CHAPTER V

RESULTS AND DISCUSSIONS

In this chapter, the results and discussions are classified into two major parts. Firstly, characterization of the prepare catalyst, zeolite Y and metal catalysts which are analysed by XRD, AAS, CO adsorption and FT-IR pyridine adsorption. The description is explained in section 5.1. Second, catalytic activity of metal catalysts on the oxidative methane coupling is explained in section 5.2.

5.1 Catalyst characterization

5.1.1 X-ray Diffraction (XRD)

X-ray Diffraction is a technique which can identify the crystal structure. Figure 5.1 illustrates the reference XRD spectrum of zeolite Y(NaY) commercial that used as reference. The XRD spectrum of NaY zeolite prepared in this research laboratory is show in figure 5.2 and will corresponding to XRD spectrum in figure 5.1. This indicates that the structure of prepared NaY zeolite is similar to that of the reference. Figure 5.3. displays the XRD spectrum of HY zeolite. In the same way this spectrum is not different from the reference. It is evident that the H form of zeolite Y does not significantly change the main structure of zeolite.

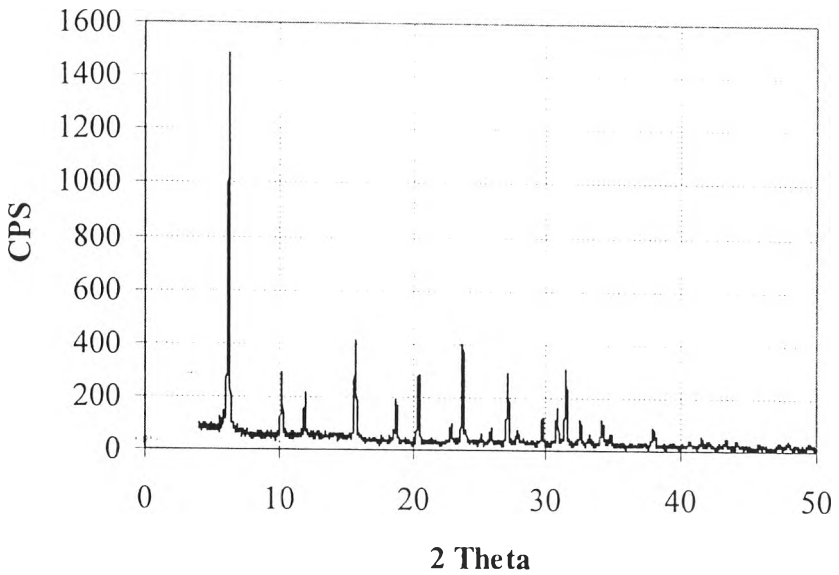

Figure 5.1. X-ray diffraction pattern of commercial NaY (JRC-Z-Y)

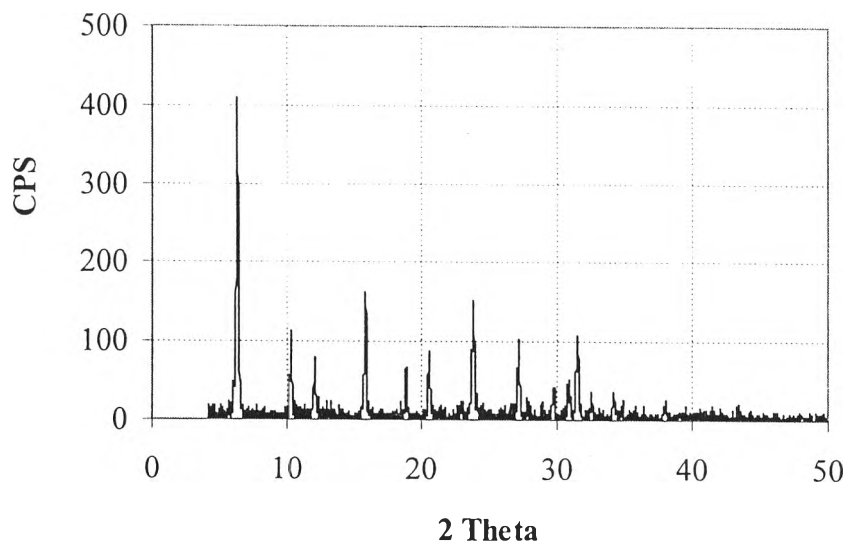

Figure 5.2. X-ray diffraction pattern of NaY

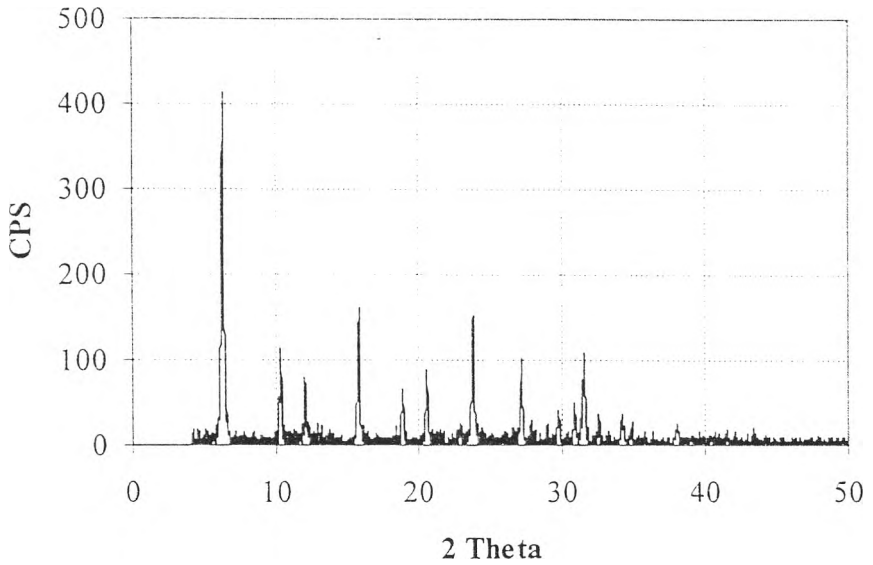

Figure 5.3. X-ray diffraction pattern of HY

5.1.2 Determination of composition content of catalyst

The results of metals loading on zeolite Y are determined by AAS which are summarized in table 5.1

Table 5.1 The compositions of Catalysts

Catalyst	% metal
10%Co/NaY_w[a]	8.60
10%Co/NaY	7.18
10%Co/HY	0.21
15%Pt/HY	3.10

[a]This catalyst was prepared by wet impregnation method.

5.1.3 CO adsorption

The results of metals catalysts from CO adsorption technique are present in Table 5.2

Table 5.2 The metal active sites of metal catalysts

Catalyst	Metal active sites (molecules CO/ g_{cat})
10%Co/NaY_w	3.86×10^{18}
10%Co/NaY	1.49×10^{18}
10%Co/HY	1.25×10^{18}

5.1.4 FT-IR pyridine adsorption

Figures 5.4 to 5.6 illustrate the relevant region of IR spectrum after exposure to pyridine as a function of temperature of evacuation on 10%Co/NaY_w, 10%Co/NaY and 10%Co/HY respectively. Admission of pyridine resulted in the appearance of a number of bands in the region of interest, between 1300 – 1700 cm^{-1}. The appearance of bands at 1540 and 1450 cm^{-1} demonstrates the presence of Brönsted and Lewis acid sites respectively[Tanabe *et al.*(1989)].

A number of changes are observed on evacuation when increasing temperature. After evacuation between room temperature and 500°C, a gradual reduction in the intensity of the pyridine bounds both at Lewis and Brönsted sites appeared.

