# CHAPTER IV
# RESULTS AND DISCUSSION

## 4.1 Catalyst Characterization

This section was devoted to the catalysts characterization results. The results were derived from variety characterization methods, including pulse chemisorption, X-ray diffraction, BET and SEM. The characteristic of the catalysts in this part will be used to explain the activity of catalysts in the next section. Moreover, the precursors, silatrane and alumatrane, were characterized and discussed in this section.

### 4.1.1 Precursor Synthesis

The silatrane and alumatrane were successfully synthesized via the Oxide-One-Pot-Synthesis (OOPS) process, as described in the previous chapter. The precursors were characterized by Thermal Gravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR).

#### *4.1.1.1 Silatrane Characterization*

Figure 4.1 shows the TGA thermogram of the silatrane, containing two mass loss transitions. The first mass loss transition, which is corresponding to organic ligand oxidation, occurred at 300°-450 °C. The other, which is corresponding to the residue char oxidation, was observed at 600-650 °C. The silatrane has percent ceramic yield of about 20%, which is slightly higher than the theoretical ceramic yield of 19% (Sathupanya *et al.*, 2003).

The IR-spectrum of the precursors is shown in Figure 4.2. It shows peaks that almost identical to the characteristic peaks of silatrane (Table 4.1), reported by Sathupanya *et al.*, 2003.

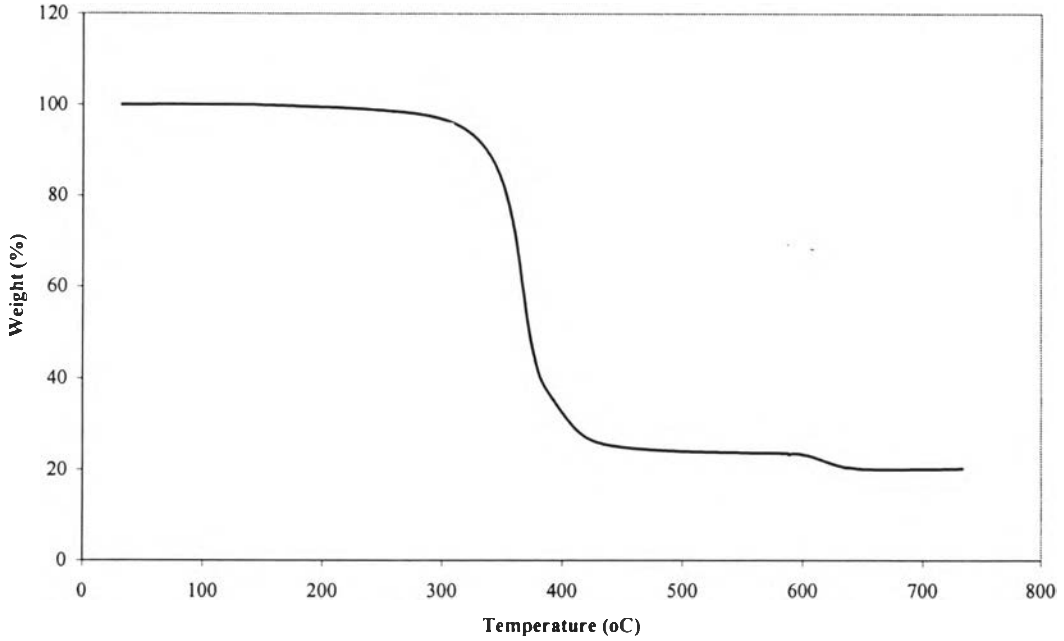

**Figure 4.1** The TGA thermogram of silatrane.

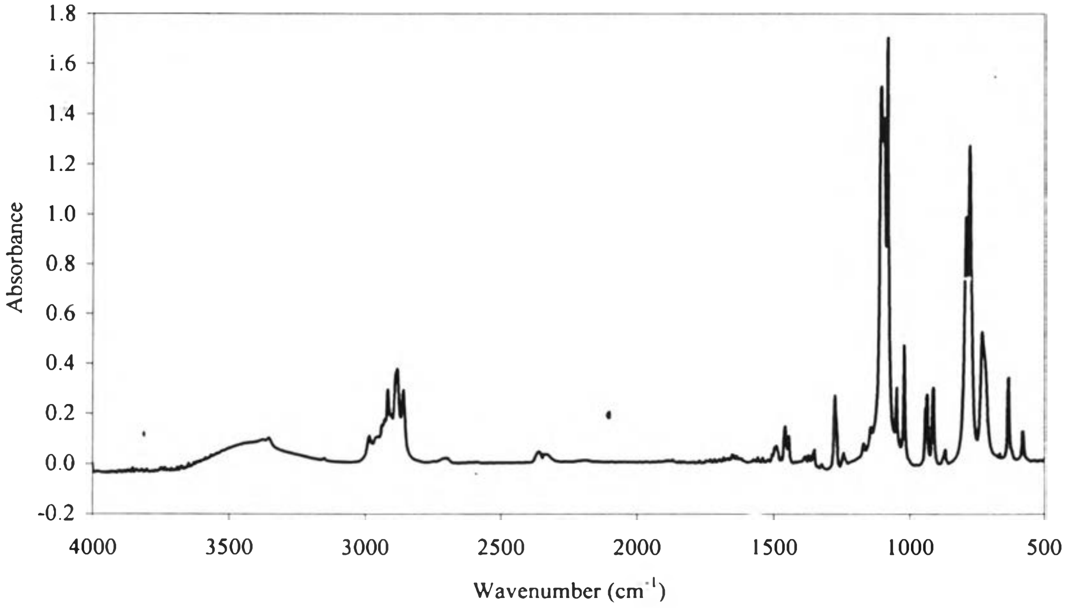

**Figure 4.2** FTIR spectrum of silatrane.

**Table 4.1** Peak positions and assignments in the FTIR spectrum of synthesized silatrane

| Peak positions ($cm^{-1}$) | Assignments |
|---|---|
| 3100-3700 | $\nu$(O–H) |
| 2800-3000 | $\nu$(C–H) |
| 1445, 1459, 1500 | $\delta$(C–H) |
| 1351 | $\nu$(C–N) |
| 1276, 1022 | $\nu$(C–O) |
| 1080-1180, 1049 | $\nu$(Si–O) |
| 1096 | $\nu$(Si–O–C) |
| 700-940 | $\delta$(Si–O–C) |
| 580 | Si←N |

