and D₄ provide the same initial CO₂ signal in the first three decoking cycles. But a decreasing CO₂ signal appears in the catalyst D₃ when it was used for a few cycles. Catalyst D₅ has a CO₂ signal level lower than the others. After the decoking procedure carried on for 5-10 min. The CO₂ signals in all catalyst types go to the same CO₂ signal amplitude and trend. These results will be discussed later in section 4.2

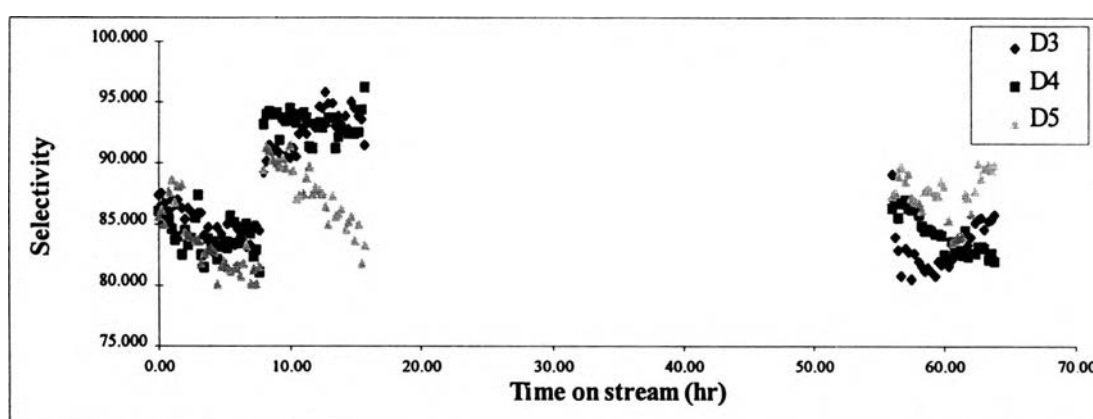


Figure 4.2 Catalyst selectivity in reaction cycle (1st, 2nd and 8th).

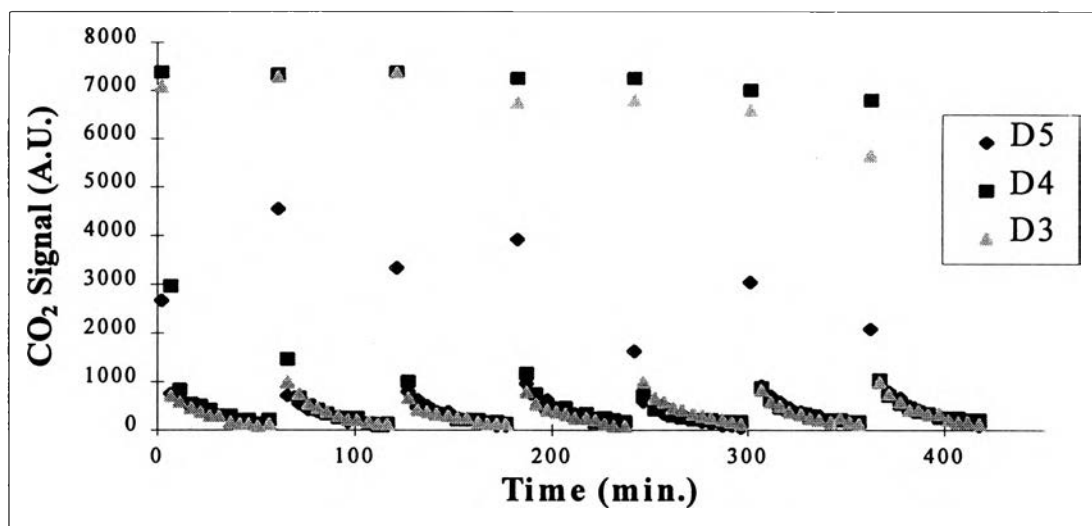


Figure 4.3 CO₂ produced in coke burning cycle.

4.1.2 Temperature Programmed Oxidation

After catalyst D₃-D₅ were operated under the same conditions for 8 reaction cycles. The spent catalyst was characterized by Temperature Programmed Oxidation (TPO) procedure. The amount of carbonaceous compounds oxidized being determined by quantification of the CO₂ formed (Bond et al., 1995). The TPO result was shown in Figure 4.4. Two coke burning zones were found which correspond to previous work (Parera et al., 1983, Barbier et al., 1985 and Reasaco et al., 1994). The first peak appears from burning temperatures 300 °C to 500 °C that match the burning of coke deposited on or near the metal site (Pt) and is efficiently catalyzed by the metal (Basso et al., 1991). The higher burning zone (500-700 °C) is due to more refractory coke deposited on the alumina support that is more polymerized and for which combustion is non-catalyzed. The difference in burning temperature zone depends on TPO conditions e.g. heating rate and concentration of oxidant gas. The area under the TPO profile can imply the coke amount on the catalyst (Lin et al., 1990).