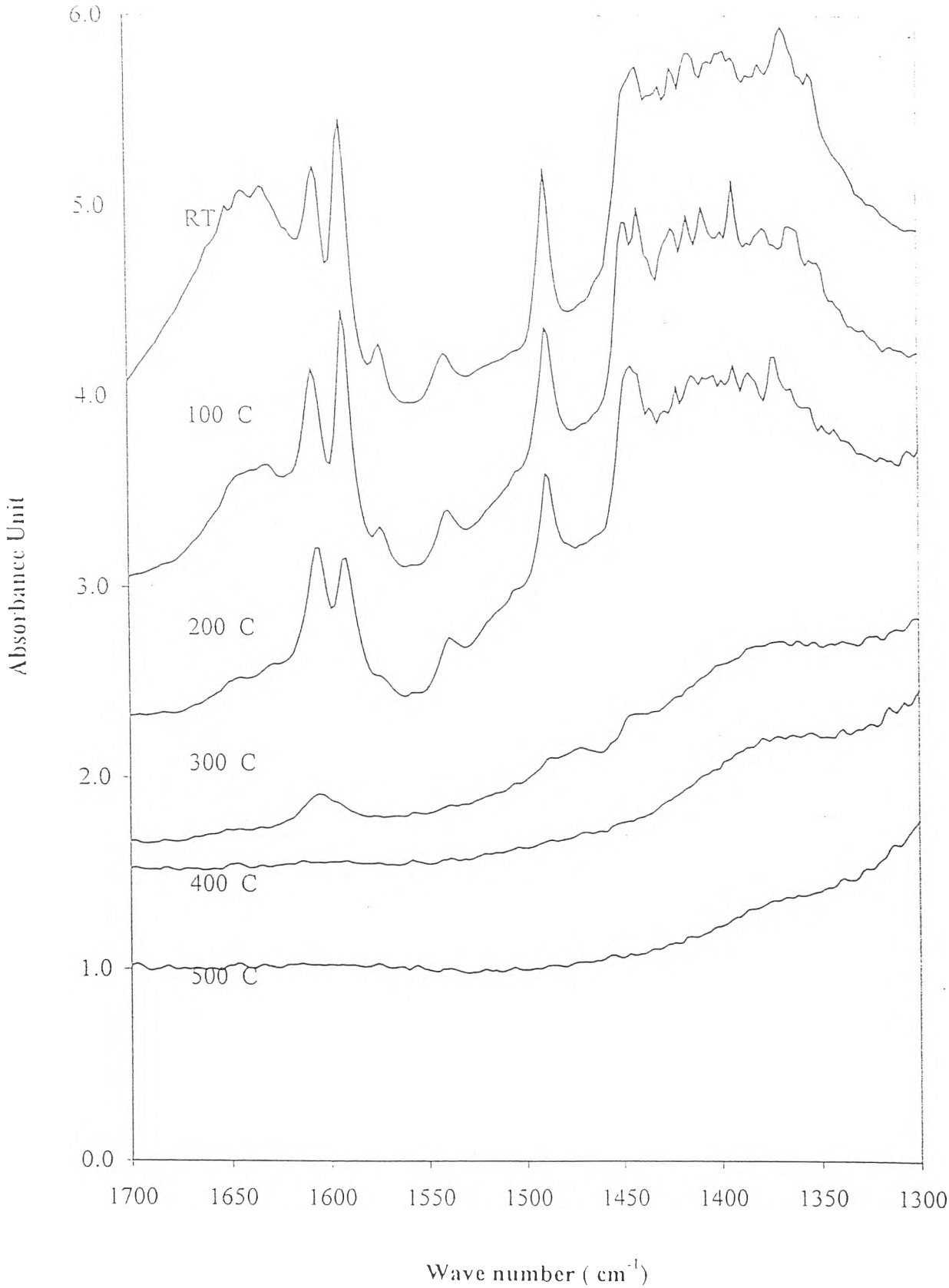

Figure 5.4 IR spectrum of 10%Co/NaYw

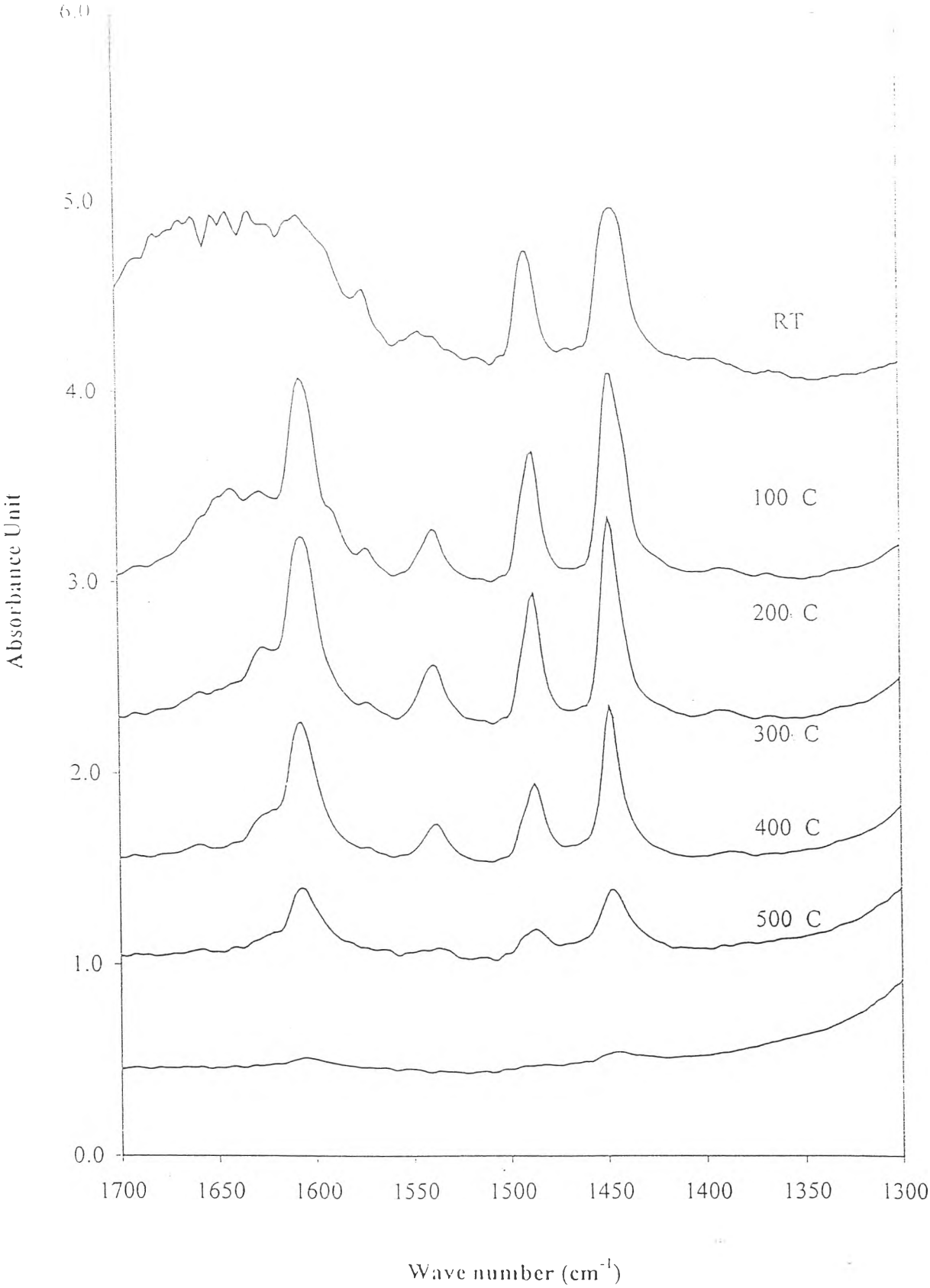

Figure 5.5 IR spectrum of 10% Co/NaY

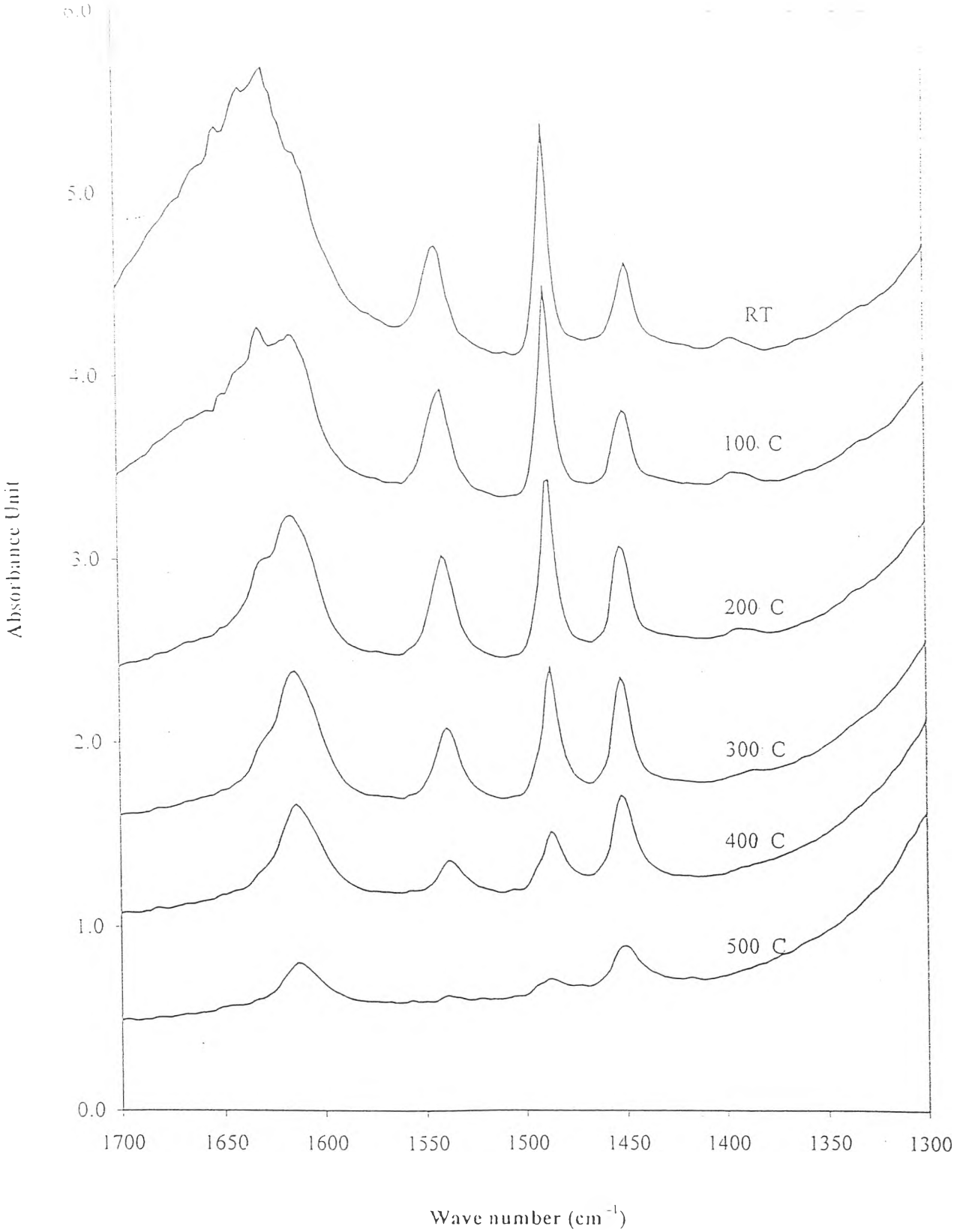

Figure 5.6 IR spectrum of 10%CoHY

The IR spectra of these catalysts identify that the intensity of Brönsted acid of 10%Co/HY is higher than 10%Co/NaY and 10%Co/NaY_w while the highest of Lewis acid intensity is belong to 10%Co/NaY. In the case of the strength of both acid sites the strength of 10%Co/HY is higher than that of 10%Co/NaY and 10% Co/NaY_w because at 500°C the band of both acid sites of 10%Co/HY still remain at 500°C. In contrast, the band of both acid sites of 10%Co/NaY disappear. For 10% Co/NaY_w, peak of both acid sites vanish at 300°C.

5.2. Catalytic Reaction

In this section, the catalytic property of metal catalysts prepare in this research is investigated by testing the non-oxidative methane coupling. The step of reaction can be suggested that methane was decomposed to adsorbed species at the first.

$$CH_{4(g)} \longrightarrow CH_{3(a)} + H_{(a)} \quad (1)$$

$$CH_{3(a)} \longrightarrow CH_{2(a)} + H_{(a)} \quad (2)$$

$$CH_{2(a)} \longrightarrow CH_{(a)} + H_{(a)} \quad (3)$$

$$CH_{(a)} \longrightarrow C_{(a)} + H_{(a)} \quad (4)$$

$$2H_{(a)} \longrightarrow H_{2(g)} \quad (5)$$

Where (a) and (g) are active sites and gas phase, respectively [Solymosi *et al.*(1994)]. After that the adsorbed species may coupling to the surface carbon species such as the vinylidene (CCH_2) species and ethylidene (CCH_3) species. Finally, the surface carbon species were hydrogenated to ethane and propane in the hydrogenation step [Lenz-Solomun *et al.*(1994)]. Furthermore, the species CH_3 and CH_2 were hydrogenated to methane [Solymosi *et al.*(1994)].

The results were reported as the amount of methane adsorbed (mole/g_{cat}) on the methane adsorption step. In the same may methane, ethane and propane produced in hydrogenation step were presented as mol/g_{cat}.

5.2.1. The effect of catalyst preparation method

The 10%Co/NaY used in this investigation was prepared by wet impregnation and ion exchange method. The results of the amount of methane adsorbed and products, methane and propane, are illustrated in table 5.3, figures 5.7 and 5.8, respectively.

The amount of methane adsorbed on the 10%Co/NaY that was prepared by wet impregnation method is higher than the other. It is supported by the results of metal active sites displaying in Table 5.2 , the 10%Co/NaY_w is higher. It can explain that the methane chemisorption occur on metal sites[Belgued *et al.* (1992), Koerts *et al.* (1992) and Wang *et al.* (1993)]. The amount of methane adsorbed of the 10%Co/NaY_w is higher. Furthermore, the amount of methane produced on hydrogenation step, figure 5.7, is more than 10%Co/NaY. On the other hand the amount of propane occurred in the reaction is lower than the other as predicted in figure 5.8. At the beginning of reaction, 0-20 min, the amount of propane on the 10% Co/NaY prepared by ion exchange method is zero. After that it increases rapidly to 2.90×10^{-20} mol/g_{cat} at 30 min and then decrease to zero at 40 min. It remains at zero until reaction time is 70 min. The amount of propane rises to 4.44×10^{-20} mol/g_{cat} at 80 min but at 90 min; it drops to zero again.

The catalytic activity of the 10%Co/NaY_w is similar to 10%Co/NaY but the amount of propane in lower. The results of FT-IR pyridine adsorption in figure 5.4 and 5.5 show that the number of Brönsted and Lewis acid on 10%Co/NaY is higher than the other. From previous results , it can be suggested that the catalytic activity depend on the metal sites and acid sites of catalyst. This catalyst is called bifunctional catalyst that was explained in Chapter III. Conclusionly, the catalytic activity of ion exchange catalyst in higher than wet impregnate catalyst.

Table 5.3 The amount of methane adsorbed on 10%Co/NaY and 10%Co/NaY_w

Catalyst	CH_4 adsorbed (mol/g_{cat})
10%Co/NaY	0.0104
10%Co/NaY_w	0.0513

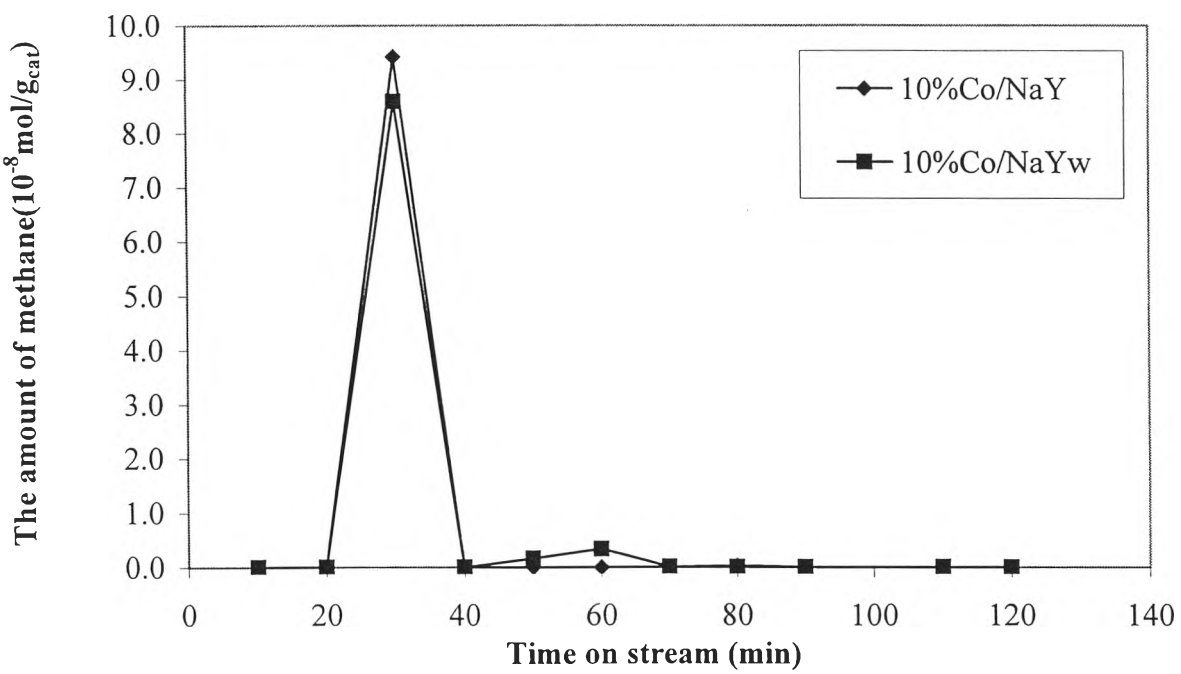

Figure 5.7 The amount of methane produced on 10%Co/NaY and 10%Co/NaY_w as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 300 °C.

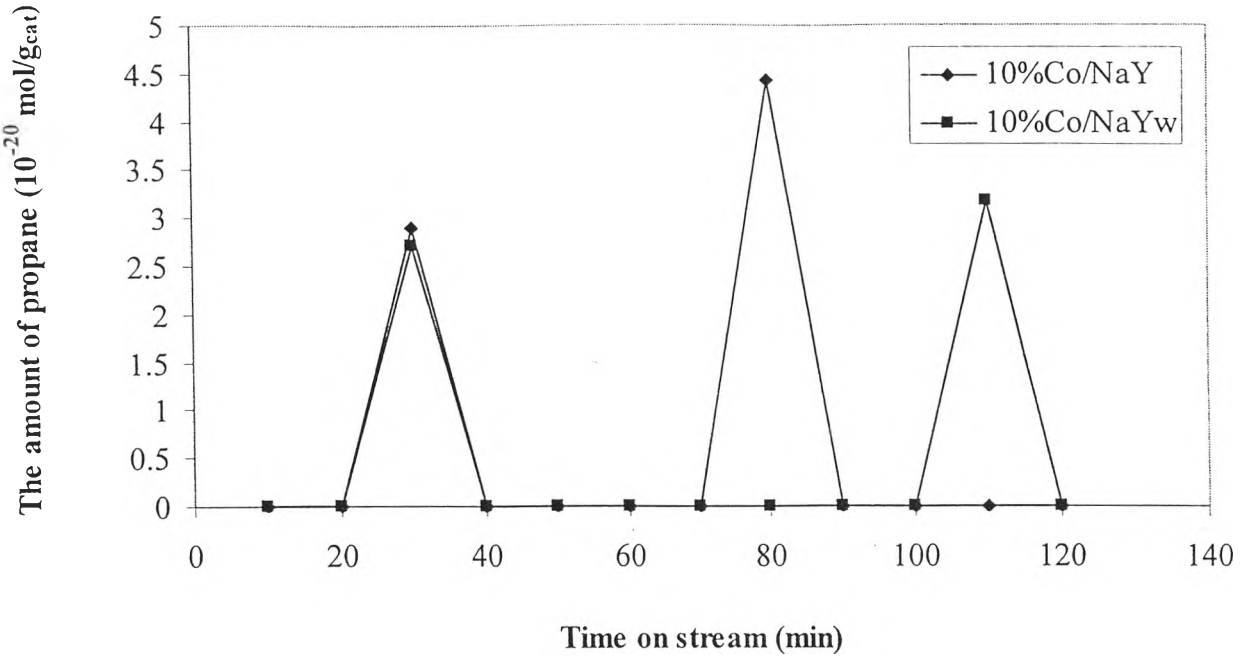

Figure 5.8 The amount of propane produced on 10%Co/NaY and 10%Co/NaY_w as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 300 °C.

5.2.2 The effect of Na-form (NaY) and H-form (HY)

Both forms of zeolite Y prepared by ion exchange with 10% cobalt were used on the non-oxidative methane coupling to study the effect of form of zeolite Y. The amount of methane adsorbed on 10%Co/HY is much more than 10%Co/NaY while the amount of methane produced is less than 10%Co/NaY, see table 5.4 and figure 5.9. Figure 5.10 indicates that at the initial time (2-30 min) the amount of propane produced on 10%Co/HY increases gradually from 0.6×10^{-19} mol/g_{cat} upto 1.44×10^{-19} mol/g_{cat}. After that it decreases slightly to 9.8×10^{-20} mol/g_{cat}. On the other hand the pattern of curve for 10%Co/NaY is similar to 10%Co/HY but the amount of propane is very lower.

Refer to table 5.2, figures 5.5 and 5.6, the metal sites of 10%Co/NaY is higher than the other while the amount of Bronsted and Lewis acid is lower. It can be suggested that methane was adsorbed on metal and acid sites [Loratsachan (1998)]. As a result 10%Co/HY gives higher the amount of methane adsorbed. Furthermore, the catalysts for non-oxidative methane coupling are necessary bifunctional catalyst that was explained in section 3.1.2.2. It can be concluded that H-form catalyst is better than Na-form catalyst.

Table 5.4 The amount of methane adsorbed on 10%Co/NaY and 10%Co/HY catalysts

Catalyst	CH_4 adsorbed (mol/g_{cat})
10%Co/NaY	0.01
10%Co/HY	3.49

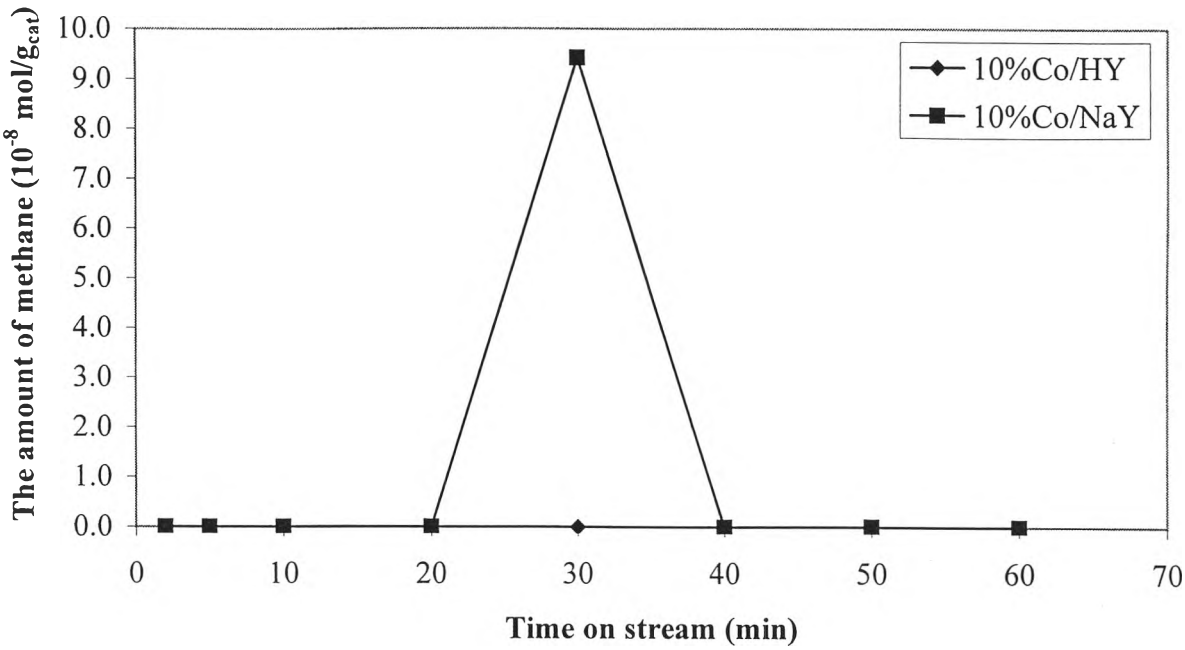

Figure 5.9 The amount of methane produced on 10%Co/HY and 10%Co/NaY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 300 °C.