### *4.1.1.2 Alumatrane Characterization*

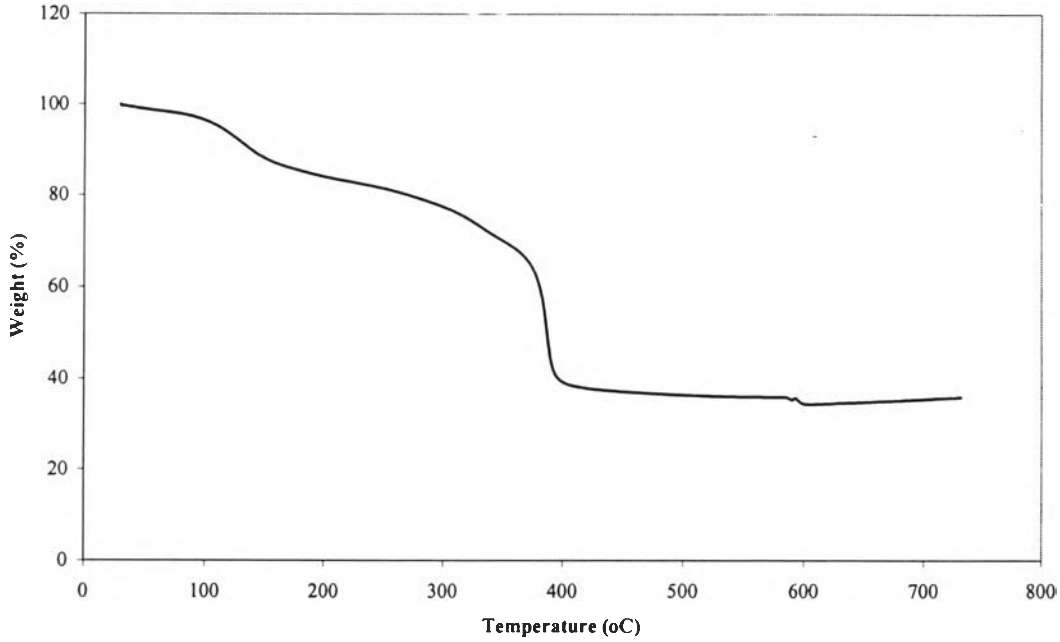

**Figure 4.3** The TGA thermogram of alumatrane.

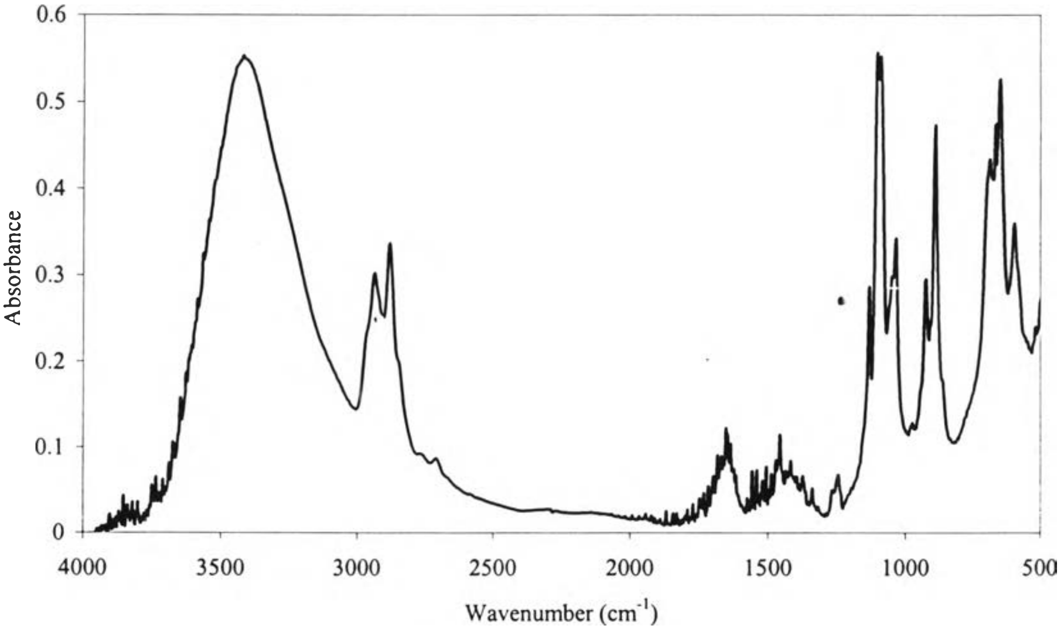

**Figure 4.4** FTIR spectrum of alumatrane.

Figure 4.3 shows the TGA thermogram of alumatrane, having three mass loss transitions at 50°-200°C, 200°-550°C and 580-600°C, which were corresponding to trapped solvent and TIS decomposition, organic ligand decomposition and residual carbon char decomposition, respectively. The percent ceramic yield of the alumatrane is about 32.6% which is higher than the theoretical ceramic yield of 23.7% reported by Sathupanya *et al.,* 2003.

Figure 4.4 shows IR spectrum of synthesized alumatrane product giving the peaks that are almost identical to the characteristic peak of alumatrane, as summarized in Table 4.2 and reported by Sathupanya *et al.,* 2003.

**Table 4.2** Peak positions and assignments in the FTIR spectrum of synthesized alumatrane

| Peak positions ($cm^{-1}$) | Assignments |
|---|---|
| 3100-3700 | $\nu$(O–H) |
| 2800-3000 | $\nu$(C–H) |
| 1653 | O–H overtone |
| 1457 | $\delta$(C–H) |
| 1133 | $\nu$(C–O) |
| 1030-1100 | $\nu$(Al–O–C) |
| 900-1000 | $\nu$(C–N) |
| 890 | $\delta$(Al–O–C) |
| 500-800 | $\nu$(Al–O) |

4.1.2 Catalyst Characterization

The $H_2$ chemisorption and BET were performed to determine the mean metal particle size, metal dispersion and surface area of the catalysts. The measurement was carried out, as described previously. The results are shown in Table 4.3.

**Table 4.3** The mean particle sizes and degree of metal dispersion measured by $H_2$ chemisorption method and BET surface area of the prepared catalysts

| Catalysts | Metal particle size (nm) | Metal Dispersion (%) | BET Surface Area ($m^2/g$) |
|---|---|---|---|
| 1%Pt/$Al_2O_3$ | 0.95 | 107.01 | 161.06 |
| 1%Pt/LTA4 | 5.75 | 17.71 | 36.26 |
| 1%Pt/LTA6 | 4.77 | 21.34 | 60.77 |
| PtFe/LTA6(Pt:Fe = 10:1) | | | - |
| PtFe/LTA6(Pt:Fe = 1:1) | 4.30 | 23.40 | - |

The mean particle sizes are consistent to those approximately calculated by the XRD peak broadening technique, which will be explained in the next part. The 1%Pt/LTA6 was about 16% smaller metal particle size than that of 1%Pt/LTA4, as shown in Table 4.3. As expected, the 1%Pt/LTA6 has higher metal dispersion which is 21.34% than 17.71% metal dispersion of Pt/LTA4, which may be a cause of different catalyst performances between 1%Pt/LTA6 and 1%Pt/LTA4. The 107% metal dispersion of Pt/$Al_2O_3$ did not reflect the real value. It was a result of $H_2$ spill over (Satterfield, 1991). However, we know that the metal particle size of 1%Pt/$Al_2O_3$ was smaller than 5 nm because it was not observed by the XRD. Moreover, loading Fe onto the catalyst was not changed the metal size and dispersion since the comparable values were obtained. There are many possibilities. It may be that the Fe covered a part of Pt and $H_2$ was chemisorbed onto the Fe just like Pt to alter and the measurement. Another possibility is the Fe separately located from the Pt and the $H_2$ was not chemisorbed on the Fe to generate the measurement result.

### 4.1.3 X-ray Diffraction Patterns

Powder X-ray diffraction method was used to confirm LTA support and also to obtain phase and crystal size of Pt metal. The XRD patterns of the unloaded LTA4, 1%Pt/LTA6, 1%Pt/LTA4, and 1%Pt/$Al_2O_3$ are shown in Figure 4.1. The LTA4 shows many sharp peaks matched to the XRD pattern of LTA reported by

Sathupanya *et al.*, (2003). The 1%Pt/commercial LTA has almost exactly the same patterns as the unloaded LTA, suggesting that the Pt particle on the LTA6 was too small to be observed by XRD. On the other hand, some additional peaks to the peaks of LTA support were observed in 1%Pt/LTA4. This suggests the bigger Pt particle size on the LTA4 is bigger than that of the LTA6. Those additional peaks observed at 2θ of 39.8° and 46.4° were corresponding to Pt(111) and PtO for CuKα (1.5406 Å) radiation, respectively (Igarashi *et. al.*, 1997). By using values of 2θ, full width half maximum (FWHM), and wave length of X-ray of CuKα together with Debye-Scherrer equation, the mean particle size of the Pt metal was estimated. For 1%Pt/LTA4, the mean particle diameter perpendicular to (111) plan was about 4.82 nm and by using geometrical correction factor the mean particle size was about 6.4 nm, which is in agreement with one that obtained from the $H_2$ chemisorption technique (Table 4.1). The 1%Pt/$Al_2O_3$ gave no peaks, as expected, due to the amorphous phase obtained, moreover, the Pt particle supported on $Al_2O_3$ was too small to significantly diffract X-ray. From XRD results described above, the difference between 1%Pt/LTA4 and 1%Pt/LTA6 was the size of Pt particle or may also be the phase of supported Pt. The different Pt particle size might lead to the different metal dispersion. The higher degree of metal dispersion means the higher accessible Pt active site which may be a cause of different selectivity between 1%Pt/LTA6 and 1%Pt/LTA4 in low temperature range. Moreover, it has been reported that the small Pt particle was more active and selective to CO oxidation due to stronger adsorption of CO on the small Pt than the larger one. Because of the relatively low heat capacity of the small particle and exothermic reaction, the microscopic temperature rose and contributed to the high activity and kept water from physical adsorption. In contrast, the large particle can adsorb more heat so the microscopic temperature was not raised much and not enough to desorbed water. The large particles were thus slowly deactivated by the accumulated water (Son *et al., 2002*). As a result of those phenomena, the selectivity of 1%Pt/LTA4 dramatically increased with temperature. In contrast, the 1%Pt/LTA6 revealed high selectivity at low temperatures.