The catalyst D₄ shows the highest aggregate of coke on the Pt site. At the same TPO conditions, the catalyst D₃ gives the highest amount of coke on the alumina support. However, the total amounts of coke are not much different. These agree with the propane conversion and dehydrogenation selectivity in section 4.1.1. Catalyst D₃ and D₄ have high propane conversion but lower selectivity in the 8th reaction cycle. These correspond to the increase in coking reaction path instead of desired reaction path on the catalyst.

Figure 4.1, 4.2 and 4.4 provide the information about the promoters (Sn) function. TPO shows the larger amount of coke on support of catalyst D₃ and D₄ and may be due to the migration of coke from the metal site. Propane conversion gives the same conversion order in all cycles. It can be implied that Sn still keeps its structure promoters function, inducing the coke to migrate to the alumina support, and consequently providing the clean active Pt sites, even with lower amounts of active metal sites. The changing of selectivity order in the last dehydrogenation and the higher coke on the metal site of catalyst correspond to the increase in unrecovered Pt active function. The inappropriate Pt landing position occurs in regeneration procedure after some agglomerated Pt can not be redispersed and blocks the migration path of the remaining active Pt.

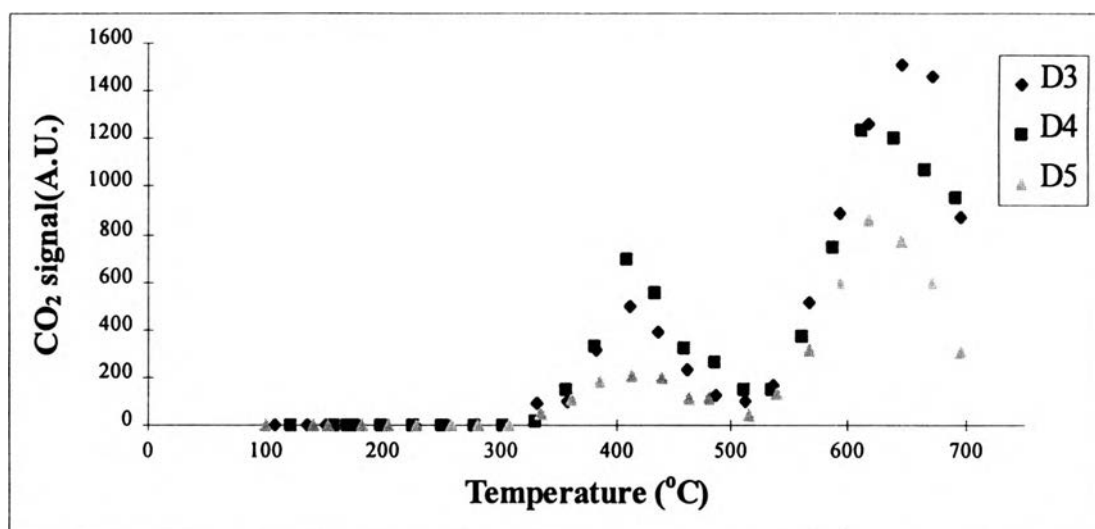


Figure 4.4 Temperature Programmed Oxidation profile of 8th cycle run catalyst

4.2 Coke partial regeneration

Catalyst D₃, D₄ and D₅ that had been coked for 8 hours in propane dehydrogenation reaction were characterized after processing in different decoking periods. Elementary Analyzer, Thermobalance and Fourier Transform Infrared (FTIR) Spectroscopy were used to investigate the partially regenerated catalyst.

Figure 4.5 shows the weight percentage of carbon remaining on the spent and partially regenerated catalysts. Spent catalyst D₅ have the highest carbon weight percentage, catalyst D₃ and D₄ have less carbon. The initial decoking rate is very high at the first 5 minutes of regeneration. After 5 minutes, the decoking rate in all types of catalyst goes down rapidly through the end of regeneration time (60 minutes). The high propylene selectivity in the first reaction cycle, figure 4.2, gives an explanation in the amount of coke deposits on the catalyst. Catalyst D₅, which has the lowest propane selectivity, also has the highest amount of coke.