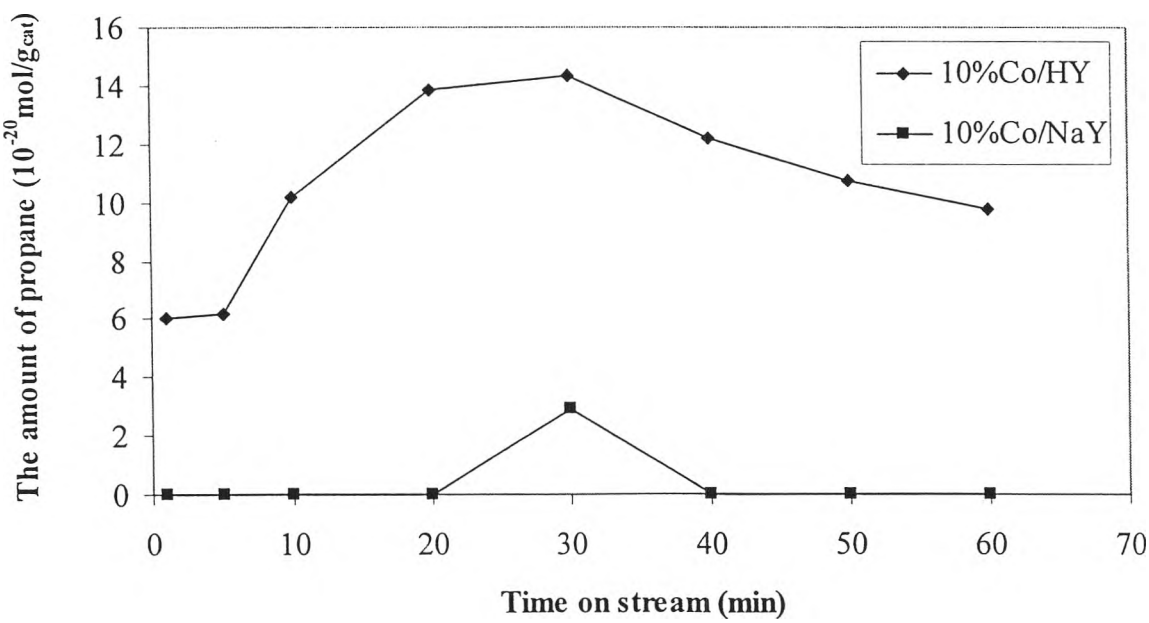

Figure 5.10 The amount of propane produced on 10%Co/HY and 10%Co/NaY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 300 °C.

5.2.3 The effect of the amount of metal loading

Co, Ru and Pt are transition metals used for preparation of metal catalysts in this research. The effect of the amount of metal loading is investigated in this section which each metal loading in HY was prepared by ion exchange method.

5.2.3.1 The amount of Co loading

The amount of Co loading in HY is varies as 5% ,10% and 15% . The effect of catalytic activity to non-oxidative methane coupling is shown in table 5.5, figures 5.11 and 5.12.

The amount of methane produced on 15%Co/HY, figure 5.11, is higher than the others. From figure 5.12, it is founded that among three catalysts, the 10%Co/HY catalyst give the maximum amount of propane. With this catalyst, the amount of propane increases slightly to a broad maximum of about 1.44×10^{-12} mol/g_{cat} at 30 min before declining to 9.8×10^{-20} mol/g_{cat} at 60 min.

On the other hand, 5%Co/HY and 15 %Co/HY catalysts give much lower amount of propane than 10%Co/HY catalyst. Additionally, 10%Co/HY has also the maximum amount of methane adsorbed that is supported by the metal active sites in table 5.5. From the above results, it is concluded that the appropriate percentage of cobalt is 10%.

Table 5.5 The amount of methane adsorbed on Co/HY catalyst

Catalyst	Metal active sites (molecules CO/g_{cat})	CH_4 adsorbed (mol/g_{cat})
5%Co/HY	5.23×10^{17}	7.60×10^{-3}
10%Co/HY	1.25×10^{18}	3.49
15%Co/HY	4.61×10^{17}	4.48×10^{-10}

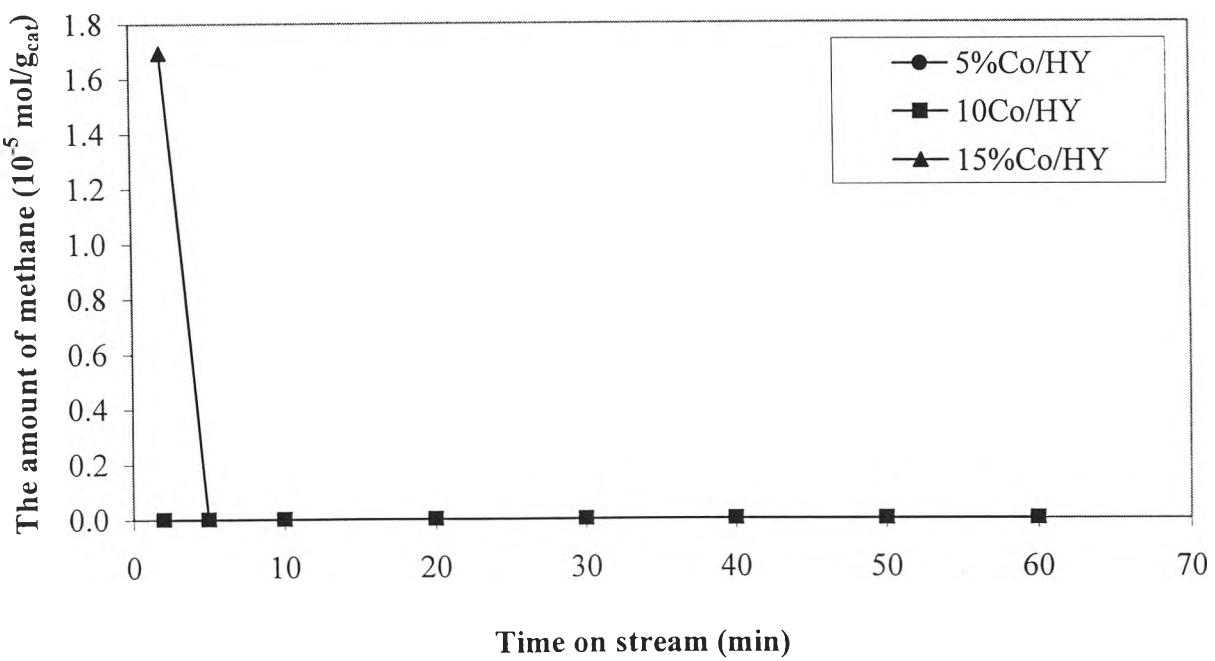

Figure 5.11 The amount of methane produced on Co/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 300 °C.

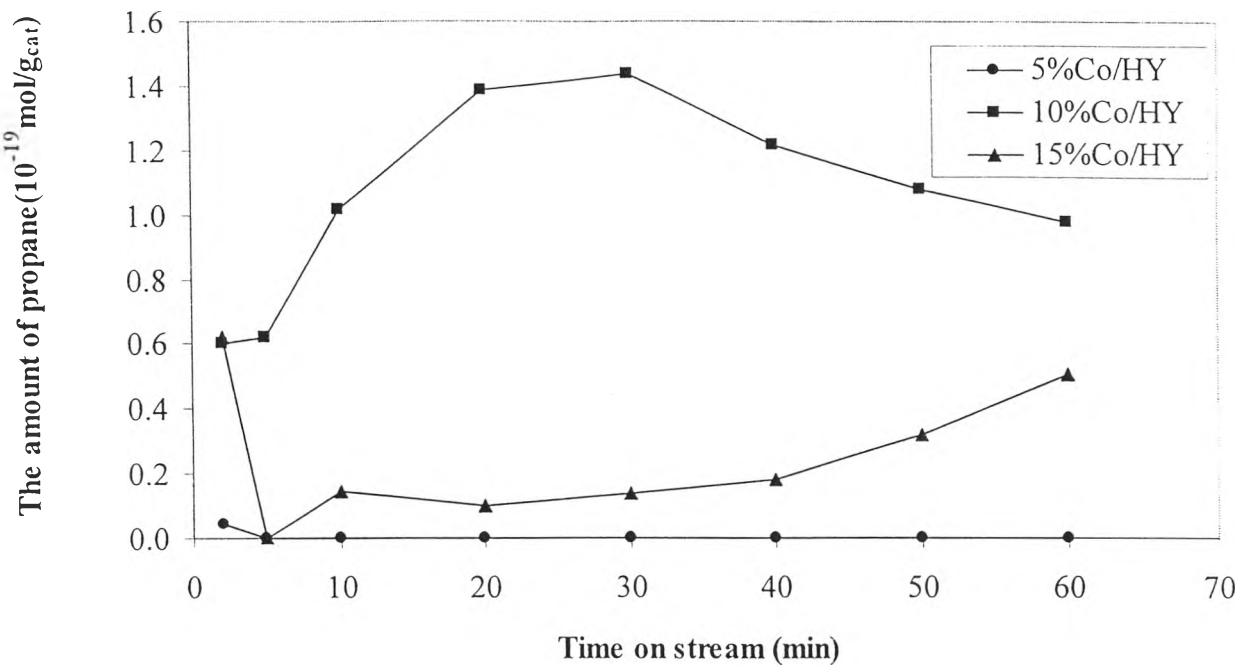

Figure 5.12 The amount of propane produced on Co/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 300 °C.

5.2.3.2 The amount of Ru loading

The metal catalysts prepared from Ru have a different metal loading as 10%, 15% and 20% . When they were tested for the non-oxidation methane coupling, it is clear that methane, ethane and propane as products are detected. Unlike Co/HY catalyst, methane and propane are produced.

The amount of methane adsorped and the metal active sites for three different metal loading catalysts are summarized in table 5.6. Figure 5.13 shows that the amount of methane produced on 20%Ru/HY is higher than the others. The 15%Ru/HY is seen to be the best catalyst for adsorbing methane. Moreover, this catalyst can produce ethane much more than both the 10%Ru/HY and 20%Ru/HY as shown in figure 5.14. It is elucidated that the maximum amount of ethane is 8.4×10^{-7}mol/g_{cat} and occur at 2 min. After that ethane decrease gradually and become

7.15×10^{-9} mol/g_{cat} at 60 min. Similar behavior was obtained with both the 10%Ru/HY and 20%Ru/HY . Figure 5.15 demonstrates the amount of propane produced in non-oxidative methane coupling. In the case of the 10%Ru/HY, propane increases dramatically in the first region of reaction time, 0-20 min, and the maximum of propane is 9.45×10^{-20} mol/g_{cat} occurring at 20 min. Subsequently, it drops rapidly to zero at 30 min and then rises slightly to 5.15×10^{-20} mol/g_{cat} at 60 min. In the case of the others, the general pattern of curves of the 15% and 20%Ru/HY is the same as that of the 10%Ru/HY. However the only difference between the curve of the 10%Ru/HY and the curves of the others is that a lower propane occurs with the latter catalyst.

From the above results, it can be conclude that the suitable percentage of ruthenium is 15 %

Table 5.6 The amount of methane adsorbed on Ru/HY catalyst

Catalyst	Metal active sites (molecules CO/g_{cat})	CH_4 adsorbed (mol/g_{cat})
10%Ru/HY	1.32×10^{19}	1.05
15%Ru/HY	5.01×10^{19}	3.39
20%Ru/HY	1.02×10^{19}	0.35

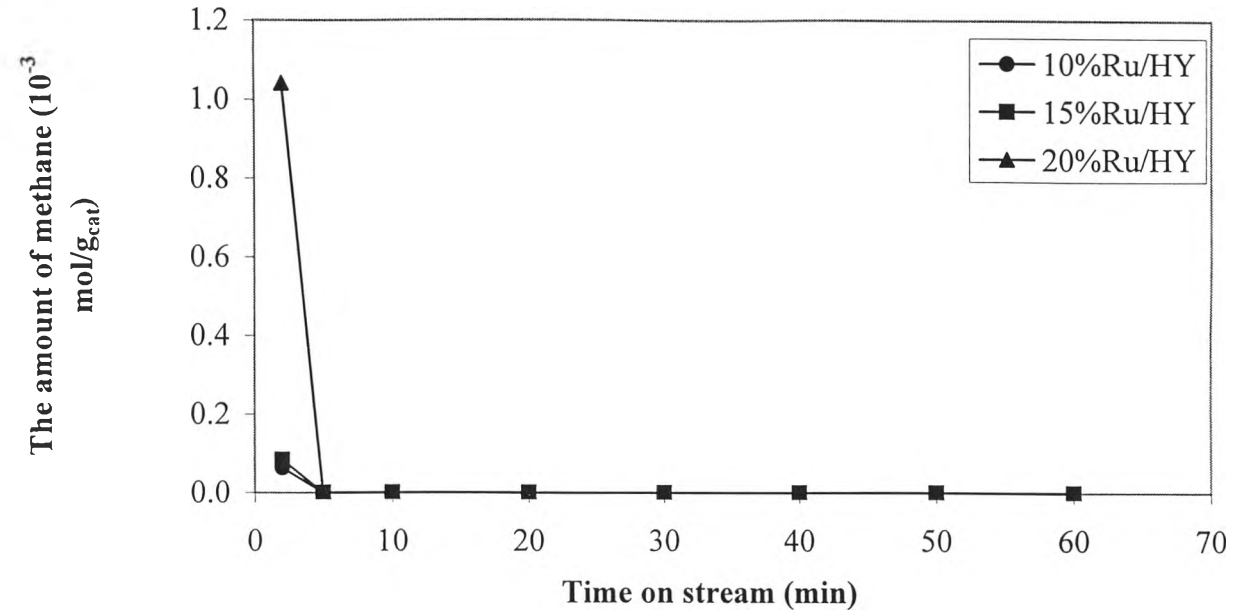

Figure 5.13 The amount of methane produced on Ru/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 200 °C.

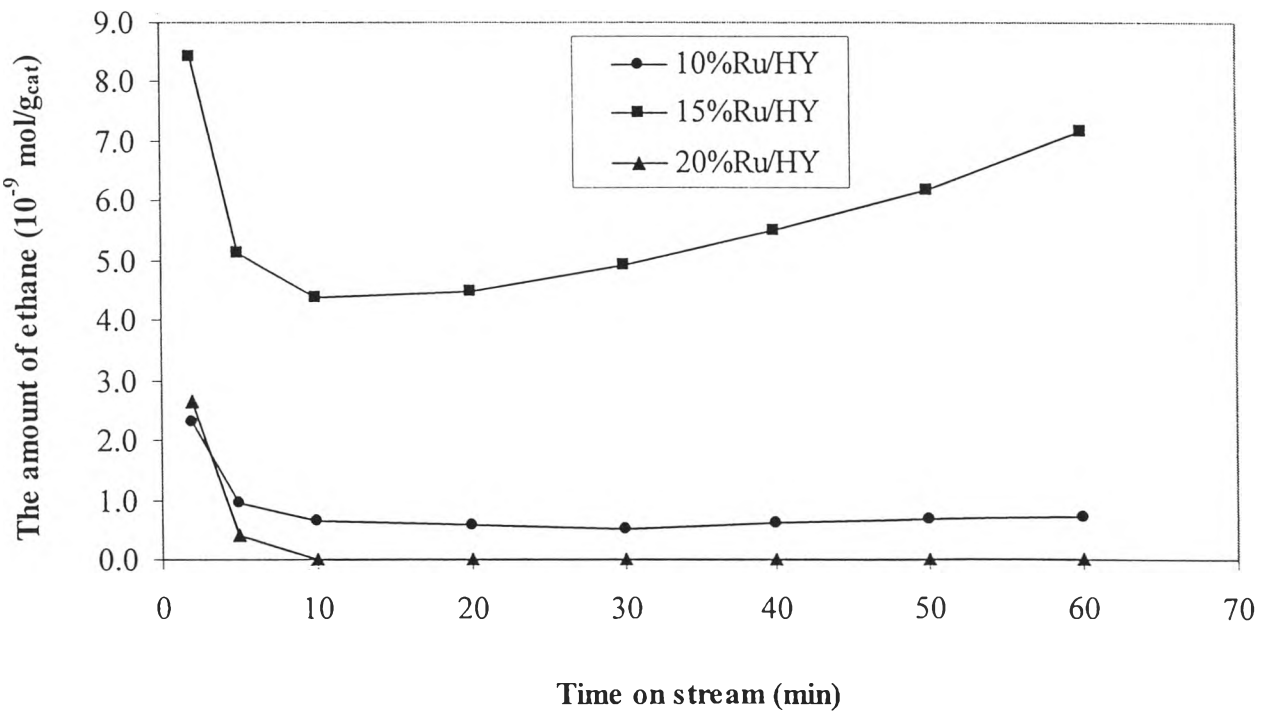

Figure 5.14 The amount of ethane produced on Ru/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 200 °C.