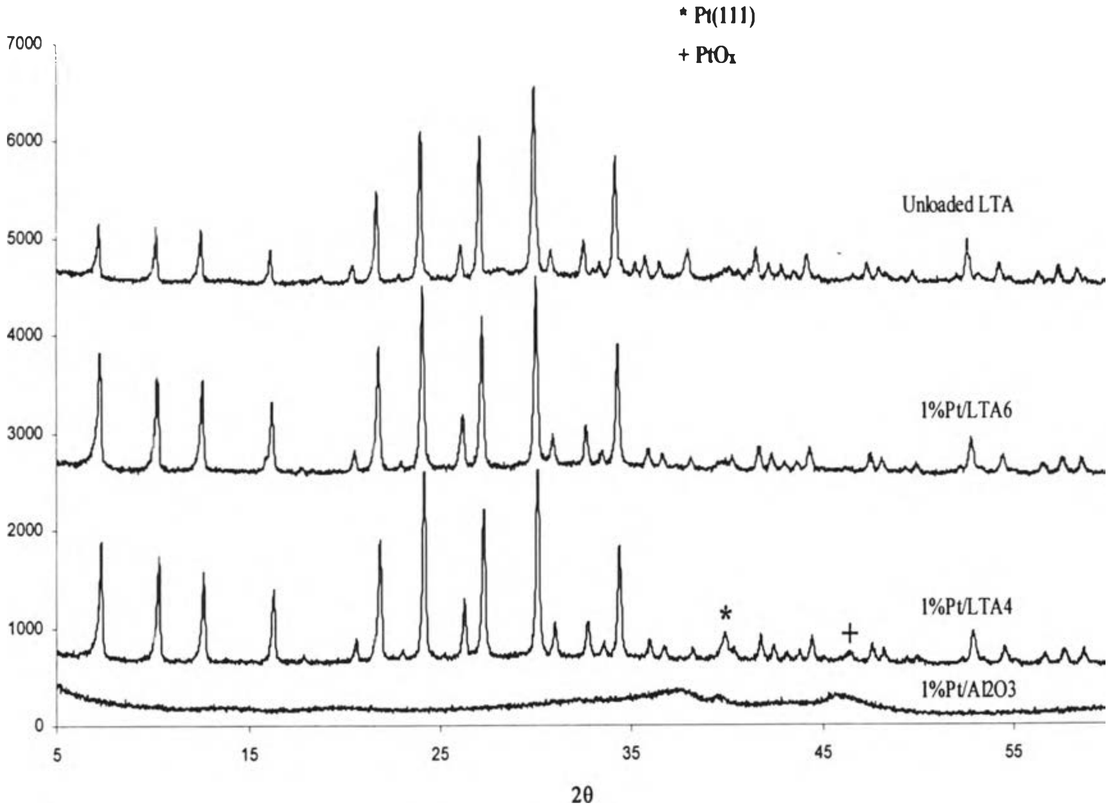

**Figure 4.5** XRD patterns for 1%Pt/$Al_2O_3$, 1%Pt/LTA4, 1%Pt/LTA6, and LTA4.

### 4.1.4 Scanning Electron Microscope (SEM)

The SEM micrographs were taken in order to observe the morphology of the LTA support. As revealed in Figures 4.6-4.7. This difference might be related to the difference of catalytic activity between 1%Pt/LTA4 and 1%Pt/LTA6.

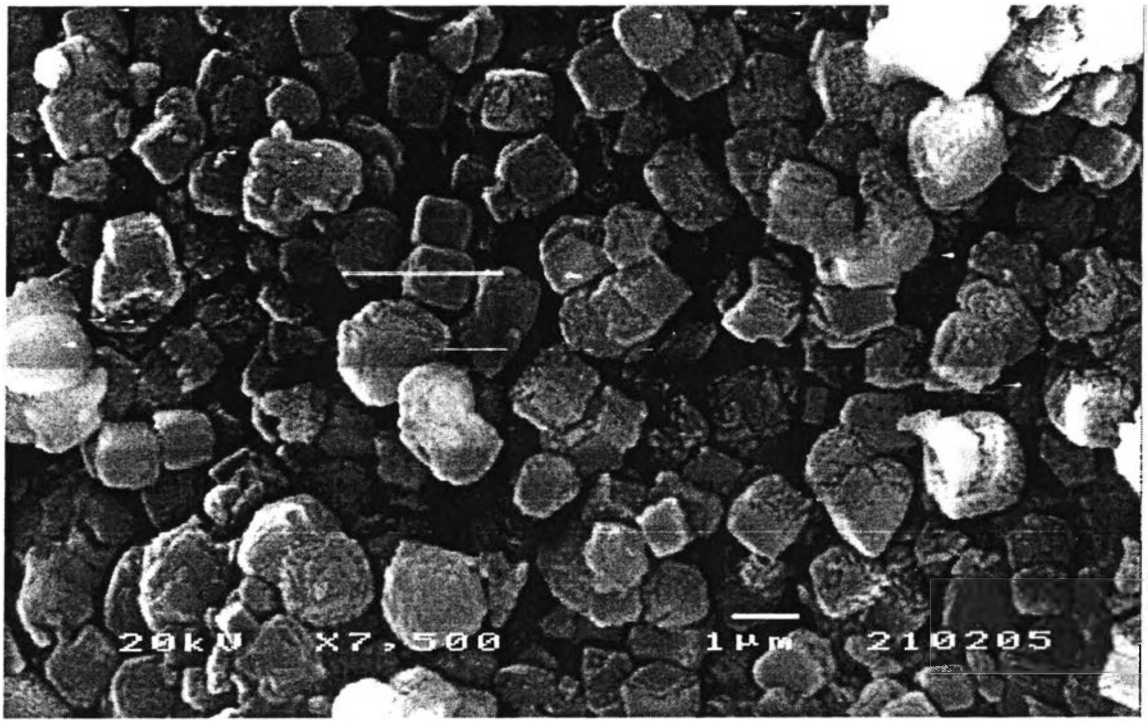

**Figure 4.6** SEM micrograph of 1%Pt/commercial LTA (LTA6).

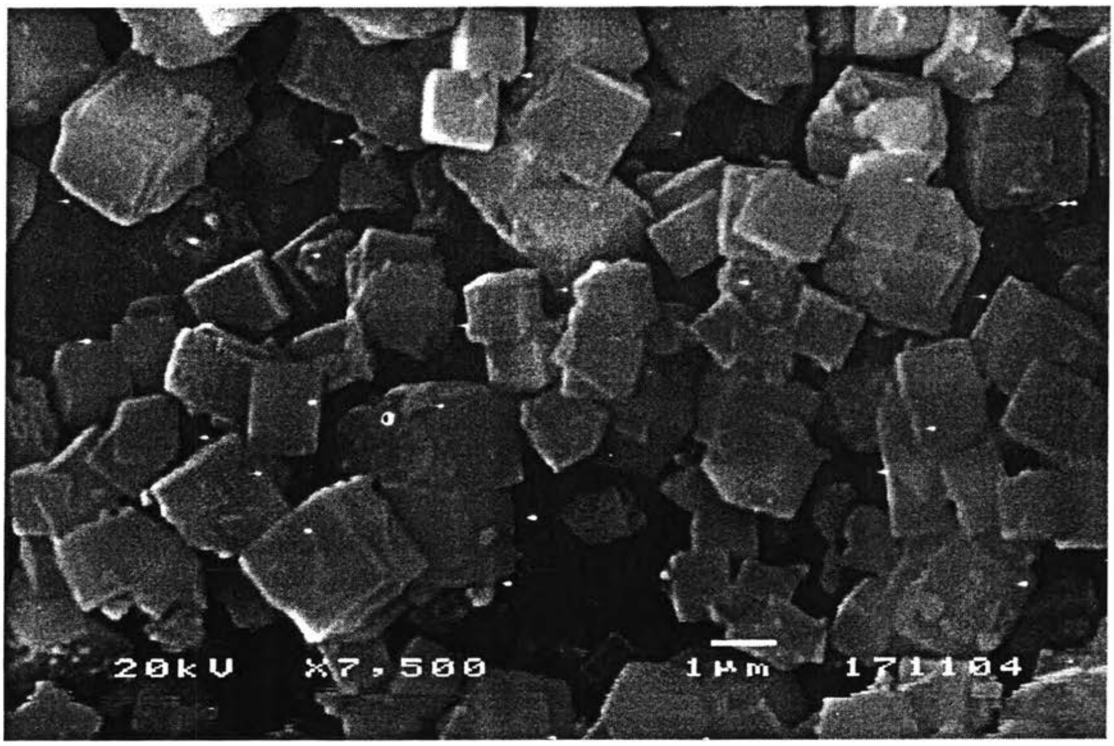

**Figure 4.7** SEM micrograph of 1%Pt/synthesized LTA (LTA4)

## 4.2 Activity Testing

In this section the results of the catalytic performance of the prepared catalysts were presented and discussed. It was divided into 4 subsections: effects of support, $H_2O$ vapor concentration, $CO_2$ concentration and the combination of $H_2O$ and $CO_2$ in the feed on the catalytic performance.

### 4.2.1 Effect of Catalyst Support

As mentioned previously, in this section the catalytic performance of Pt supported on three different supports were exhibited. The catalytic activities of 1%Pt supported on the synthesized LTA (abbreviated LTA4) and commercial LTA (abbreviated LTA6) were plot against the 1%Pt/$Al_2O_3$, the conventional catalyst for this reaction.

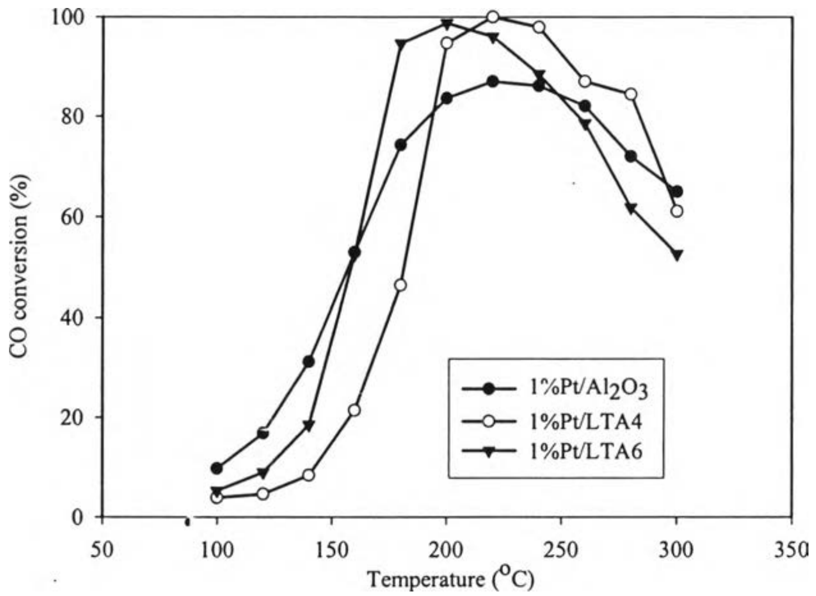

**Figure 4.8** CO conversion of 1%Pt/$Al_2O_3$ (●), 1%Pt/LTA4 (synthesized) (○), and 1%Pt/LTA6 (commercial) (▼). Reactant composition is 1% CO, 1% $O_2$, and He (balance).