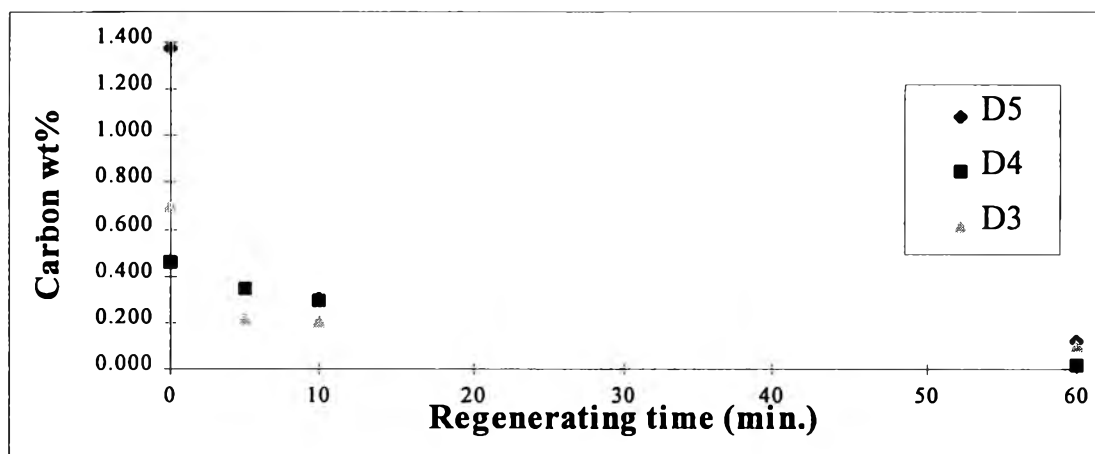


Figure 4.5 Carbon weight percentage of catalyst D₃-D₅ in different regenerating time.

The amounts of carbonaceous deposits on the spent and partially regenerated catalysts are also tested by the thermobalance. The spent 8 hour catalysts have 3 weight-loss zones in the thermobalance diagram. The first zone (appear within the temperature less than 150 °C) represents the loss of moisture in the catalyst pore. According to the TPO discussion in section 4.1 the second weight-loss zone (200-350 °C) and the third weight-loss zone (400-550 °C) shows the weight loss due to the combustion of coke deposits on the metal sites and alumina support, respectively. The coke remaining on the metal and support sites after partial regeneration are shown in Table 4.1.

The total coke amount was based upon the total removed coke from both metal and support sites. The order of total coke from this analyzer is the same as estimated from the Elementary analyzer ($D_5 > D_3 > D_4$).

All coke on the metal sites, different in initial amount, was completely removed within 5 minutes of regeneration and the coke deposits on the support sites continue to decrease. The coke on support of catalyst D₃ can be burnt faster than those of catalysts D₄ and D₅ respectively due to the effect of

promoter (Sn). The coke deposits on the alumina support require O₂ dissociative adsorption on the metal site and diffusion to the alumina to complete the combustion reaction. When metal alloy occur at high promoter (Sn) loading catalysts, the O₂ dissociation to the Pt atom were inhibited (Paffett et al., 1990)

Infrared spectroscopy has often been used to characterize the structure of the coke deposits (Rayo et al., 1994). Figure 4.6 a, b, c show FTIR (1200-1800 cm⁻¹) spectra of the original spent catalyst and the partially regenerated sample.

Table 4.1 The coke (investigated by the thermobalance in weight percentage) on metal site and alumina support of spent catalyst (Coke) and partially regenerated catalyst for 5 minutes (PAR5) and 10 minutes (PAR10). The N represents no coke remaining on the site

Type	Position	Initial coke	PAR5	PAR10
D ₅	Metal	0.6	N	N
	Support	0.8	0.3	0.1
D ₄	Metal	0.3	N	N
	Support	0.5	0.2	0.05
D ₃	Metal	0.3	N	N
	Support	0.7	0.1	N