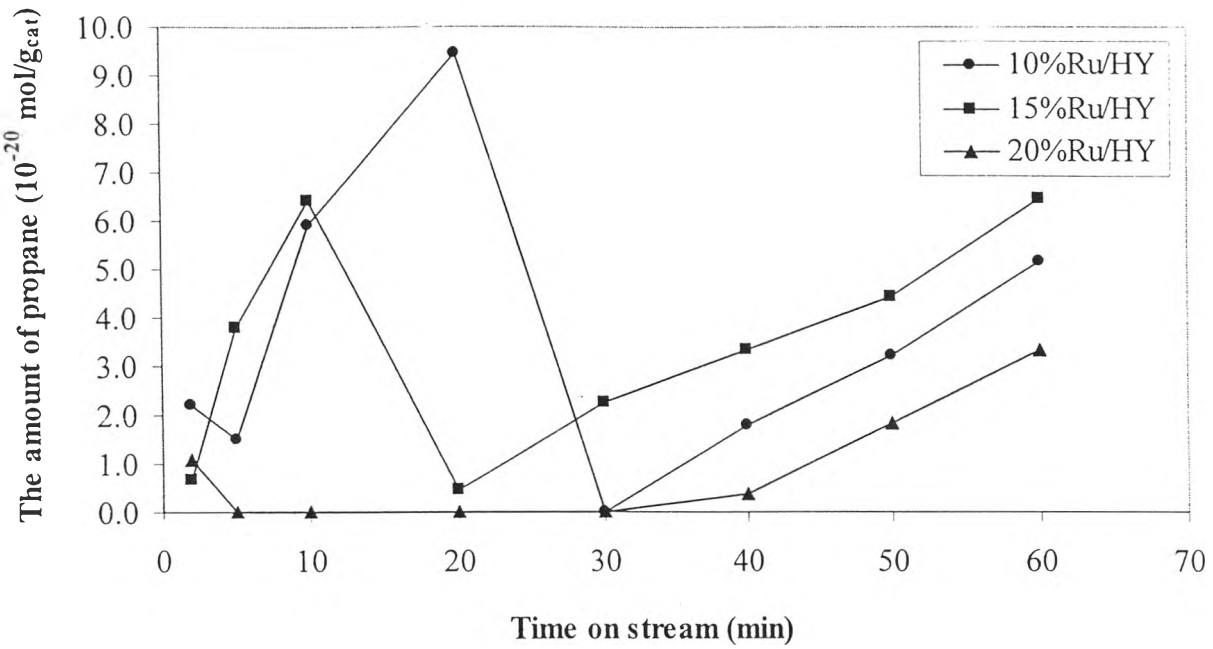

Figure 5.15 The amount of propane produced on Ru/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 200 °C.

5.2.3.3 The amount of Pt loading

The amount of Pt loading in HY zeolite is set to as 10%, 15% and 20%, like that of Ru loading. With these catalysts, it significant that the major difference between the Pt/HY and either Co/HY or Ru/HY is that ethane is produced in methane adsorption step with former catalyst. Table 5.7 give also the amount of ethane occurring in this step. Figures 5.16, 5.17 and 5.18 indicate the amount of methane, ethane and propane produced in hydrogenation step

It is clearly seen that the 15%Pt/HY gives the maximum amount of adsorbed methane, the metal active sites and emits the most ethane as shown in table 5.7. Figure 5.16 presents the amount of methane adsorbed, on 10% Pt/HY is higher than the others. Figure 5.17 exhibits the amount of ethane produced in hydrogenation step as a function with reaction time. It is found that the 15%Pt/HY give the amount of ethane more than the others. As reaction time is 2 min, the maximum amount of

ethane is detected to be 1.76×10^{-18} mol/$g_{cat.}$ After that ethane decreases substantially to zero at 5 min and is constant at this value until the reaction time as 60 min. The 10%Pt/HY and 20%Pt/HY show the pattern of curve to be similar to the 15%Pt/HY. Propane produced on the 15%Pt/HY is more than that produced on the other in the first region of reaction time, 0-5 min, and the maximum amount of propane become 3.51×10^{-19} mol/g_{cat} at 2 min. Subsequently, it decreases to zero at 10 min and then it increases gradually to $4.8\text{x}10^{-21}$ mol/g_{cat} at 60 min. Hence, at 20 min, the 20%Pt/HY give the amount of propane lower than the 15%Pt/HY which at 5-60 min, the oppoate is observed, However, in both these reaction time regions, the 10%Pt/HY give the lowest amount of propane.

It is concluded from all experiment results that the most suitable catalyst becomes 15%Pt/HY.

Table 5.7 The amount of methane adsorbed and ethane evolved on Pt/HY catalyst

Catalyst	Metal active sites (molecules CO/g_{cat})	CH_4 adsorbed (mol/g_{cat})	C_2H_6 (mol/g_{cat})
10%Pt/HY	1.04×10^{19}	0.0062	-
15%Pt/HY	1.51×10^{19}	0.50	3.57×10^{-18}
20%Pt/HY	1.07×10^{19}	0.03	-

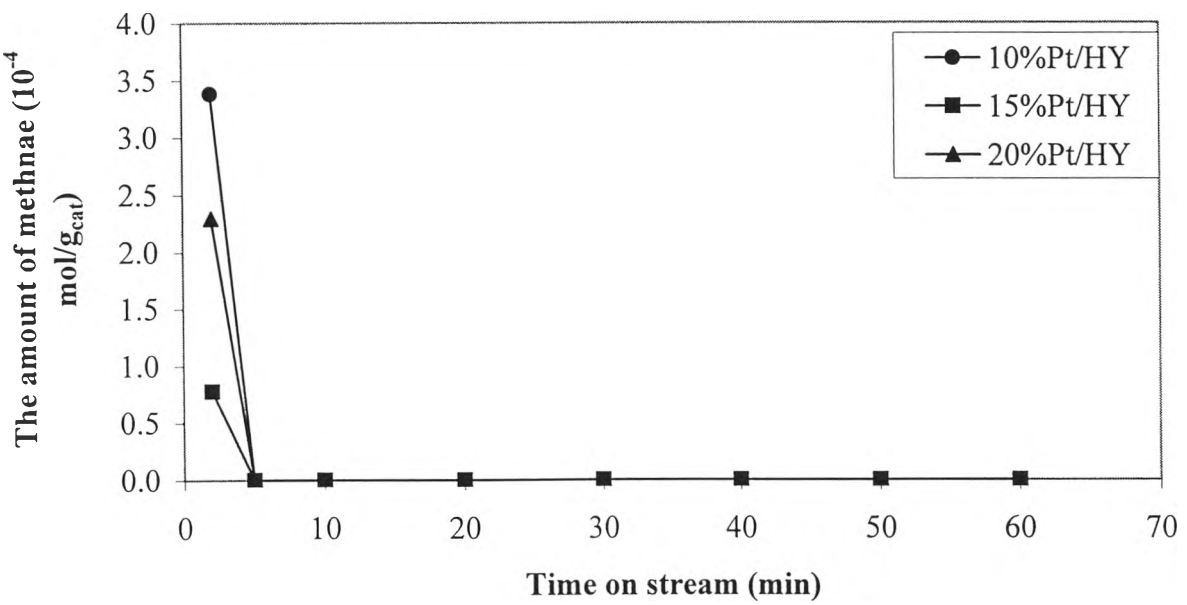

Figure 5.16 The amount of propane produced on Pt/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 200 °C.

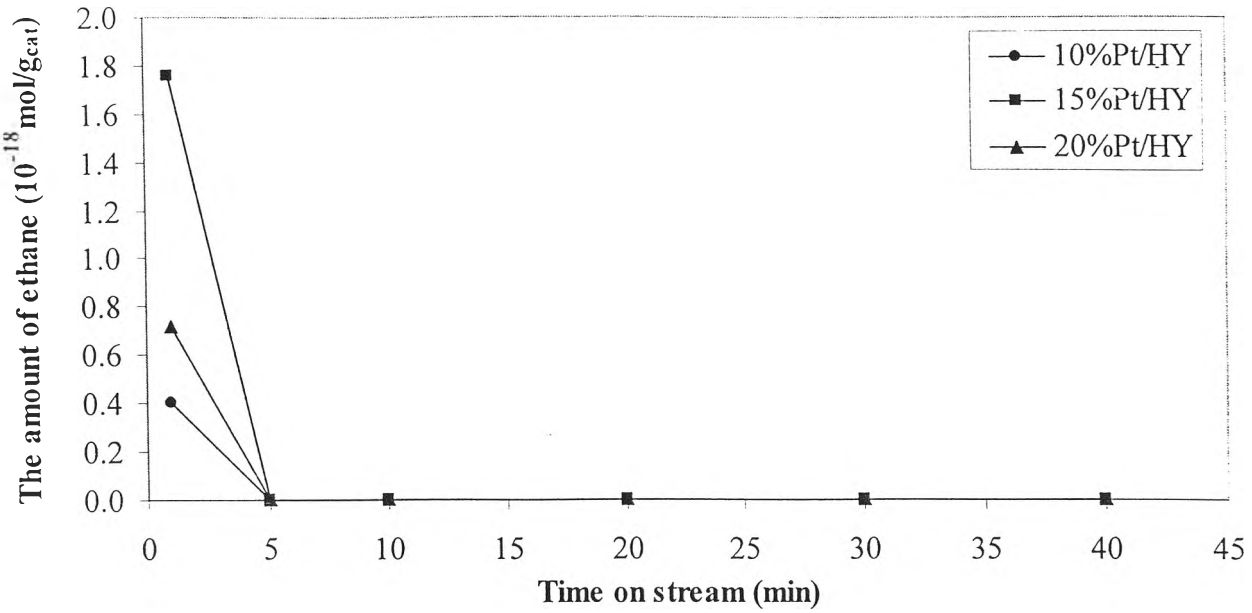

Figure 5.17 The amount of ethane produced on Pt/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 200 °C.

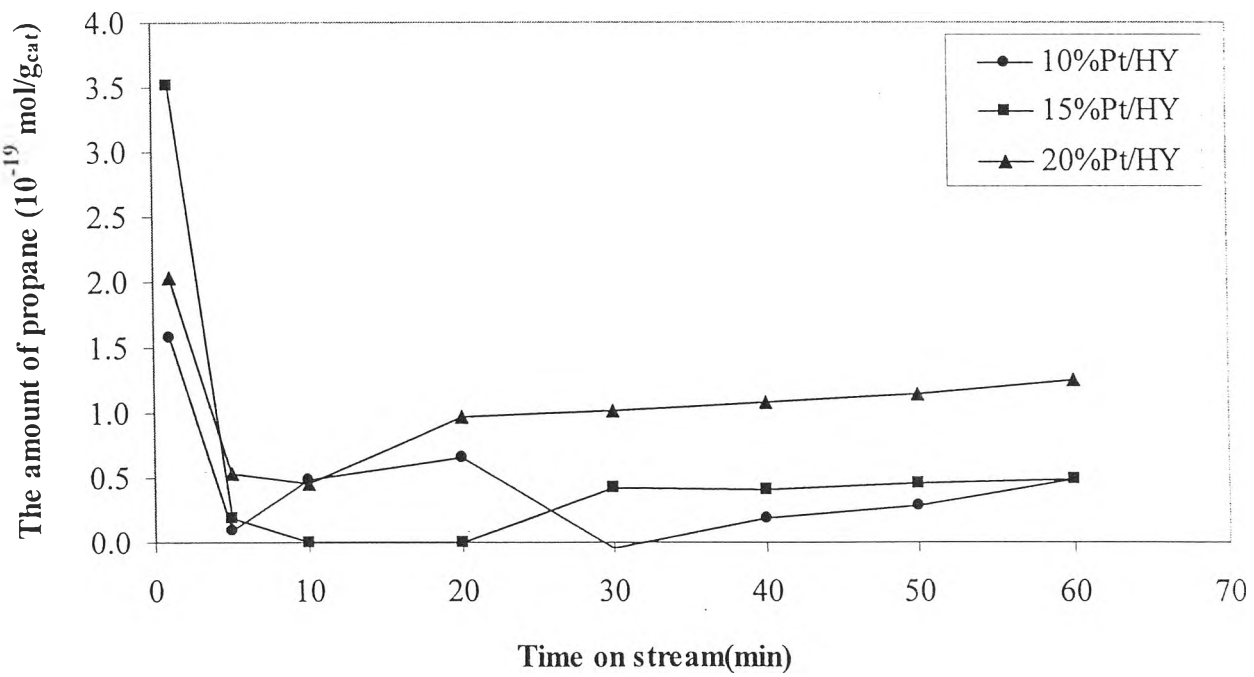

Figure 5.18 The amount of propane produced on Pt/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. Reaction temperature : 200 °C.

5.2.3.4 Discussion

There is the best percentage metal loading for each catalyst. It is clearly seen that the catalytic activity decreases when the percentage metal loading is higher or lower than the appropriate value. It can be explained that the lower metal loading gives a small amount of metal sites. On the other hand, the amount of metal is so high in a upper metal loading and it can be suggested that pore sites of catalyst are covered with the clustering of metal atoms. So, the amount of metal sites is decline that were shown in tables 5.5, 5.6 and 5.7.

5.2.4 The effect of reaction temperature

The reaction temperature is one of the important variable which affects significantly catalytic activity of metal catalysts. In order to find the optimum temperature for operating each catalyst, the further set of experiment about the effect of reaction temperature to catalytic activity is observed by using three different metal catalyst, i.e. 10%Co/HY, 15%Ru/HY and 15%Pt/HY.

5.2.4.1 The effect of reaction temperature on 10%Co/HY

The reaction temperature used for testing in this section is set as 200, 300 and 400°C. The catalytic activity of the 10%Co/HY at different temperature is summarized in table 5.8, figures 5.19 and 5.20.

It is observed that 10%Co/HY having the maximum amount of methane adsorbed become 3.49 mol/g_{cat} at 300°C as shown in table 5.8. In hydrogenation step, the amount of methane and propane produced at different temperature against reaction time is indicated in figure 5.19 and 5.20, respectively. Figure 5.20 shows the pattern of curves for 10%Co/HY at all temperatures has almost similarity. Using the reaction temperature as 300°C , the amount of propane increases slowly with increasing reaction time until the maximum amount of propane, 2.79×10^{-19} mol/g_{cat}, is reached at 60 min. Although the amount of methane adsorbed on 200°C as same as 400°C, the amount of propane produced is higher. Since, the amount of methane produced on 400°C much more than 200°C that was shown in figure 5.19. It is concluded that the

optimum temperature for operating 10%Co/HY on the non-oxidative methane coupling is around 300°C

Table 5.8 The amount of methane adsorbed on 10%Co/HY catalyst

Reaction temperature (°C)	CH_4 adsorbed (mol/g_{cat})
200	0.04
300	3.49
400	0.05

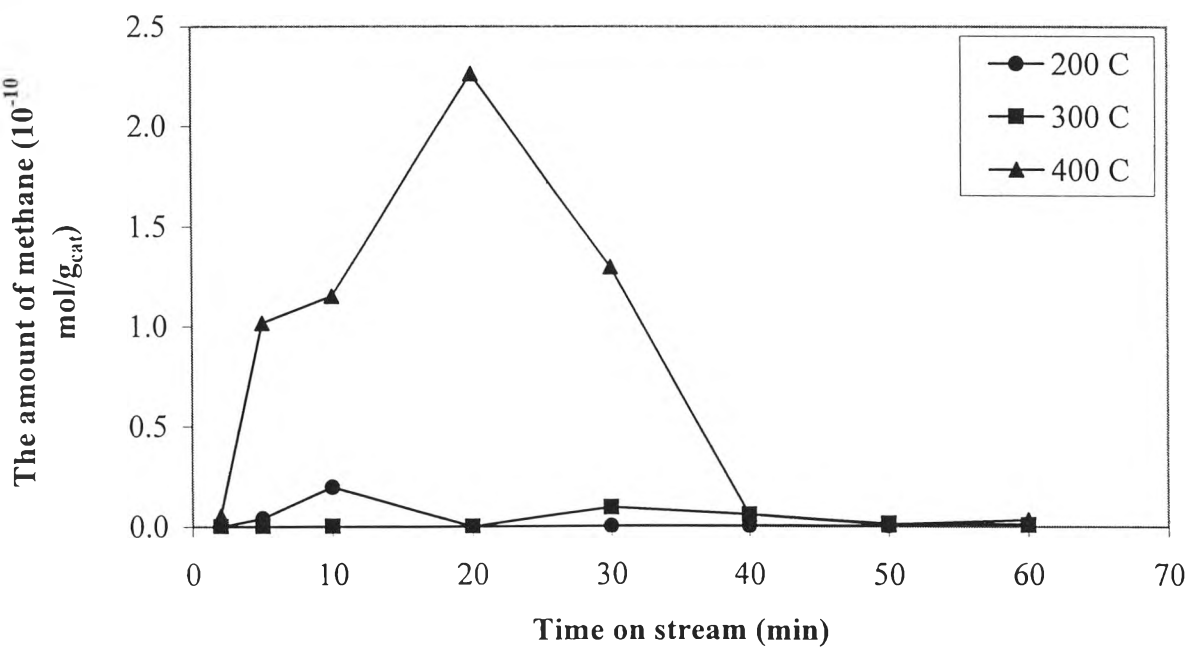

Figure 5.19 The amount of methane produced on 10%Co/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}.