Figures 4.8-4.10 display the CO conversions, CO selectivity and $O_2$ conversions of 1%Pt supported on $Al_2O_3$, LTA4 and LTA6, respectively. Peaks of CO conversion were observed on all of the catalysts. Among them, the CO conversions were in the order of Pt/LTA4 > Pt/LTA6 > Pt/$Al_2O_3$ (Figure 4.8). The CO conversion profile of 1%Pt/LTA4 was very similar that of the 1%Pt/LTA6, however, the temperature at which the maximum CO conversion occurred was shifted to 20°C higher. The CO was completely converted to $CO_2$ by the 1%Pt/LTA4 at 220 °C while the 1%Pt/LTA6 gave the maximum temperature at about 200 °C. In contrast, the 1%Pt/$Al_2O_3$ could not achieve CO conversion of 100%, it gave the maximum CO conversion of about 88% at 220 °C. The CO conversion of 1%Pt/LTA4 can be divided to in two regions which are increasing sharply from about 5% to 100% at temperature range from 100 °C to 220 °C and then dramatically decreasing at temperatures above 220 °C. The Pt/LTA6 gave the same feather of CO conversion as the Pt/LTA4 except higher CO conversion at lower maximum temperature. As the temperature was raised up the CO conversion of Pt/LTA6 exponentially increased, the ignition temperature was observed at 160°C. At 200°C the Pt/LTA6 almost completely oxidized CO to $CO_2$, 99% maximum CO conversion. Above 200 °C, the CO conversion dramatically decreased to about 50% at 300 °C. These observations are consistent with the work reported by many authors, including Kahlich *et al.*, (1997), Manasilp and Gulari (2002), and Son *et al.*, (2002). In the work of Kahlich *et al.*, they conducted the experiment with 0.5% Pt/$Al_2O_3$ and 5% Pt/$Al_2O_3$. They investigated the CO oxidation over 0.5%Pt/$Al_2O_3$ with and without $H_2$ in the reactant gas. The oxidation of 1%CO with 1%$O_2$ in the absence of $H_2$ was measured as a function of temperature. The CO conversion was very low at temperatures below 125 °C. As the temperature was raised the CO conversion first slowly increased then suddenly went up and reached 100% conversion at 225 °C. In order to study the CO oxidation in $H_2$-rich environment, they added 75% $H_2$ into the reactant gas. In the $H_2$-rich environment, the ignition temperature was reduced by about 30 °C from 200° to 170 °C. The CO conversion was very low at temperatures below 100 °C and sharply increased to about 80% in the temperature range of 100°-225 °C, about 10% less than our work which may be due to lower metal loading. Then, the CO conversion exponentially decreased from 80% to about 30% at 350 °C.

This phenomena has been explained by Kahlich *et al.* that in the absence of $H_2$, only the CO and $O_2$ were competed for the metal active sites and the CO oxidation took place only at the interface of the adsorbed CO ($CO_{ads}$) and dissociated the adsorbed $O_2$ ($O_{ads}$). At low temperatures the metal surface was dominated by $CO_{ads}$, more than 90%, therefore, the $O_{ads}$ is a limiting factor of this reaction. As the temperature went up more $O_{ads}$ was available which made the CO conversion increase until it reached maximum at 100% CO conversion. In the presence of $H_2$, the $H_2$ came to competition with CO and $O_2$ for the metal active sites. The CO, however, is much stronger adsorbed on the metal active site, as a result, the metal surface was still dominated by $CO_{ads}$. As the temperature increased, the dissociation of the adsorbed $H_2$ ($H_{ads}$) was also increased, resulting in loss of CO selectivity. This is a major cause of a decrease in CO conversion at the temperature range beyond maximum CO conversion. Manasilp and Gulari, (2002) investigated the catalytic performance of 1% and 2% $Pt/Al_2O_3$ catalysts prepared via sol-gel method. Their results have the same feather as our work except lower maximum CO conversion of about 75% and about 80% for 1%$Pt/Al_2O_3$ and 2%$Pt/Al_2O_3$, respectively. The temperature at which the maximum conversion was observed also different. Their catalysts reached the maximum CO conversion at 170 °C while our 1%$Pt/Al_2O_3$ catalysts reached maximum CO conversion at 220 °C. Those differences are the results of different catalysts preparation method, which led to the metal dispersion and metal particle size and different amount of metal loading. The 5%$Pt/Al_2O_3$ was tested for the selective CO oxidation in the $H_2$-rich, 1%CO, 1%$O_2$ by Son *et al.*, (2002). They also observed the same CO conversion and selectivity feathers as our work. The CO conversion was first quite low at around 5-10% at the temperature lower than 100 °C, and was suddenly increased in the temperature range of 100-200 °C from ~10% to ~90%. Their observations can be understood by the same explanation of Kahlich.

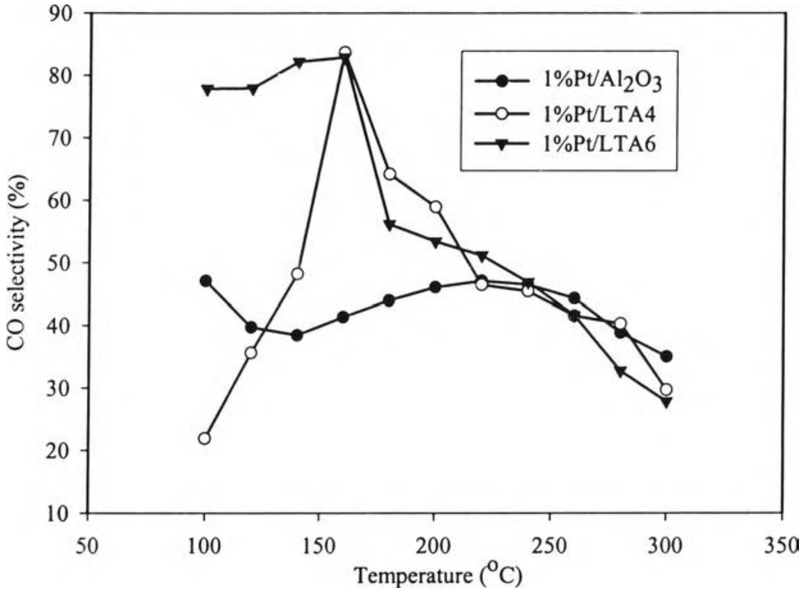

**Figure 4.9** CO selectivity of 1%Pt/$Al_2O_3$ (●), 1%Pt/LTA4 (synthesized) (○), and 1%Pt/LTA6 (commercial) (▼). Reactant composition is 1% CO, 1% $O_2$, and He (balance).

The 5%Pt/$Al_2O_3$ of Son achieved the maximum CO conversion of 90% even they loaded higher amount of the Pt metal, which gave metal particle size of about 16 nm. Comparing to the metal particle size of our 1%Pt/$Al_2O_3$, the 16 nm of 5%Pt/$Al_2O_3$ of Son was much bigger and led to lower metal dispersion. However, the higher metal loading of Son's catalyst may provide comparatively absolute number of metal active sites to our catalysts.

All catalysts showed different characteristic of selectivity at temperature lower than 220 °C. The differences at low temperatures are illustrated in Figure 4.9. This feather of Pt/LTA catalyst is quite different from the Pt/$Al_2O_3$ catalyst on which the selectivity is steeply lowered as increasing the CO conversion at temperature of 220 °C. On the other hand, the selectivity of Pt/$Al_2O_3$ was approximately constant, it slightly swings between 35-48% all over the temperature range of interest. The selectivity of Pt/LTA4 was totally different from the one of Pt/LTA6. It sharply increased from about 20% at 100 °C to about 80% at 160 °C. At temperature above 160 °C, the selectivity of Pt/LTA4 was sharply dropped to about

30% at 300 °C. The different of the CO conversion profile and selectivity between 1%Pt/LTA4 and 1%Pt/LTA6 might be a result of different metal dispersion, 21% in 1%Pt/LTA6 and 18% in 1%Pt/LTA4. The Pt/LTA6 showed very high selectivity of about 80% at low temperatures. It was the ignition temperature where the selectivity started suddenly dropped to 55% at 180 °C and almost linearly decreased to 35% at 300 °C. The Pt/LTA6, unlike Pt/$Al_2O_3$, gave very high selectivity, about 80%, in the temperature range of 100-160 °C. Beyond 160 °C, the selectivity rapidly dropped to about 65% at 180 °C. In the temperature range above 220 °C, the selectivities of Pt/$Al_2O_3$ and Pt/LTA6 were not much different. The structure of LTA (type zeolite) has pore, in this work Na-A type has pore size about 0.40 nm, which can contain gas molecules like $H_2O$, $O_2$, etc, (Igarashi *et al.,* 1997). The difference in selectivity may be a result of sieving capability of the LTA support. It may be that the $H_2$ molecules could get into the pore much easier compared to the CO and $O_2$ molecules, therefore, the $H_2$ was crowded inside the pore and made CO and $O_2$ have more opportunity to access the metal active site which is located outside the pore. On the other hand, the $H_2$ molecules in the LTA's pore might reduce the amount of $H_{ads}$ because lower number of $H_2$ can access the metal active sites. Igarashi *et al.*, (1997) studied the catalytic performance of Pt supported on various supports, including A-type zeolite, X-type zeolite, mordenite zeolite and $Al_2O_3$. They reported that the selectivity of their catalysts varied indirectly to the pore size of the supports. The 6%Pt/LTA prepared by ion-exchange method also showed similar CO conversion profile. However, the CO conversion and selectivity of 6%Pt/LTA were much lower than our Pt/LTA catalyst. The selectivity started about 20% at 150 °C then increased to the maximum selectivity of 60% at 200 °C. Above 200 °C the selectivity linearly decreased to about 30% at 350 °C. The differences of catalytic performance between 6%Pt/LTA of Igarahsi and 1%Pt/LTA in our work might be the location of Pt metal on the support and the amount of Pt loading. In our work, the incipient wetness impregnation method was used, and by this method the metal would sit outside the pore of LTA on the surface of the support. While, by ion-exchange method the Pt metal might locate inside the pore of LTA and lead to lower performance of the catalyst.