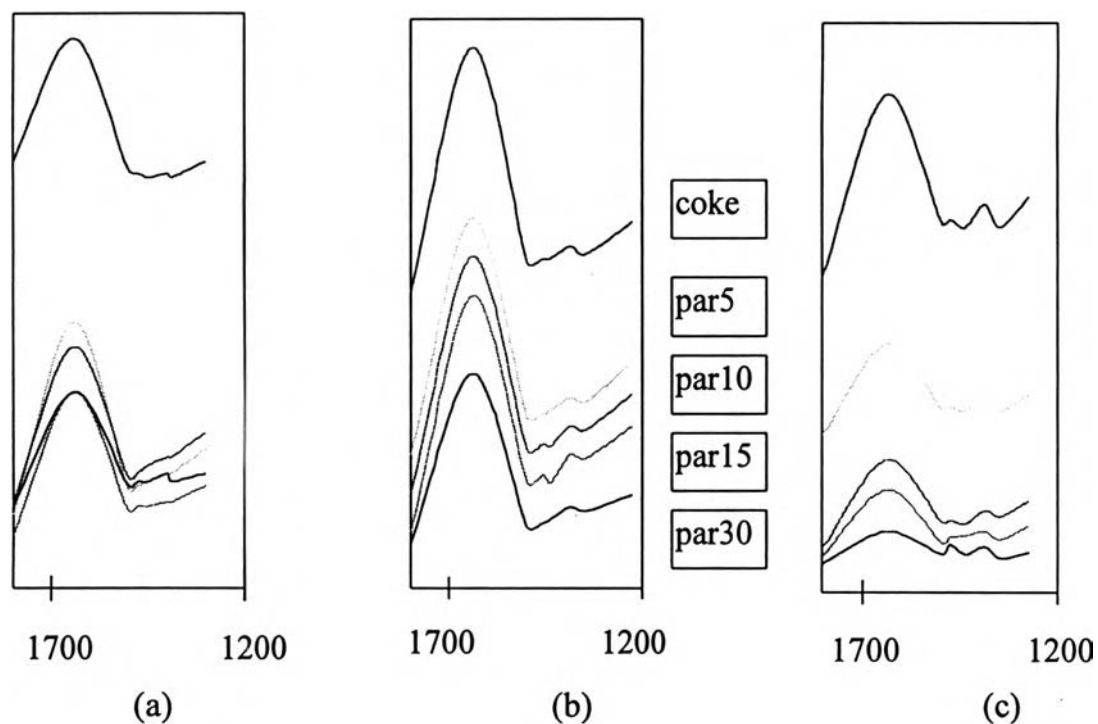


Figure 4.6 FTIR spectra of coke and partially regenerated catalyst in the aromatic carbon stretching zone and in the aliphatic bending zone (a) Catalyst D₃, (b) Catalyst D₄ and (c) Catalyst D₅

Using the computer software to give the same intensity to the peak at 1580-1680 cm^{-1} in all coked catalyst spectra in order to show as reference peak. The absorption band appears between 1580-1680 cm^{-1} referred to the stretching of the C=C bond belonging to aromatic rings, polyaromatics and olefins. The peak at about 1400 cm^{-1} represents the C-H bond stretching in C-(CH₃) or C-(CH₃)₂ groups (Parera et al., 1992). All catalyst types show the decrease in both aromatic and aliphatic bands. The catalyst D₅ show the highest change in both functional groups from spent catalyst to the first 5 minutes of partially regenerated catalyst. But the slower change occurs in the last 15 minutes of the partial regeneration procedure. Catalyst D₄ gives the consistent decreasing pattern in absorbance band through the minimum absorbance level. Catalyst D₃ shows the unchanged in aromatic carbon

stretching after passing 15 minutes regeneration time. The FTIR results can confirm the previous analysis about the decoking rate.

C=O and C-OH functional groups were not found by IR, may be due to the high coke burning temperature (500 °C). These intermediate groups were changed to the complete combustion product (Parera et al., 1992).

From catalyst characterizations, the role of promoter (Sn) in decoking procedure was established. The Elementary analyzer and thermobalance show the fast initial decoking rate and coke deposits on the metal sites were removed within 5 minutes regeneration time. The high burning temperature (500 °C) cause the coke burning process to behave like non-selective burning (Pieck et al., 1992). At the initial regenerating time, coke on both metal sites and alumina supports were burnt at the same time. The amount of coke removed on both sites present the total coke burning rate. However, coke deposits on the metal still burn in catalyzed condition, Pt-O form, (Basso et al., 1991) and give a fast decoking rate. At this period, Sn plays an unclear function due to the different amount of initial coke deposits. After coke on the metal sites was completely burnt off, the decoking rate only comes from coke that still was burning on the alumina supports. At this time (after 5 minutes regeneration), from all catalyst characterization procedures, the different amount of promoter (Sn) loading cause the different decoking rates. The metal (Pt) always surrounded by the significant amount of promoters (Sn) with the electrical interaction. The Sn in the higher Sn loading catalyst could block the O₂ diffusion path due to its geometric function.