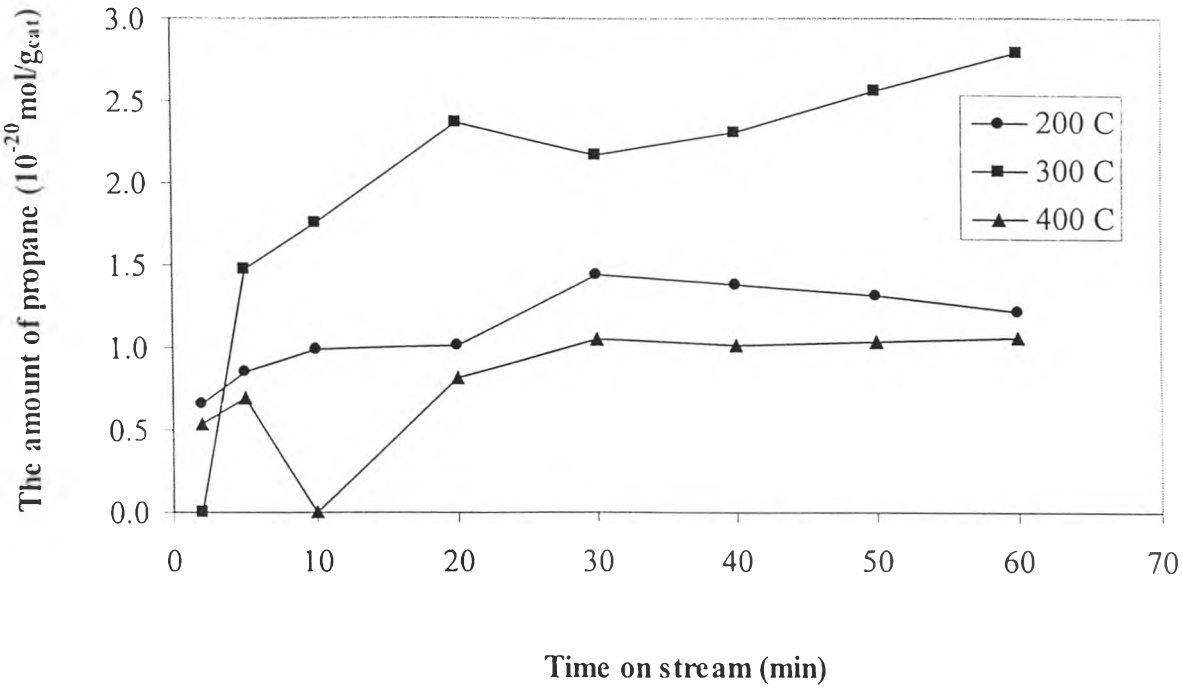

Figure 5.20 The amount of propane produced on 10%Co/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}.

5.2.4.2 The effect of reaction temperature on 15%Ru/HY

In this section, the effect of reaction temperature on 15%Ru/HY is investigated to obtain the optimum temperature for operating 15%Ru/HY on the non-oxidation methane coupling using temperature as 100, 200 and 300°C.

The coincident occurrence of the maximum amount of methane adsorbed, that of ethane and propane produced from hydrogenation step indicated in table 5.9, figures 5.22 and 5.23, respectively , is observed at 200°C. At this temperature, 8.4×10^{-9} mol/g_{cat} of ethane is produced at 2 min and then it fall gradually with increasing reaction time until it become 7.15×10^{-9} mol/g_{cat} at 60 min. On the other hand, propane increases rapidly to start form 6.75×10^{-21} mol/g_{cat} at 2 min to 6.40×10^{-20} mol/g_{cat} at 10 min and then it decrease to the 4.72×10^{-21} mol/g_{cat} at 20 min. Finally, the amount of propane increases again until it is 6.45×10^{-20} mol/g_{cat} at 60 min.

Therefore, it is suggested that the 15%Ru/HY can considerably operate as well at 200°C

Table 5.9 The amount of methane adsorbed on 15% Ru/HY catalyst

Reaction temperature (°C)	CH_4 adsorbed (mol/g_{cat})
100	7.42×10^{-7}
200	1.05
300	5.40×10^{-5}

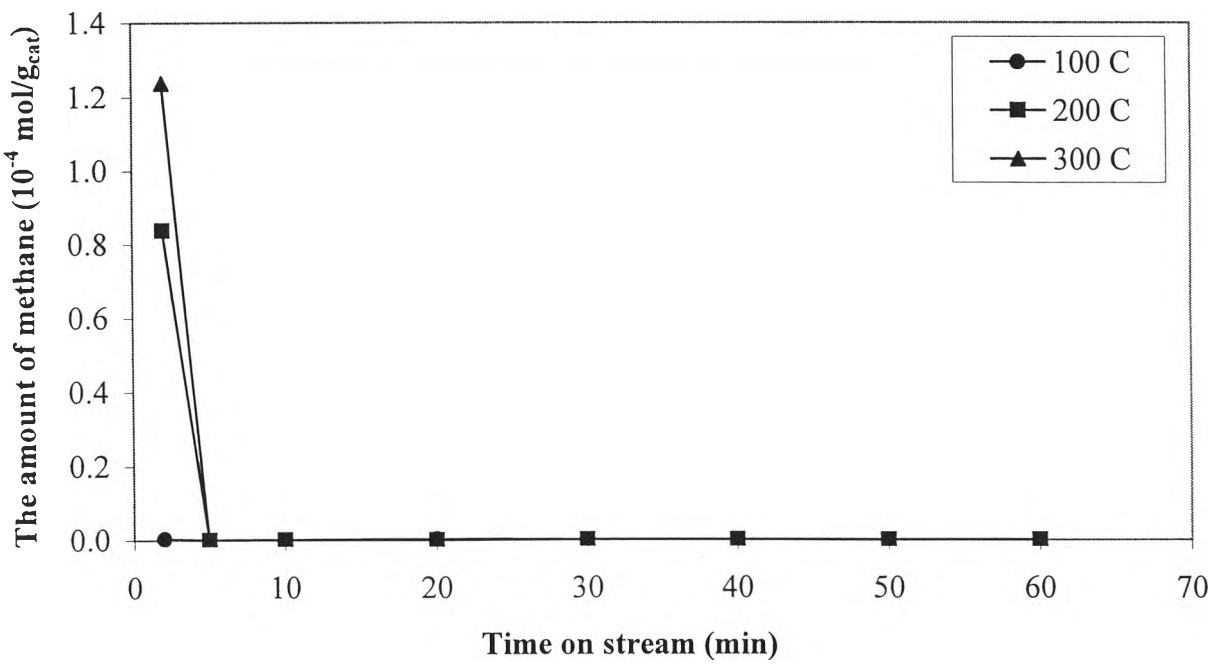

Figure 5.21 The amount of methane produced on 15%Ru/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}.

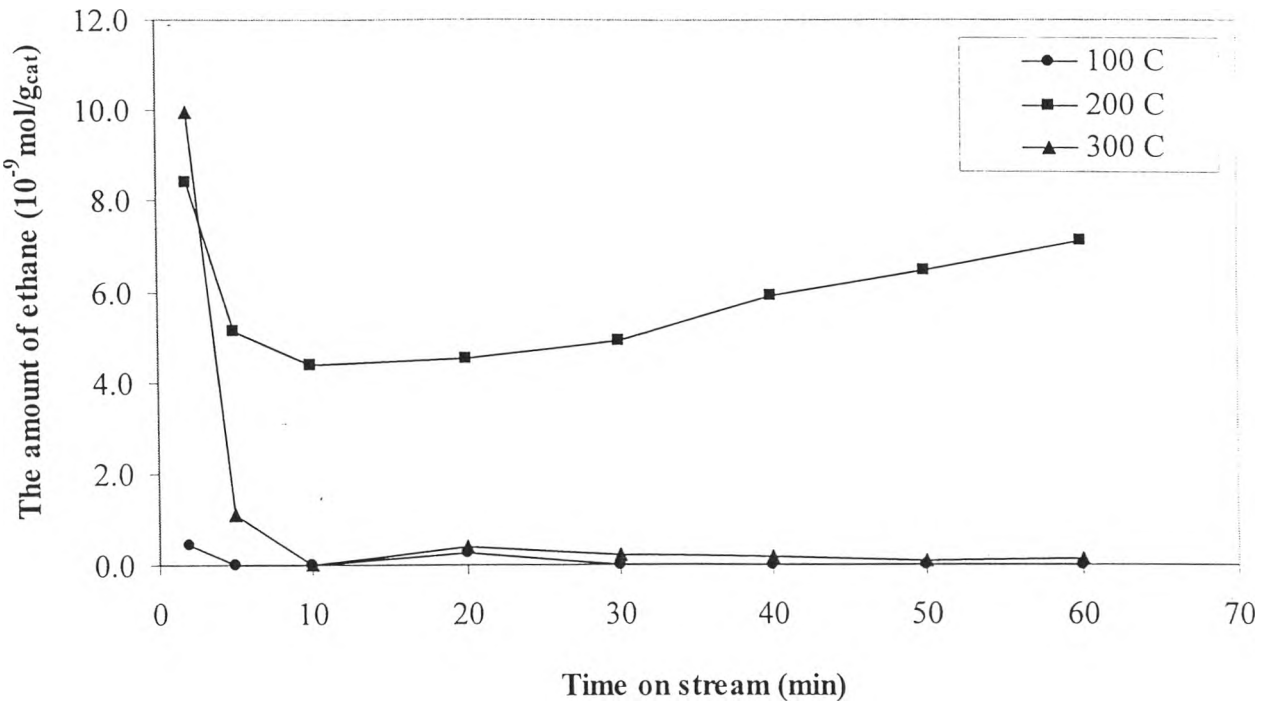

Figure 5.22 The amount of ethane produced on 15%Ru/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}.

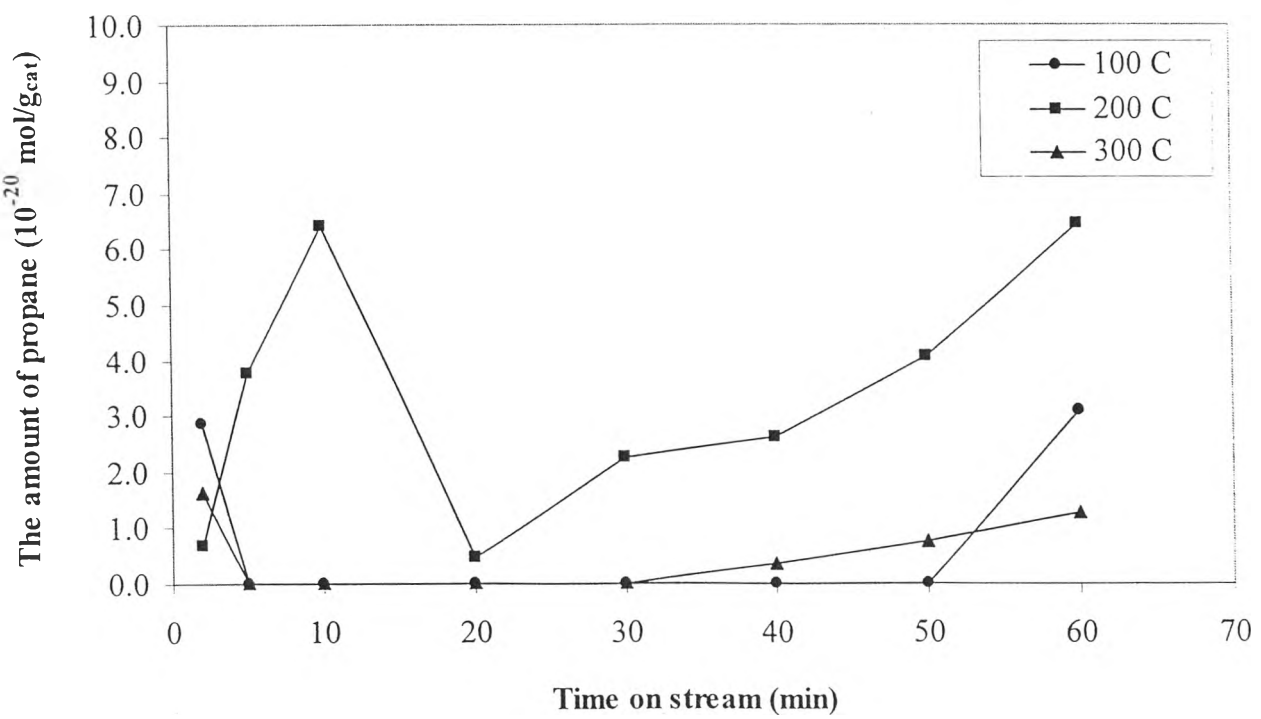

Figure 5.23 The amount of propane produced on 15%Ru/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}.

5.2.4.3 The effect of reaction temperature on 15%Pt/HY

The investigation of the effect of reaction temperature on the catalytic activity in the non-oxidative methane coupling on 15%Pt/HY is obtained from varying reaction temperature as 300, 400 and 500°C. The experimental results are reported as follows:

1. In the methane adsorption step, the amount of methane adsorbed is exhibited in table 5.10.

2. In the hydrogenation step, the amount of methane, ethane and propane evolved is shown in figures 5.24, 5.25 and 5.26, respectively.

The reaction temperature having the amount of methane adsorbed on 15% Pt/HY in the methane adsorption step in order from higher to lower is at 500°C > at 400°C > at 300°C. While the order of the reaction temperature occurring the amount of ethane emitted on this catalyst is as follows : at 400°C > 300°C and 500°C. Figure 5.25 indicates that in the hydrogenation step, ethane is produced at 400°C much more than at both 300 and 500°C . The amount of ethane becomes 4.28×10^{-8} mol/g_{cat} at 2 min and then drops gradually until it is 2.11×10^{-9} mol/g_{cat} at 60 min. Figure 5.26 demonstrates the amount of propane produced on the 15%Pt/HY in the hydrogenation step. It is obviously seen that all of reaction time ,0-60 min, the 15%Pt/HY gives the amount of propane produced at 400°C more than that of propane produced at the other temperature. The maximum amount of propane occurs at 2 min and then propane increases dramatically until the 3.79×10^{-20} mol/g_{cat} of propane is detected at 10 min. Subsequently, it increases slightly from 3.89×10^{-20} mol/g_{cat} at 30 min to 9.8×10^{-20} mol/g_{cat} at 60 min. The amount of methane adsorbed on 500°C is higher than the other as same as the amount of methane produced in hydrogenation step. Therefore, the amounts of ethane and propane produced are lower than the others which are presented in figures 5.25 and 5.26. As the above results, it suggests that the appropriate reaction temperature for non-oxidative methane coupling on 15%Pt/HY is 400°C.