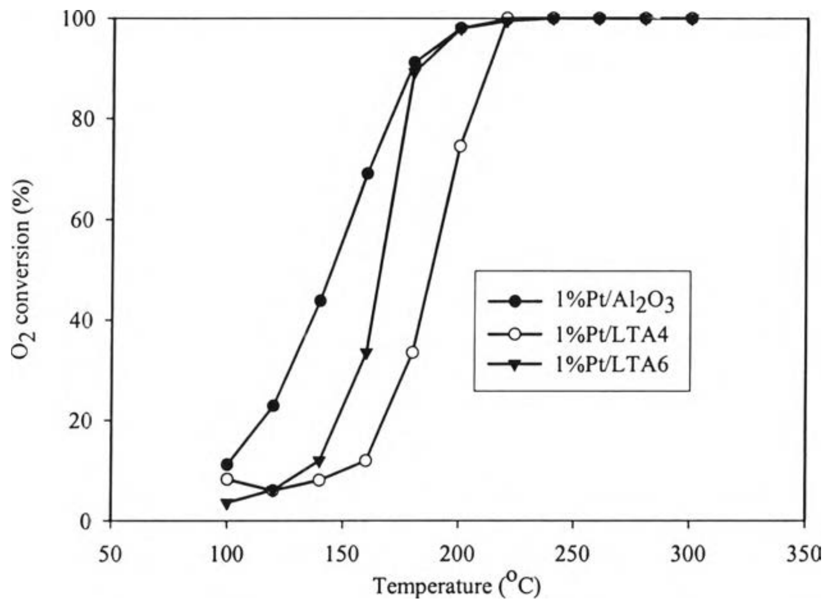

**Figure 4.10** Oxygen conversion of 1%Pt/$Al_2O_3$ (●), 1%Pt/LTA4 (synthesized) (○), and 1%Pt/LTA6 (commercial) (▼). Reactant composition is 1% CO, 1% $O_2$, and He (balance).

The $O_2$ conversions simply increased with increasing the temperature for all catalysts (Figure 4.10). The oxygen consumption was in order of Pt/$Al_2O_3$ > Pt/LTA6 > Pt/LTA4. The different oxygen consumption rate among those three catalysts was a result of different selectivity of the catalysts.

### 4.2.2 Effect of $CO_2$ Concentration

Normally, the reformate stream from the steam reformer unit contains some amount of $CO_2$, therefore, the effect of $CO_2$ on the catalytic activity of the catalysts was studied. To study the effect of $CO_2$ on the catalytic performance, 10% $CO_2$ was added to the reactant gas to make the reactant gas composition of 10% $CO_2$, 1% CO, 1% $O_2$, 40% $H_2$, balance He. As shown in Figures 4.11-4.13 that the presence of $CO_2$ has a positive effect on the CO conversion of the 1%Pt/LTA6. It booted up the CO conversion of the 1%Pt/LTA6 catalyst all over temperature range and reduced the 100 % conversion temperature by 20 degree from 200 °C to 180 °C, however, the ignition temperature was observed at the same temperature. For oxygen conversion, having $CO_2$ in the reactant gas has no significant effect on the $O_2$ conversion profile of the 1%Pt/LTA6. As consequence of increasing in CO conversion, no change in $O_2$ conversion was observed. The CO selectivity was significantly increased over entire temperature range of interest, especially below 160 °C.

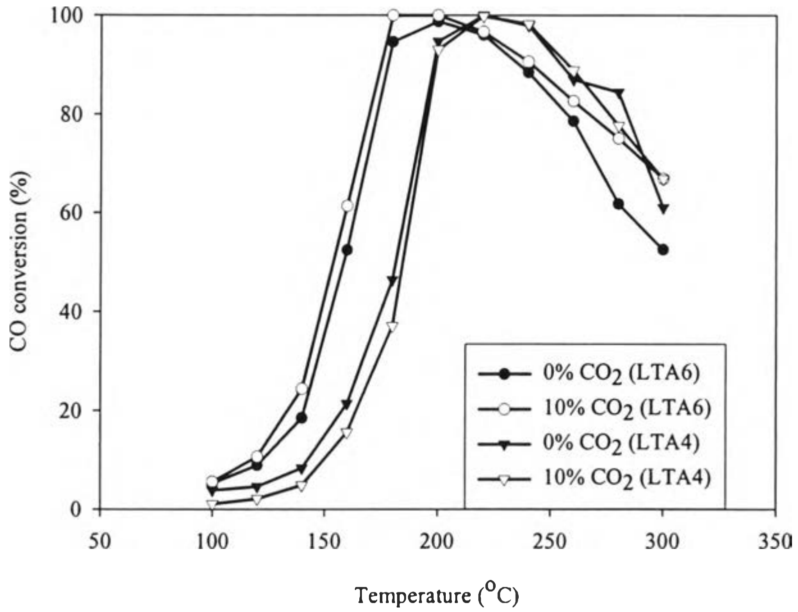

**Figure 4.11** Effect of $CO_2$ concentration on CO conversion of 1% Pt/LTA6(commercial) catalyst; 0% $CO_2$ (●), 10% $CO_2$ (○), and 1%Pt/LTA4(synthesis); 0% $CO_2$ (▼), 10% $CO_2$ (▽). Reactant composition is 1%CO, 1%$O_2$, 0-10%$CO_2$, 40% $H_2$ and He (balance).

On the other hand, the 1%Pt/LTA4 was negatively affected by the presence of the $CO_2$ in the feed, as shown in Figures 4.11-4.13. The CO, $O_2$ conversions were slightly reduced when adding 10%$CO_2$ into the feed. The selectivity was slightly changed in term of maximum selectivity temperature. It was shifted 20°C from 160°C to 180°C, as shown in Figure 4.13.

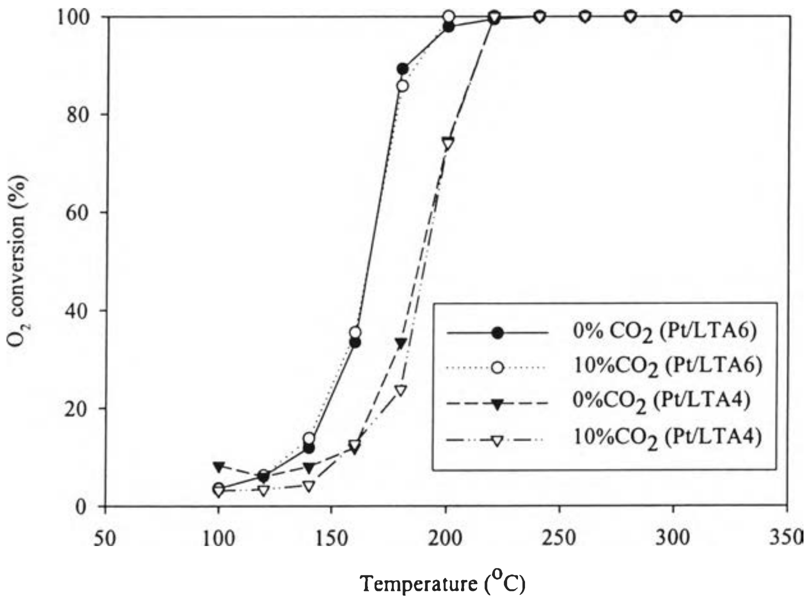

**Figure 4.12** Effect of $CO_2$ concentration on $O_2$ conversion of 1%Pt/LTA6(commercial) catalyst; 0% $CO_2$ (●), 10% $CO_2$ (○) and 1%Pt/LTA4(synthesis); 0% $CO_2$ (▼), 10% $CO_2$ (▽). Reactant composition is 1%CO, 1%$O_2$, 0-10%$CO_2$, 40% $H_2$ and He (balance).