Table 5.10 The amount of methane adsorbed and ethane evolved on 15%Pt/HY catalyst

Reaction temperature (°C)	CH_4 adsorbed (mol/g_{cat})	C_2H_6 evolved (mol/g_{cat})
300	0.10	5.10×10^{-7}
400	0.50	1.83×10^{-6}
500	2.22	4.43×10^{-7}

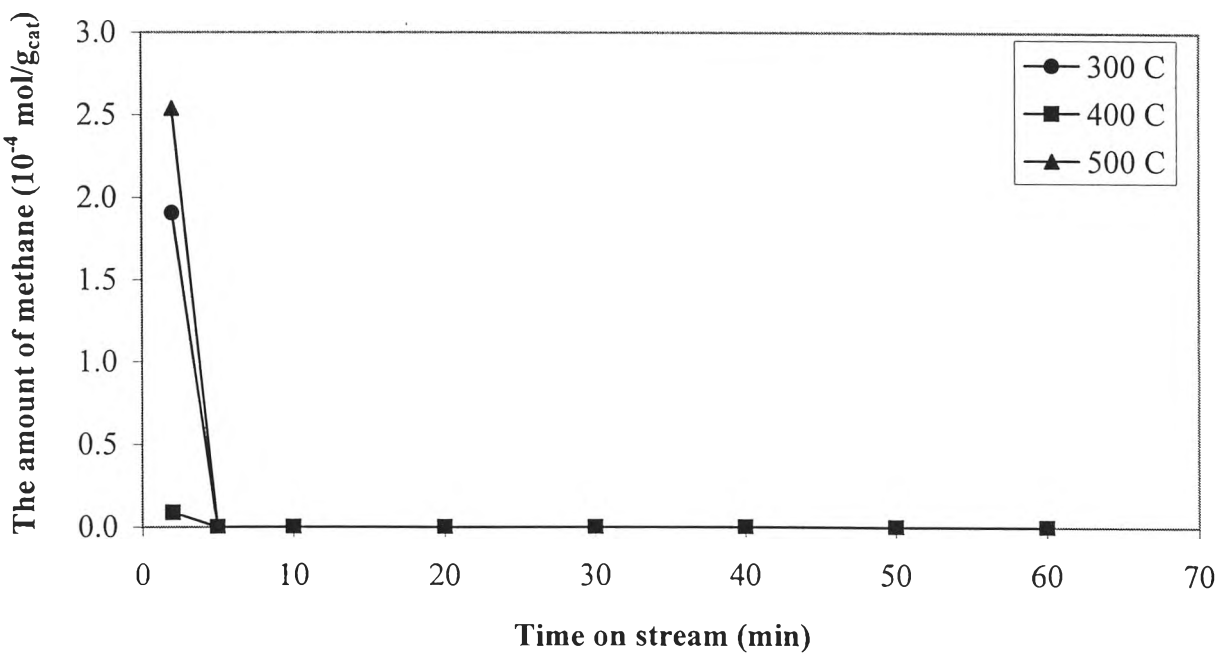

Figure 5.24 The amount of methane produced on 15%Pt/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}.

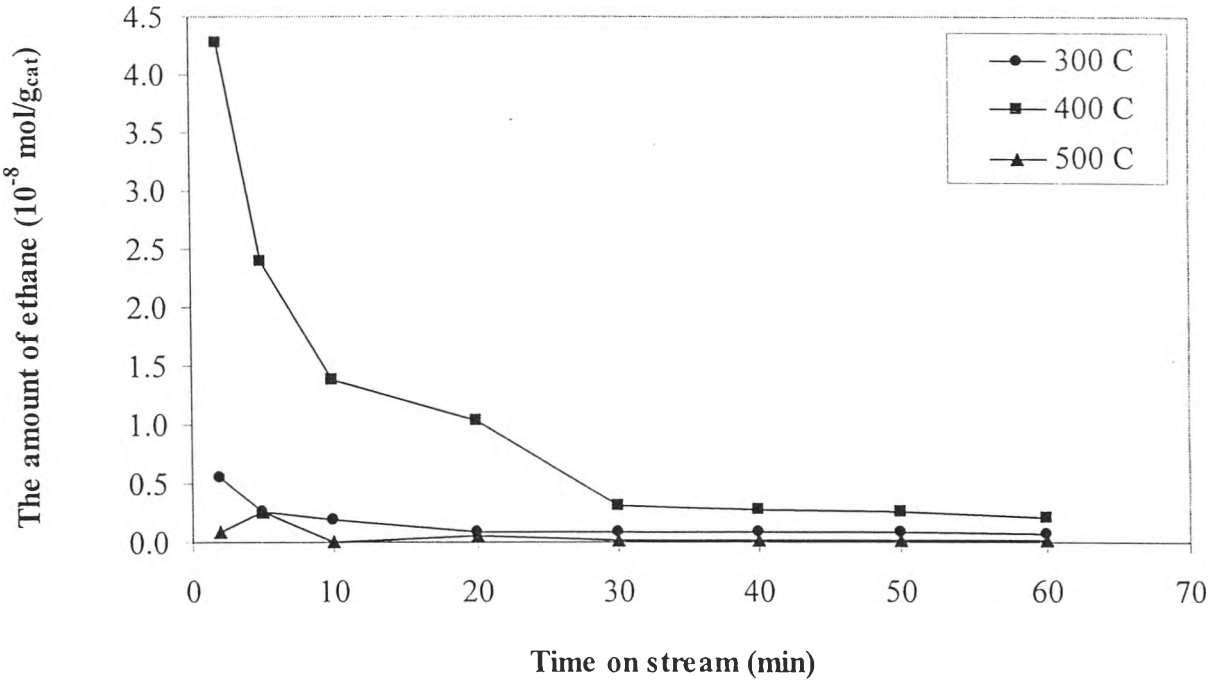

Figure 5.25 The amount of ethane produced on 15%Pt/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}.

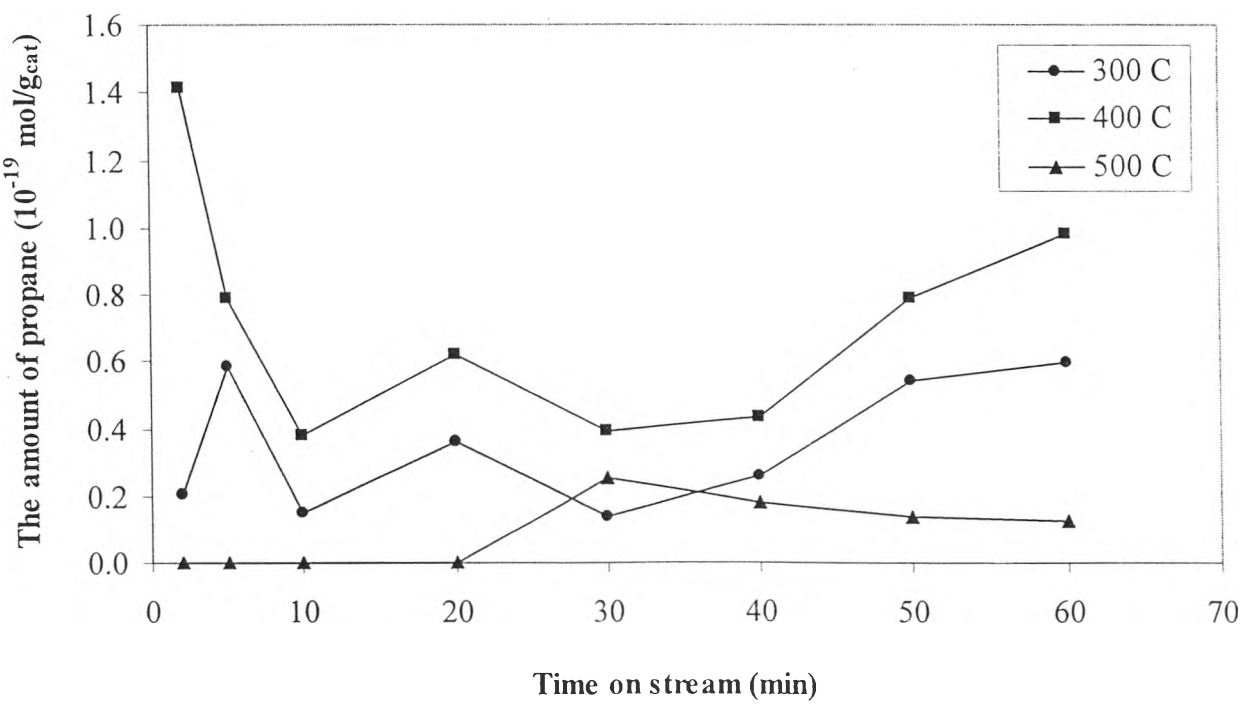

Figure 5.26 The amount of propane produced on 15%Pt/HY as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}.

5.2.4.4 Discussion

The above results illustrate that the suitable reaction temperature is depended on transition metal. Since each metal catalyst has the most suitable reaction temperature for non-oxidative methane coupling, at a lower or higher temperature the catalytic activity is less than a suitable temperature. It can be a suggested that the decomposition of methane is endothermal. On the other hand, the hydrogenation is exothermal. Futhermore, the desorption of surface carbon species can be occured in the hydrogenation step at high temperation [Amariglio *et al.* (1998)] As a result, methane is incompletely decomposed at lower temperature while the hydrogenation activity is decreases at higher temperature.

5.2.5 The effect of GHSV of methane

The previous experimental results exhibit the appropriate percentage metal loading and reaction temperature of each catalyst. After that it is focused on the effect of methane flow rate which strongly influence the conversion of the adsorbed methane and the distribution of products as well.

5.2.5.1 The effect of GHSV of methane on 10%Co/HY

This study is set up to investigate the effect of GHSV of methane on 10%Co/HY at 300°C. The catalytic activity is shown in table 5.11,figures 5.27, 5.28 and 5.29.

The amount of methane adsorbed and propane observed are predicted in table 5.11 and figure 5.29. The results suggest that the quantity of methane adsorbed on both GHSV of methane are not difference. The amount of propane are maximum at methane GHSV 4960 h^{-1} while the amount of methane produced at GHSV 6200 h^{-1} is higher. From figure 5.29, it is clear that the amount of propane produced on GHSV 4960 h^{-1} slightly increases from zero in 2 min to 2.79×10^{-19} in 60 min.

Table 5.11 The amount of methane adsorbed on 10% Co/HY catalyst

GHSV of CH_4 (h^{-1})	CH4 adsorbed (mol/g_{cat})
4960	3.49
6200	3.28

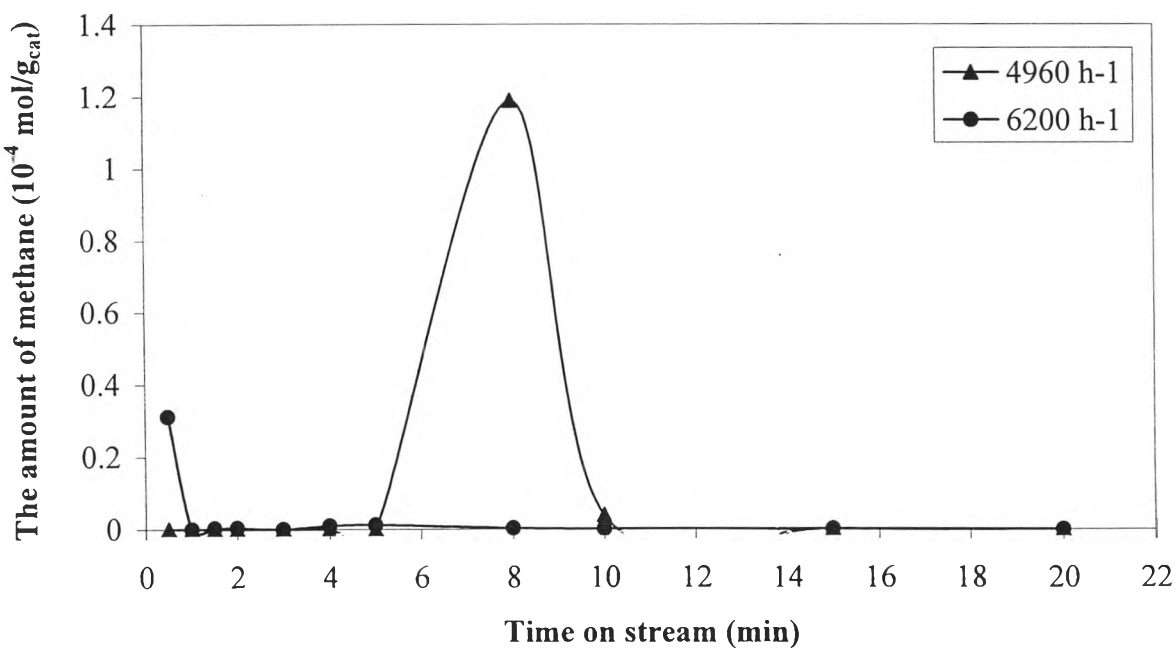

Figure 5.27 The amount of methane adsorbed on 10%Co/HY as a function of time on stream. GHSV of H_2 : 4958.17 h^{-1}. Reaction temperature 300 °C.

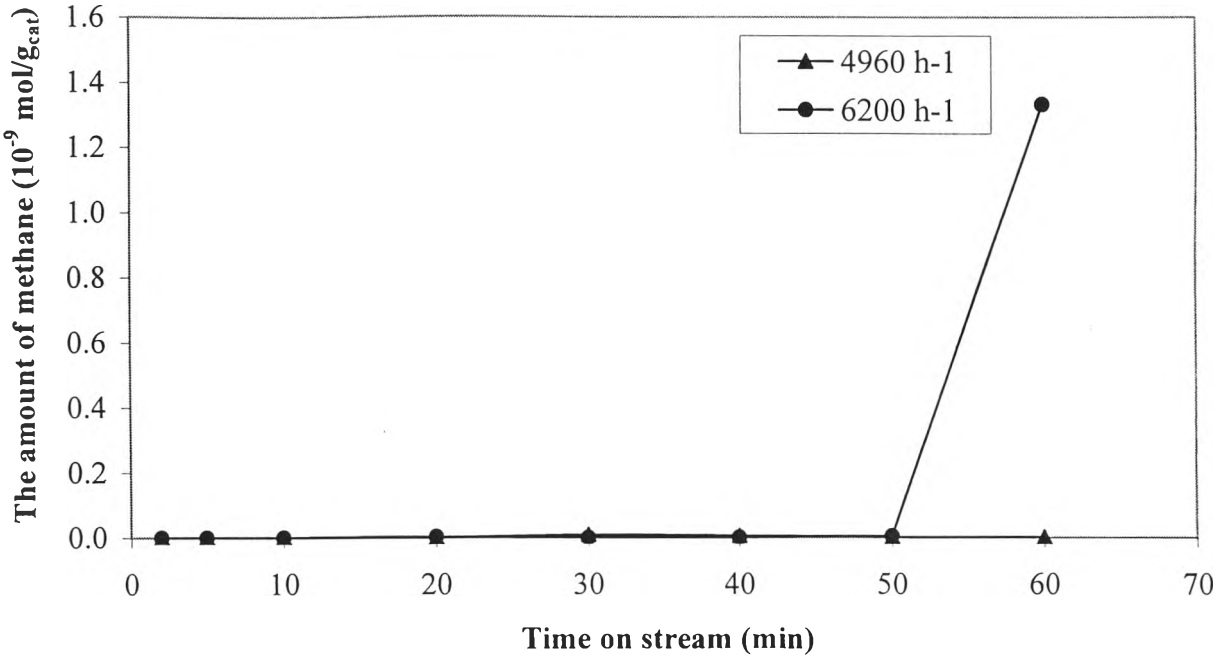

Figure 5.28 The amount of methane produced on 10%Co/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 300 °C.