The effect of $CO_2$ concentration on the performance of catalyst was also investigated by others using on the Pt/$Al_2O_3$ catalyst. Manasilp and Gulari (2002) studied the effect of $CO_2$ concentration on the 2% Pt/$Al_2O_3$. They found that by adding 25% $CO_2$ in the reactant gas, consisted of 1% CO, 1% $O_2$, 60% $H_2$ and He balance, the CO conversion was suppressed all temperature range of interest. Especially, at the temperatures above maximum temperature of 170 °C, the CO conversion rapidly dropped from about 65% to about 10%. In the presence of $CO_2$, the CO selectivity was booted up to the peak conversion of 170 °C, then, it was sharply dropped to lower than the selectivity of the one without $CO_2$ at temperature over 170 °C. The $O_2$ conversion was lower in the presence of $CO_2$ over the complete range of temperature studied, which suggested that the $CO_2$ in the reactant gas slowed the oxidation of both CO and $H_2$. To explain the phenomena, they proposed the

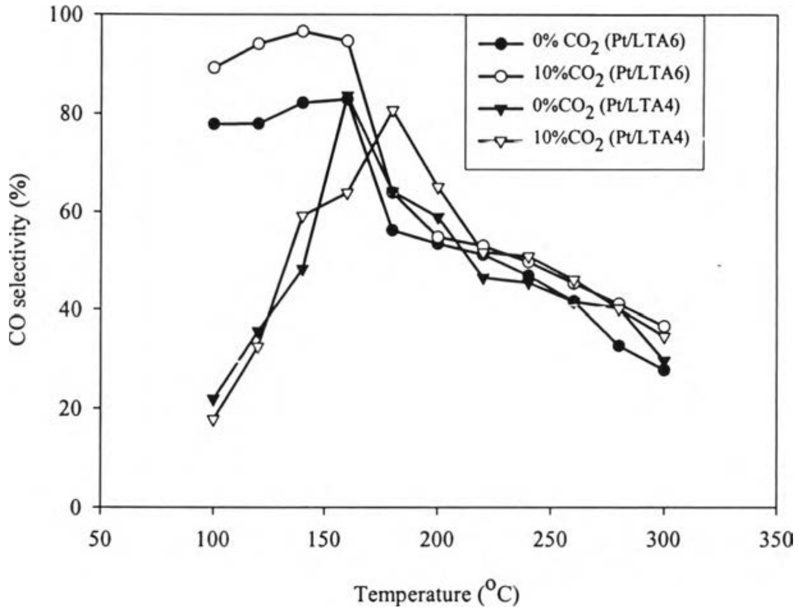

**Figure 4.13** Effect of $CO_2$ concentration on CO selectivity of 1% Pt/LTA6(commercial) catalyst; 0% $CO_2$ (●), 10% $CO_2$ (○), and 1%Pt/LTA4(synthesis); 0% $CO_2$ (▼), 10% $CO_2$ (▽). Reactant composition is 1%CO, 1%$O_2$, 0-10%$CO_2$. 40% $H_2$ and He (balance).

hypothesis that the reverse water gas shift reaction may take place and cause a limit of the catalyst performance at high temperature range. Another possible explanation is that the $CO_2$ dissociated adsorption on Pt, providing a higher effective CO concentration on the catalyst surface and, thus, reducing the rate of oxidation. The positive effect of $CO_2$ on 1%Pt/LTA6 catalyst for the selective CO oxidation implied that the LTA support could inhibit the occurrence of reverse water gas shift reaction. Regarding to the RWGS inhabitation, it might be due to the structure of the A zeolite. Since the pore size of A zeolite is close to the diameter of $CO_2$ molecule (about 2.5 ) which could cause the difficulty of the $CO_2$ admittance into zeolite pores. On the other hand, it still promoted the oxidation of CO to $CO_2$. Since the $O_2$ conversion was not changed whether it had $CO_2$ in the feed stream or not, while the CO conversion increased, thus, the $H_2$ oxidation rate was slowed down while the CO oxidation rate was speeded up. This unusual behavior of Pt/LTA catalyst is good for using in the PROX unit and is the advantage of Pt/LTA catalyst over the conventional Pt/$Al_2O_3$ catalyst. The reasons for this are still not clear. Further study on this behavior is still needed.

### 4.2.3 Effect of $H_2O$ Vapor Concentration

Generally, not only $CO_2$ was produced from the reforming reaction, but also $H_2O$ vapor was present in the stream. This is a very critical point for the practical application of zeolite, therefore, it is interesting to study the effect of $H_2O$ vapor on the catalytic activity of Pt/LTA catalysts. To investigate the effect of $H_2O$ vapor on the performance of Pt/LTA catalysts, about 10% $H_2O$ vapor was added to the reactant gas. From Figures 4.14-4.17, it was obvious that the presence of water vapor had a negative effect on the performance of the catalyst. From the CO conversion profiles from Fig 4.14, they are shifted both in absolute temperature and relative to each other for different catalyst supports. In the presence of 10%$H_2O$ vapor in the feed, the CO conversion of the 1%Pt/LTA6 catalyst decreased about 3% from 99% at 200 °C to 96% at 220°C. It is seemed that the presence of $H_2O$ vapor only shifted the CO conversion profile 20°C higher all over the temperature range, as shown in the Figure 4.14. Moreover, the $O_2$ consumption rate of 1%Pt/LTA6 was slowed down (Figure 4.15). The $O_2$ conversions of 1%Pt/LTA6 reached 100% at the same temperature of 240°C. The CO selectivity of the 1%Pt/LTA6 was also reduced by the $H_2O$ vapor at the temperature below 180°C. It dropped down from around 80% to around 65%. However, at the temperature above 180°C the CO selectivity of systems with and without $H_2O$ vapor in the feed stream seemed to converge and independent to the feed composition.

The 1%Pt/LTA4 catalyst had similar effect to the $H_2O$ vapor in the feed stream. The CO conversion was reduced as well. The highest CO conversion was decreased from about 100% to about 75% at 220°C. The $O_2$ consumption of the 1%Pt/LTA4, unlike 1%Pt/LTA6, was faster at temperature below 200°C, on the other hand, over 200°C it was slowed down. However, it reached 100% $O_2$ conversion at 240°C as well as 1%Pt/LTA6. For the CO selectivity was also decreased all over the temperature range of interest. The peak CO selectivity of 1%Pt/LTA4 was reduced from 80% to 60 at 160°C.

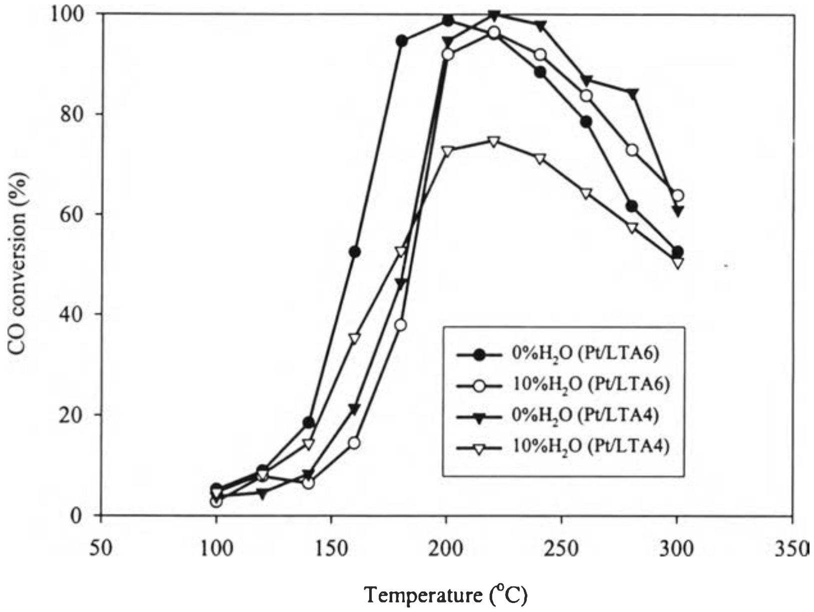

**Figure 4.14** Effect of $H_2O$ vapor concentration on CO conversion of 1% Pt/LTA6 (commercial); 0% $H_2O$ (●), 10% $H_2O$ (○), and 1%Pt/LTA4(synthesis); 0% $H_2O$ (▼), 10% $H_2O$ (▽). Reactant composition is 1% CO, 1% $O_2$, 0-10% $H_2O$, and He (balance).