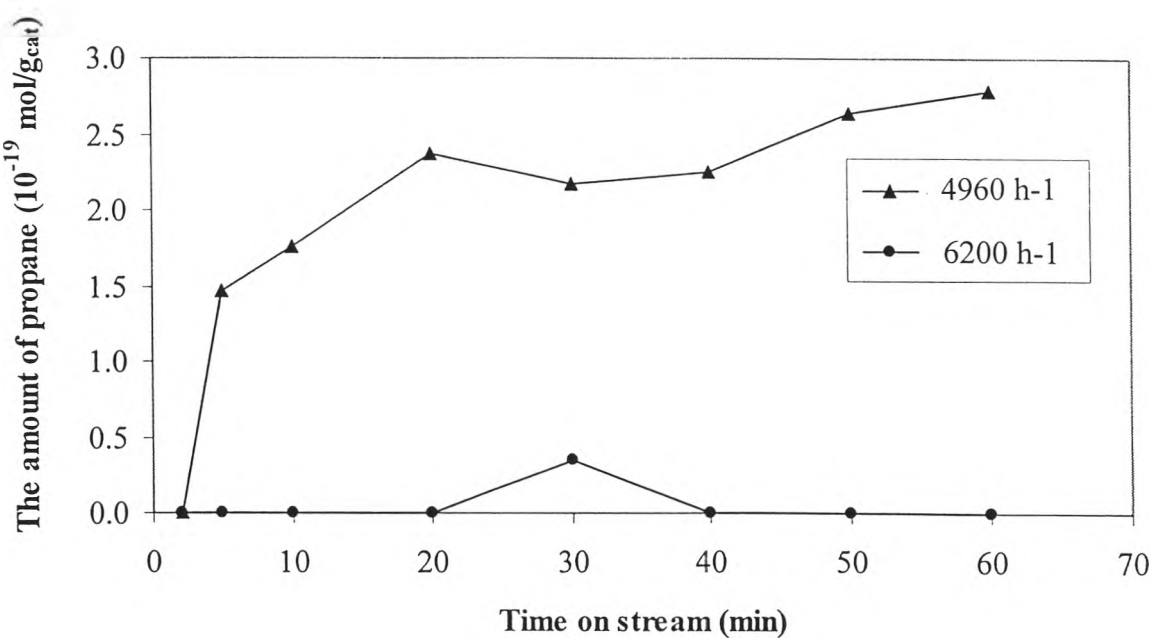

Figure 5.29 The amount of propane produced on 10%Co/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 300 °C.

5.2.5.2 The effect of GHSV of methane on 15%Ru/HY

The effect of GHSV of methane (4960 and 6200 h^{-1}) on 15%Ru/HY is studied in this section.

Table 5.12 exhibits the amount of methane adsorbed. It is found that at GHSV 4960 h^{-1} is higher. Moreover, the great deal of ethane at reaction time during 0-60 min is shown in figure 5.32. It is clearly seen that the amount of ethane of three flow rates gives high value at 2 min. After that the amount of ethane decreases rapidly in 5 min. As a results, the amount of ethane produced at the GHSV of methane at 4960 h^{-1} reaches a maximum at 9.45×10^{-10} mol/$g_{.cat}$. Then, it keeps a constant value until 60 min. Figure 5.33 illustrates the amount of propane which is maximum at 4960 h^{-1} of methane GHSV. The amount of propane dramatically increases at initial during 5-20 min and reaches a maximum value at 9.45×10^{-20} mol/g_{cat} at 20 min. Then the amount of propane decreases substantially at 30 min and increases again until reaching 5.15×10^{-20} mol/g_{cat} at 60 min. On the other hand, the GHSV of methane at 6200 h^{-1} has high value of propane at initial, but decrease to zero when the reaction time is 5 to 60 min. Furthermore, from figure 5.31 the amount of methane produced on GHSV 6200 h^{-1} is higher than other. From this study, it is concluded that the GHSV of methane at 4960 h^{-1} and reaction temperature at 200°C are the appropriate conditions of 15%Ru/HY on non-oxidative methane coupling.

Table 5.12 The amount of methane adsorbed on 15% Ru/HY catalyst

GHSV of CH_4 (h^{-1})	CH_4 adsorbed (mol/g_{cat})
4960	3.39
6200	3.08

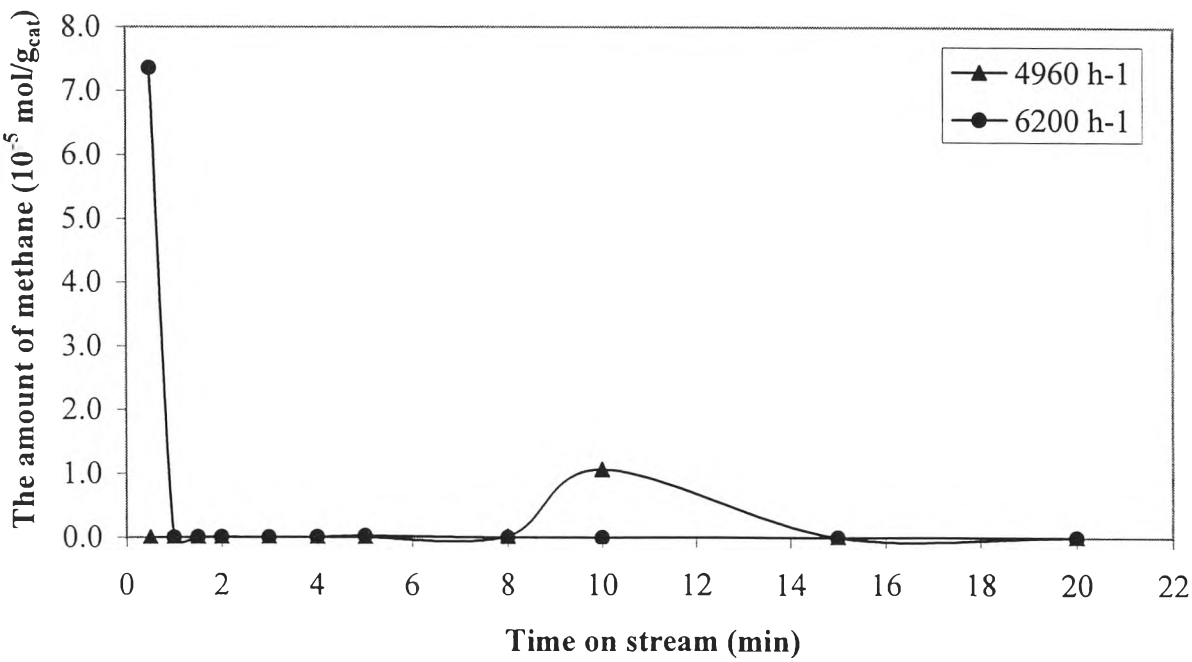

Figure 5.30 The amount of methane adsorbed on 15%Ru/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 200 °C.

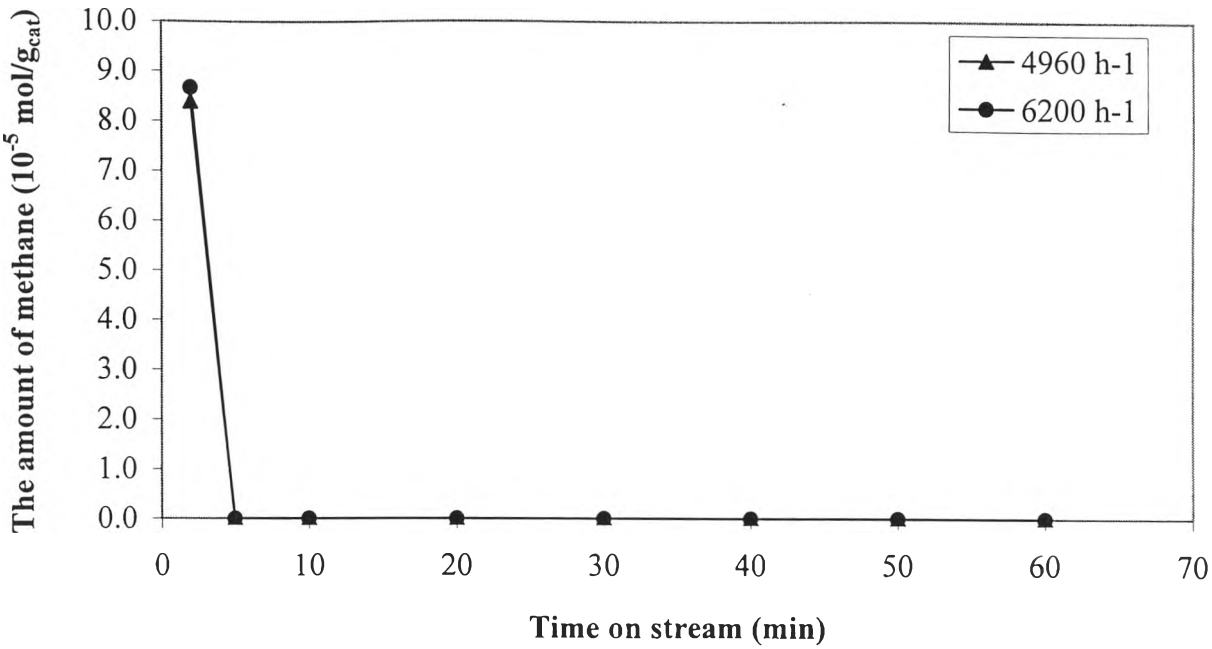

Figure 5.31 The amount of methane produced on 15%Ru/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 200 °C.

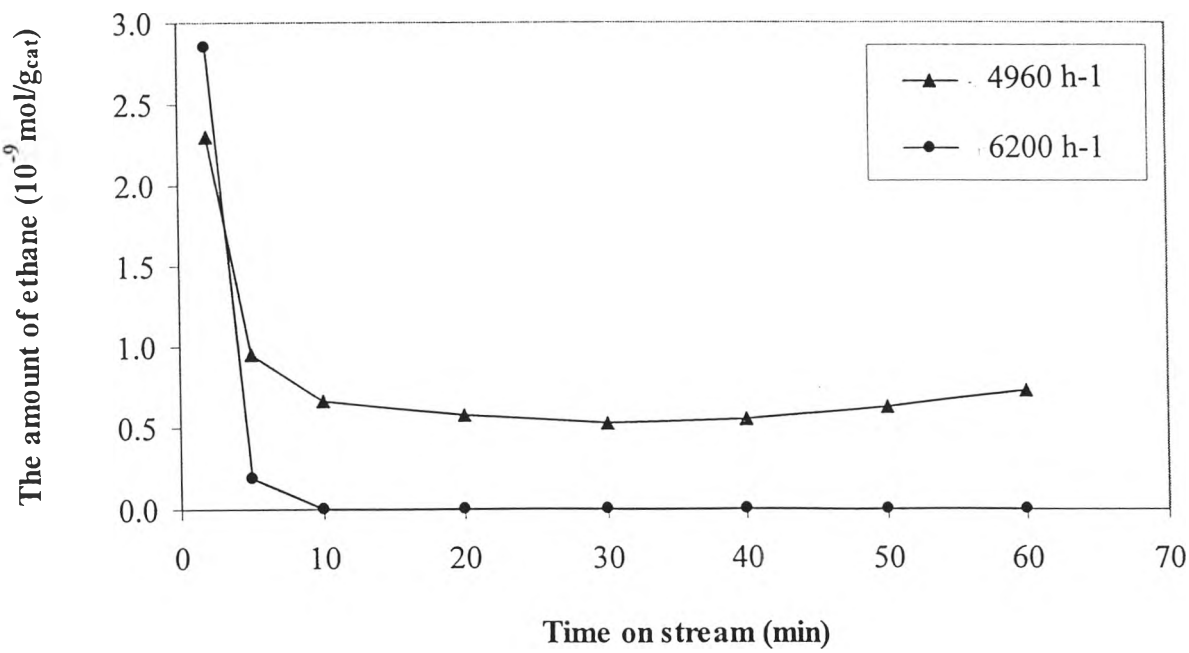

Figure 5.32 The amount of ethane produced on 15%Ru/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 200 °C.

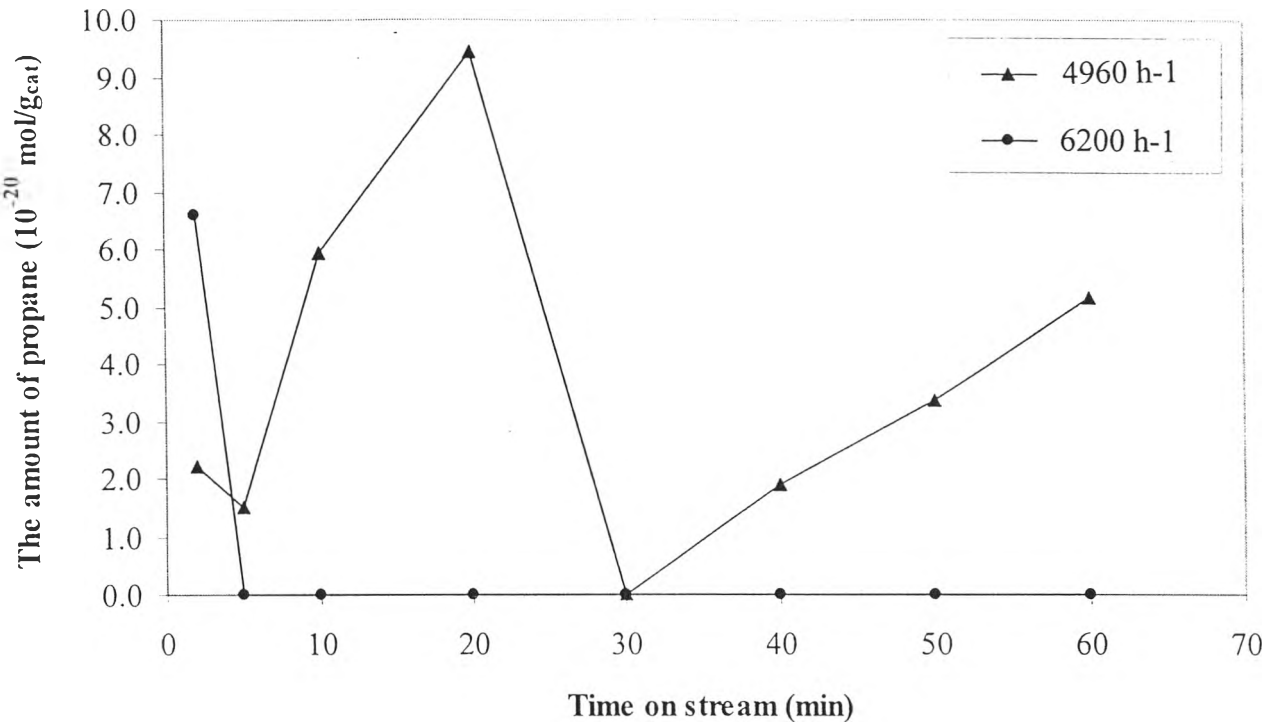

Figure 5.33 The amount of propane produced on 15%Ru/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 200 °C.

5.2.5.3 The effect of GHSV of methane on 15%Pt/HY

The GHSV of methane for 15%Pt/HY is investigated. The amount of methane adsorbed and ethane evolved of various the GHSV of methane as 4960 and 6200 h^{-1} are presented in table 5.13. The amount of methane, ethane and propane produced in hydrogenation step were shown in figures 5.35, 5.36 and 5.37, respectively.

The amount of methane adsorbed on 15%Pt/HY when the GHSV of methane is 4960 h^{-1} as same as 6200 h^{-1}. However the maximum amount of ethane evolved becomes 2.15×10^{-6} mol/g_{cat} at 6200 h^{-1}. The GHSV of methane at 6200 h^{-1} gives the maximum value of methane and ethane produced on hydrogenation step. The amount of ethane at the maximun is about 5.75×10^{-8} mol/g_{cat} at 2 min. and decreases very rapidly after 8 min. to zero. Then, it increases to about 5.85×10^{-9} mol/g_{cat} at 60 min.

Figure 5.37 indicates that the amount of propane at GHSV 4960 h^{-1} is maximum at the reaction time 30-60 min. These results suggests that the GHSV of methane at 4960 h^{-1} is appropriate value for 15%Pt/HY.