These results are consistent with Igarashi *et al.,* they reported that negligible degradation of activity occurred on Pt/mordenite when 20% $H_2O$ was added to the feed. Although when 20%$H_2O$ was added, the CO conversion and the $O_2$ conversion slightly decreased at the initial stage. In contrast to watanabe et al., they found that in the presence of 20% $H_2O$, the activity of the supported metallic catalyst and the mordenite support were extremely stable for 24 hrs. However, this is opposite to Pt/$Al_2O_3$ catalyst reported by Manasilp and Gulari (2002). For Pt/$Al_2O_3$, many authors proposed the possible mechanism on this phenomena. Schubert *et al.,* (1997) reported the result of in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscpy (DRIFTS) that this reaction was strongly enhanced by water. Kahlich *et al.*, (1997) proposed that the formate group formed on the $Al_2O_3$ support may participate the reaction and increase the CO conversion. Manasilp and Gulari (2002) proposed three possibility on this system. First, the water gas shift promoting, the

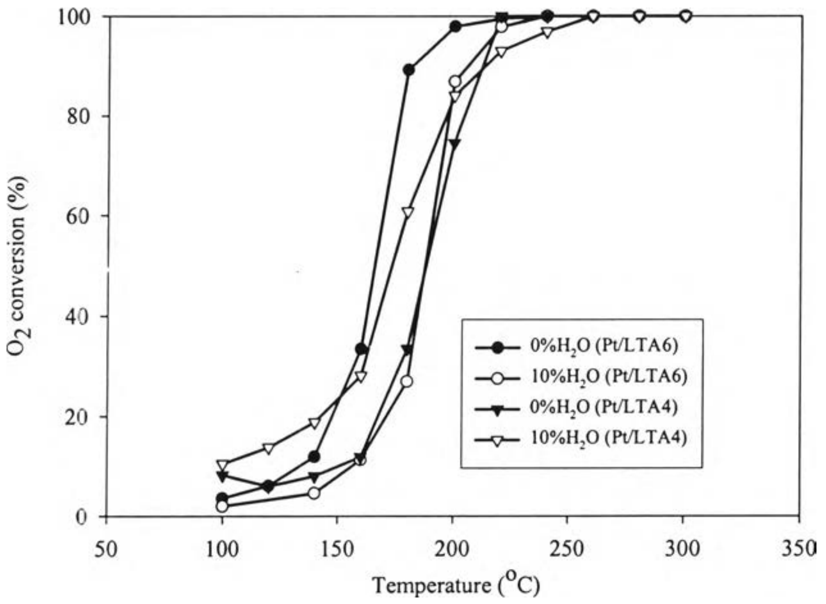

**Figure 4.15** Effect of $H_2O$ vapor concentration on $O_2$ conversion of 1% Pt/LTA6 (commercial); 0% $H_2O$ (●), 10% $H_2O$ (○), and 1%Pt/LTA4(synthesis); 0% $H_2O$ (▼), 10% $H_2O$ (∇). Reactant composition is 1% CO, 1% $O_2$, 0-10% $H_2O$, and He (balance).

presence of $H_2O$ in the feed stream enhanced the forward water gas shift reaction which increased CO conversion and also made additional $H_2$. Second, the $H_2O$ provided hydroxyl group on the catalyst. Those hydroxyl groups were a better oxidant than the $O_2$, and increased oxidation rate of CO and $H_2$. Third, the $H_2O$ vapor altered the $Pt^o$ and $PtO_x$ ratio which could directly influence on activity and selectivity of the $Pt/Al_2O_3$ catalyst. In contrast, those did not happen or not significant in Pt/LTA catalyst. In this work, the decreased CO conversion in the presence of $H_2O$ may be linked to the catalyst active sites by adsorbed water, as well as, the formation CO-$H_2O$ surface complexes or the water gas shift reaction might be suppressed by the more strong effect of sieving capability of LTA on this reaction or $H_2O$ vapor was accumulated in the pore of LTA, which is acting a very good molecular sieve for $H_2O$ vapor and the accumulated $H_2O$ was simply not available for sieving $H_2$. This caused reduction of selectivity of the catalyst. One evidence that supports this hypothesis is that in $Pt/Al_2O_3$ the $H_2O$ had slightly effect on the selectivity, even it had a strongly effect on the CO and $O_2$ conversions.

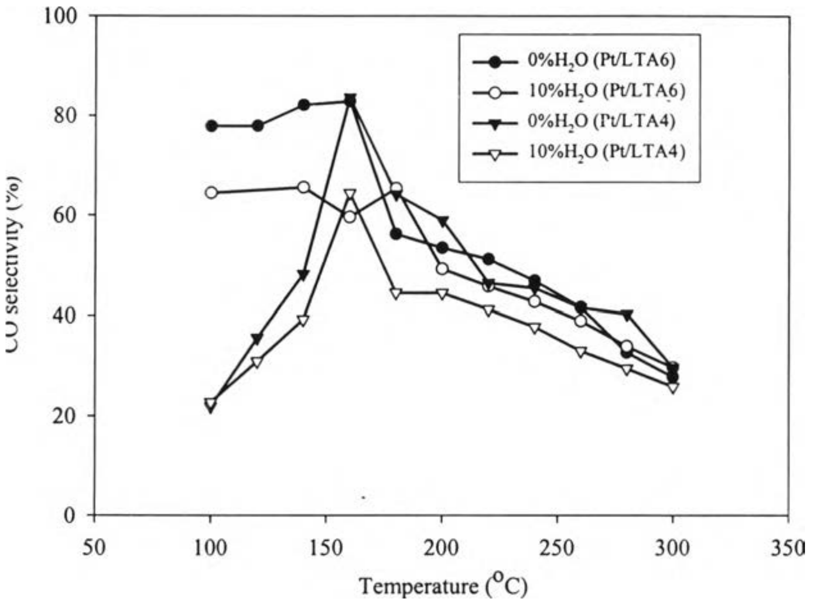

**Figure 4.16** Effect of $H_2O$ vapor concentration on CO selectivity of 1% Pt/LTA6 (commercial); 0% $H_2O$ (●), 10% $H_2O$ (○), and 1%Pt/LTA4(synthesis); 0% $H_2O$ (▼), 10% $H_2O$ (▽). Reactant composition is 1% CO, 1% $O_2$, 0-10% $H_2O$, and He (balance).

### 4.2.4 Effect of Combination of $H_2O$ and $CO_2$

To investigate the overall effect of $H_2O$ vapor concentration and $CO_2$ concentration, the combination of 10% $H_2O$ vapor and 10% $CO_2$ was added to the reactants gas consisting of 1% CO, 1% $O_2$ and 40% $H_2$ balanced in He. For 1%Pt/LTA6, even the CO conversion was promoted by $CO_2$, but in the presence $CO_2$ together with $H_2O$ the CO conversion was significantly retarded, as shown in Figure 4.17. This suggests that the $H_2O$ has stronger influence to the catalytic performance of the 1%Pt/LTA6 catalyst than the $CO_2$. Comparing to the activity of Pt/Fe-mordenite catalysts studied by Watanabe *et al.* (2003), they observed that the performance of Pt/Fe-mordenite slightly decreased from 100 to 99.1% at 200°C due to a reverse water gas shift reaction in the presence of $CO_2$. This effect on the catalytic performance of $Pt/Al_2O_3$ was also studied by Manasilp and Gulari (2002). They fed 1% CO, 1% $O_2$, 0-10% $H_2O$, 0-25% $CO_2$, 60% $H_2$ and He as balance to the reactor. They found that the combination of 25% $CO_2$ and 10% $H_2O$ had dramatically positive effect on the CO conversion of their $Pt/Al_2O_3$ catalyst, even the CO conversion was retarded by the $CO_2$ alone.

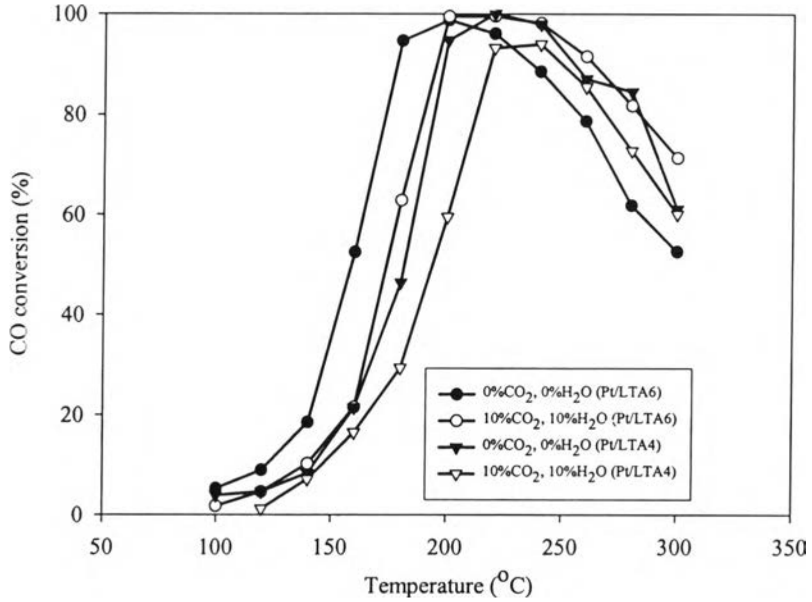

**Figure 4.17** Effect of combination of 10% $CO_2$ and 10% $H_2O$ vapor on CO conversion of 1% Pt/LTA6 (commercial). Reactant composition was 1% CO, 1% $O_2$, 0-10% $H_2O$, 0-10% $CO_2$, 40% $H_2$ and He (balance).

This indicates the stronger effect of $H_2O$ to the catalytic activity of the $Pt/Al_2O_3$ catalyst compared to the $CO_2$, which is consistent to our work. However, the effect of $H_2O$ on the 1%Pt/LTA6 catalyst and on the $Pt/Al_2O_3$ catalyst was come from different sources. As proposed by Manasilp and Gulari (2002), the changing of CO conversion due to the effect of $H_2O$ was a result of water gas shift reaction enhancement, hydroxyl group formation and modification of the ration of Pt to $PtO_x$, as mentioned previously. In contrast, the $H_2O$ on the 1%Pt/LTA6 filled the pore of the LTA support and blocked the $H_2$ molecules to access the pores.