Table 5.13 The amount of methane adsorbed and evolved on 15% Pt/HY catalyst

GHSV of CH_4 (h^{-1})	CH_4 adsorbed (mol/g_{cat})	C_2H_6 evolved (mol/g_{cat})
4960	2.21	$1.83x10^{-6}$
6200	2.10	$2.15x10^{-6}$

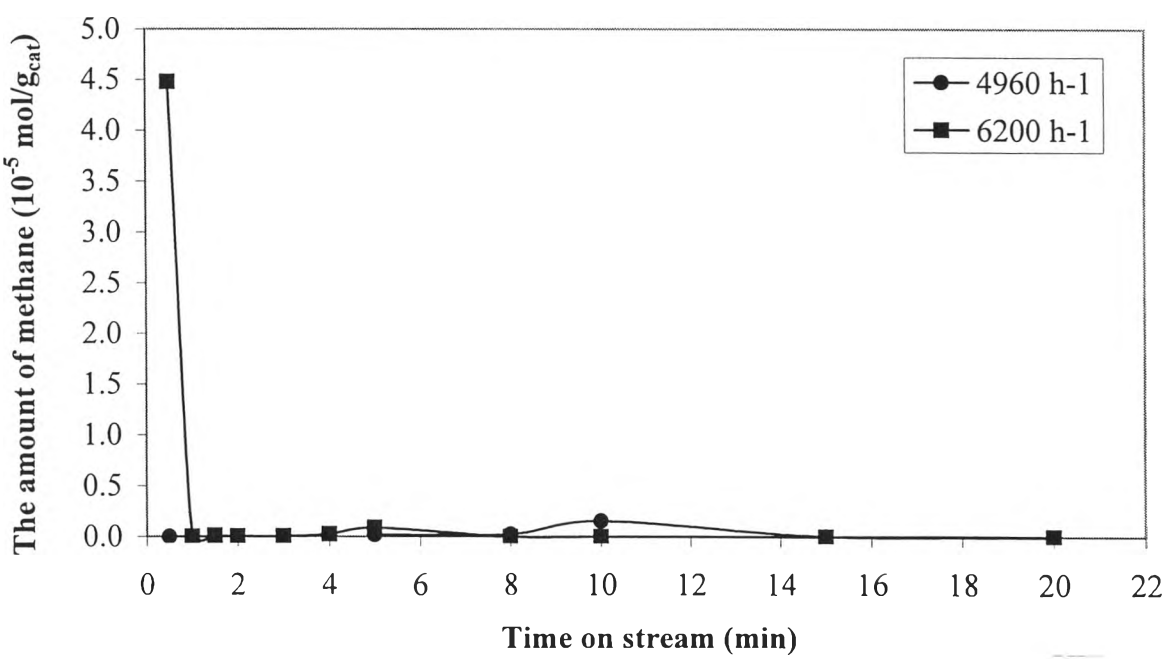

Figure 5.34 The amount of methane adsorbed on 15%Pt/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 400 °C.

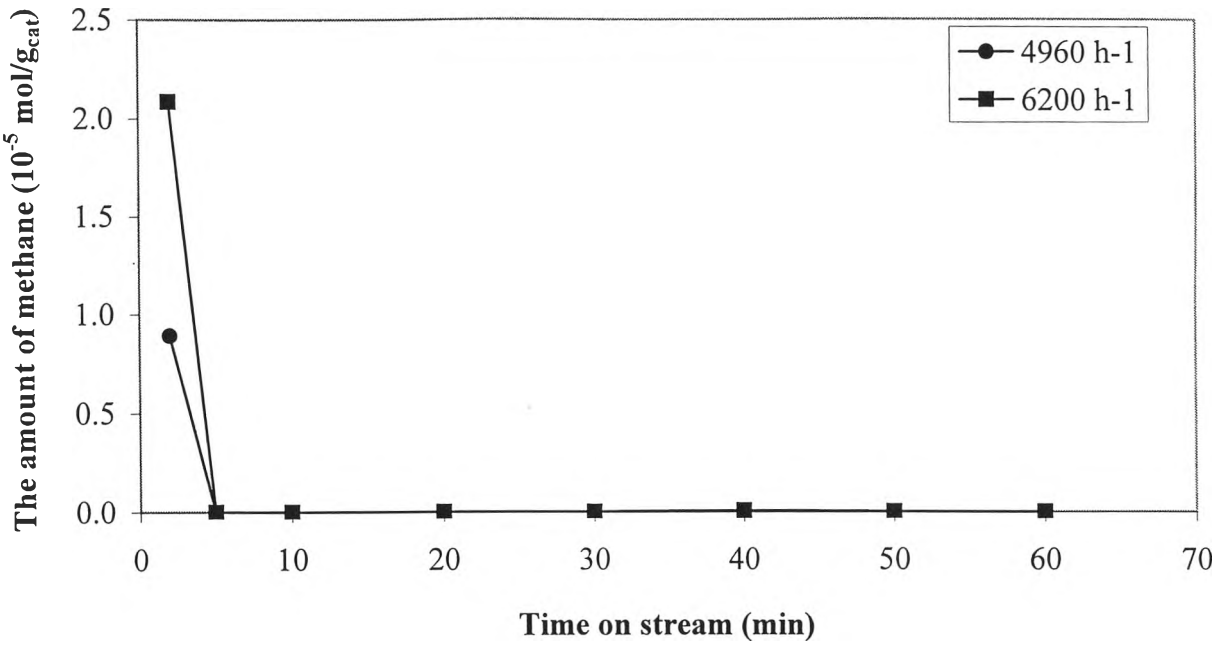

Figure 5.35 The amount of methane produced on 15%Pt/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 400 °C.

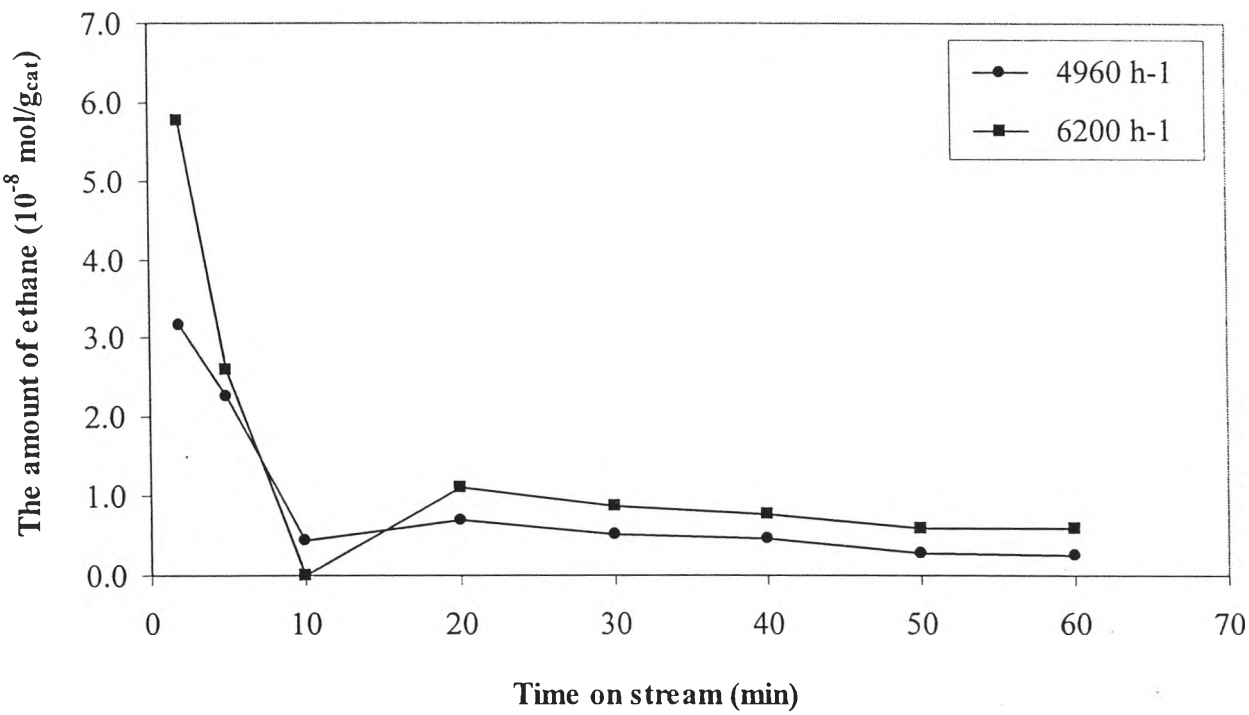

Figure 5.36 The amount of ethane produced on 15%Pt/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 400 °C.

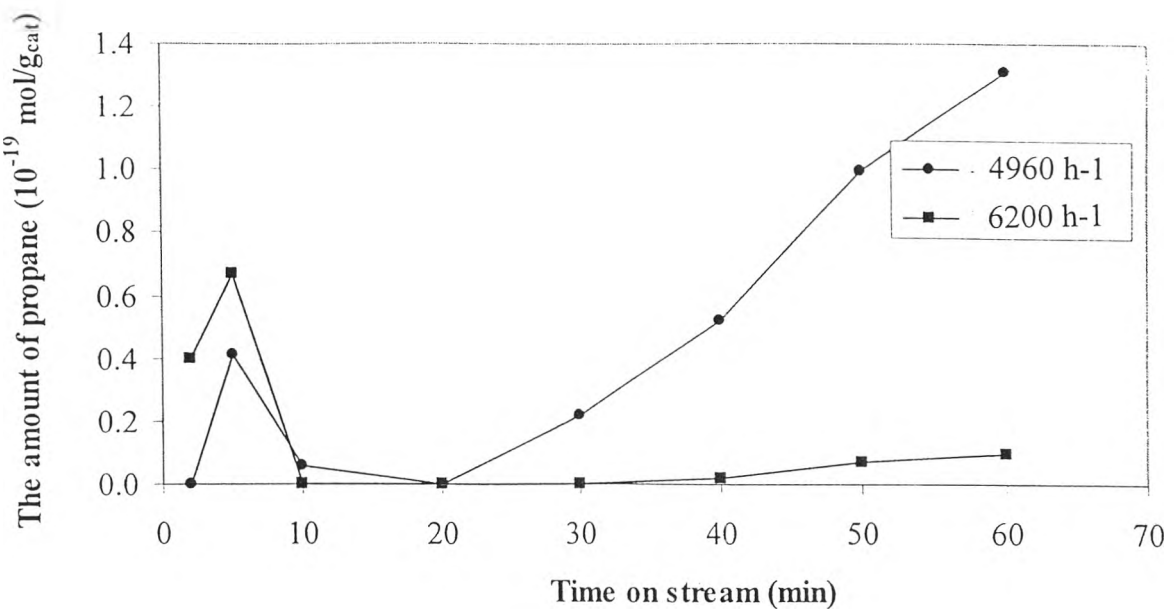

Figure 5.37 The amount of propane produced on 15%Pt/HY as a function of time on stream. GHSV of H_2 : 4960 h^{-1}. Reaction temperature 400 °C.

5.2.5.4 Discussion

It is clearly seen that the GHSV of methane influences the distribution of products [Belgued *et al.* (1992)]. It can be suggested that the pattern of the amount of methane adsorbed, figures 5.27, 5.30 and 5.34, affects the adsorbed species on active sites of catalysts.

5.2.6 The effect of hydrogenation gas

5.2.6.1 Comparison between argon and hydrogen

The effect of argon and hydrogen used as hydrogenation gas in the hydrogenation step on 10% Co/HY is reported in this section.

Figure 5.38 illustrates that the amount of propane in argon stream is much higher than in hydrogen stream. This phenomenon can be explained in the following way. When methane is adsorbed some hydrogen is evolved and cover hydrogen deficient adsorbed species on catalyst surface. It would inhibit coupling of adsorbed species [Pareja *et al.* (1994)]. For that reason, argon act as the carrier gas of the evolved hydrogen. Although argon is carrier gas, propene can be produced. It can be suggested that adsorbed species agglomerate on the surface of catalyst, giving rise to C_xH_y species. And the C_xH_y species are hydrogenated by the hydrogen evolved in gas phase.

5.2.6.2 The effect of time on stream

This section observed the effect of time on stream on 10%Co/HY. Argon was used as the hydrogenation gas. Figure 5.39 illustrates the amount of propane produced on hydrogenation step by argon. It increases rapidly from zero to the optimum value and then decreases dramatically to zero. The propane produced gives the same pattern until reaction time is 830 min. With this phenomenon, it can be suggested that the adsorbed species on active sites of catalysts are differences. The coupling of adsorbed species to propane may be occurred as a chain reaction.

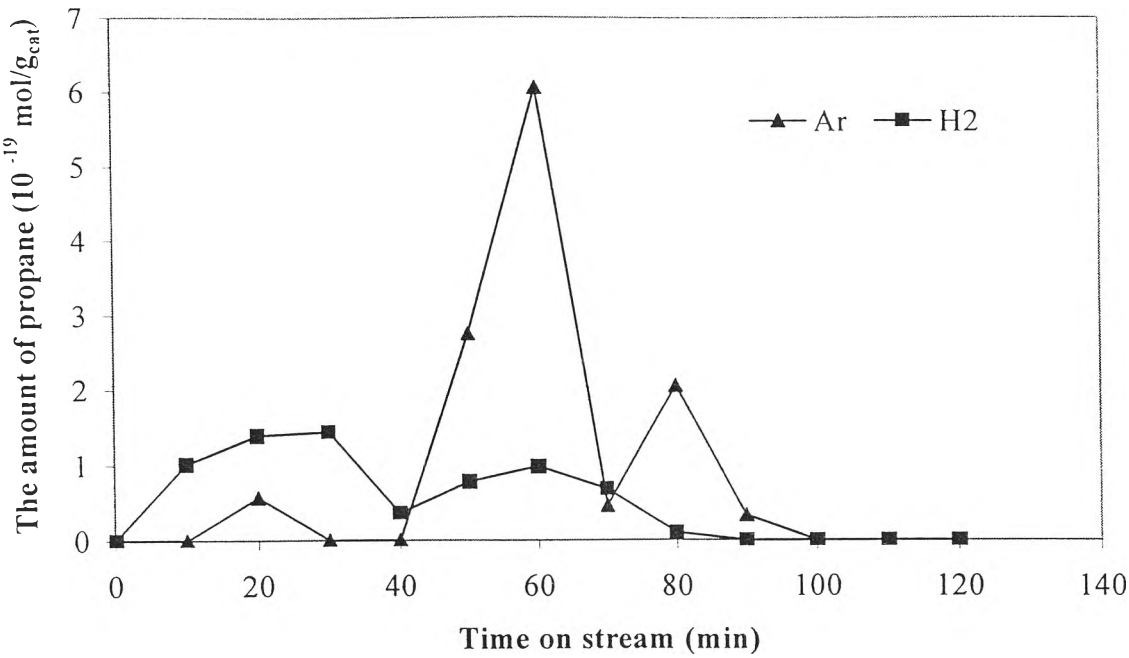

Figure 5.38 The amount of propane produced on 10%Co/HY catalyst as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of H_2 : 4960 h^{-1}. GHSV of Ar : 4960 h^{-1}. Reaction temperature : 300 °C.

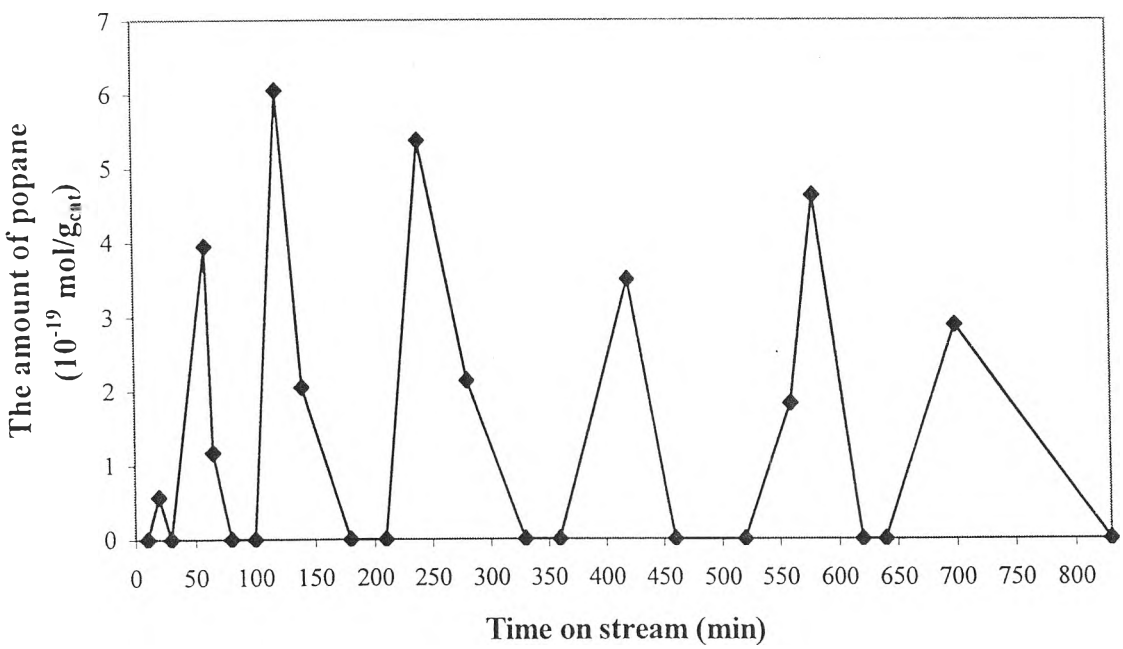

Figure 5.39 The amount of propane produced on 10%Co/HY catalyst as a function of time on stream. GHSV of CH_4 : 4960 h^{-1}. GHSV of Ar : 4960 h^{-1}. Reaction temperature : 300 °C.