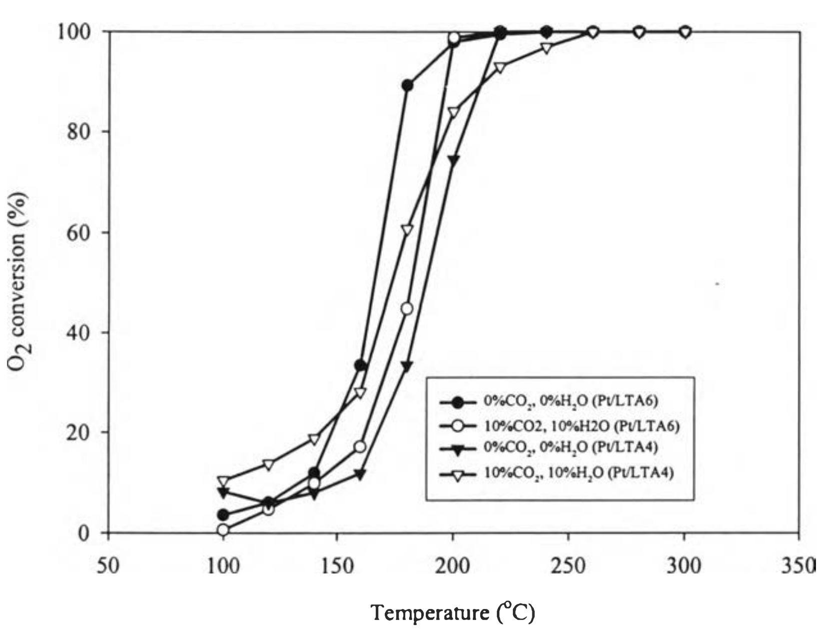

**Figure 4.18** Effect of combination of 10% $CO_2$ and 10% $H_2O$ vapor on $O_2$ conversion of 1% Pt/LTA6 (commercial). Reactant composition of 1% CO, 1% $O_2$, 0-10% $H_2O$, 0-10% $CO_2$, 40% $H_2$ and He (balance).

The $O_2$ conversion of the 1%Pt/LTA6 catalyst was affected by the combination of $CO_2$ and $H_2O$ in the same way as the CO conversion, as shown in Figure 4.18. This is also consistent with the observation for the $Pt/Al_2O_3$ by Manasilp and Gulari, 2002. The $O_2$ conversion was consumed much faster in the presence of $H_2O$ in the feed stream for the $Pt/Al_2O_3$

For the selectivity towards CO oxidation, it was found that the CO selectivity of 1%Pt/LTA6 was significantly suppressed at the temperature range lower than 180 °C. Above 180 °C, it seems like that the selectivity was independent of reactant composition. This supports the idea of the $H_2O$ molecules accumulated in the pore of LTA support and consequently reduced the selectivity of the catalyst. Moreover, the $H_2O$ has a stronger effect, again, compared to the $CO_2$ effect.

The 1%Pt/LTA4 showed the same behaviors to the effect of the combination of 10%$CO_2$ and 10%$H_2O$ on the catalytic activity. The values of CO conversion, $O_2$ conversion, and CO selectivity of the 1%Pt/LTA4 being affected by the presence of $CO_2$ and $H_2O$ vapor together were in between those values which were the effect by $CO_2$ or $H_2O$ alone. The above data suggests a conclusion that the decrease of CO conversion in the presence of $CO_2$ and $H_2O$ may be attributed to reverse water gas shift reaction, blockage of catalyst active sites by adsorbed water or the formation of CO-$H_2O$ surface complexes which are less active than adsorbed CO.

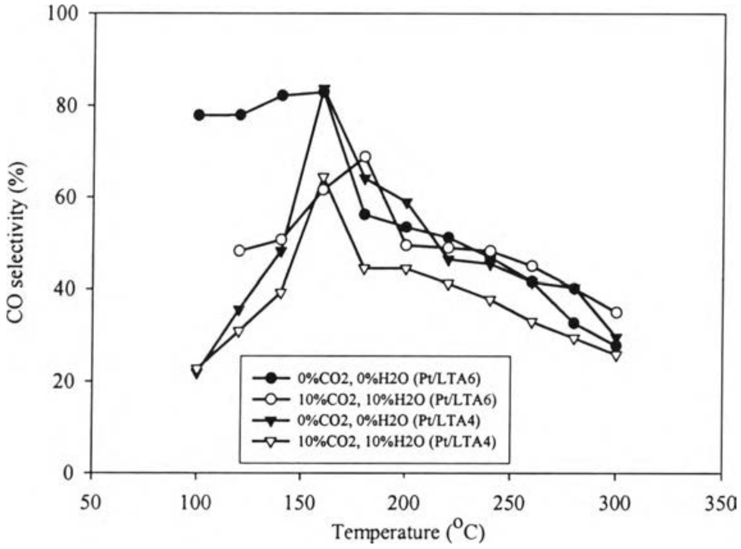

**Figure 4.19** Effect of combination of 10% $CO_2$ and 10% $H_2O$ vapor on $O_2$ conversion of 1% Pt/LTA6 (commercial). Reactant composition was 1% CO, 1% $O_2$, 0-10% $H_2O$, 0-10% $CO_2$, 40% $H_2$ and He (balance).

### 4.2.5 Effect of Fe Promoting on the Performance of 1% Pt/LTA Catalyst

Since there are many reports about Fe promoted the Pt catalysts, it was thus interesting to study the effect of Fe promoting on our Pt/LTA catalyst. As a result, we promoted our 1%Pt/LTA6 with 0.1% and 1% Fe and investigated their performance. The reactant gas consisted of 1%CO, 1%$O_2$, 40%$H_2$ and balance He was used for the reaction. It was found that promoting the 1%Pt/LTA6 catalyst with Fe did not improve the performance of the catalyst, in contrast, it significantly reduced the performance of the catalysts both in terms of CO conversion and CO selectivity as shown in Figures 4.10-4.11, respectively. In Figure 4.10, the CO conversion profiles of 1%Pt0.1%Fe/LTA6 and 1%Pt1%Fe/LTA6 were shown comparing to the un-promoted 1%Pt/LTA6. The maxima CO conversion were reduced from almost 100% to about 70% and 60% for 1%Pt1%Fe/LTA6 and 1%Pt0.1%Fe/LTA6, respectively. In addition, the maximum CO conversion temperature of the 1%Pt1%Fe/LTA6 was shifted 20% down from 200 °C to 180 °C. Adding 1%Fe into the 1%Pt/LTA6 catalyst made the $O_2$ be consumed faster. Promoting the 1%Pt /LTA6 with 0.1%Fe, however, insignificantly altered the $O_2$ consumption rate of the catalyst, as shown in Figure 4.11. As shown in Figure 4.12, the CO selectivity of the Fe promoted 1%Pt/LTA6 catalysts was totally changed comparing to the un-promoted one. Normally, the CO selectivity profile of the supported Pt catalyst had peak, but no peak was observed in the CO selectivity profile of the Fe promoted 1%Pt/LTA6 catalyst. In the work of Lui *et al.*, (2002), they did the structural study of Fe oxide promoted $Pt/Al_2O_3$ catalyst in the selective catalytic oxidation of CO in $H_2$ by using several techniques, including, Fourier Transform Infrared Spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS),

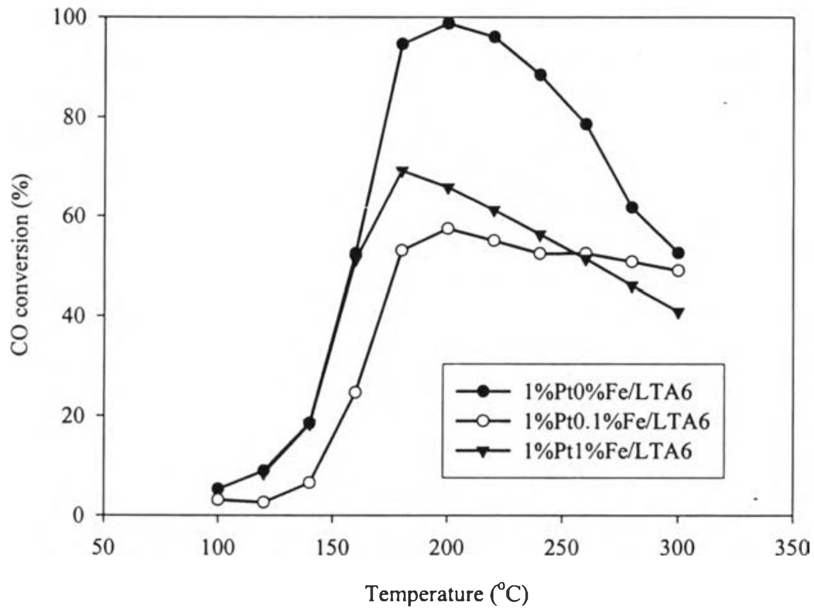

**Figure 4.20** Effect of Fe promoted 1% Pt/LTA6(commercial) on the CO conversion; 0%Fe (●), 0.1%Fe (○), and 1%Fe (▼). Reactant composition was 1% CO, 1% $O_2$, 40% $H_2$ and He (balance).

high-resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray analysis (EDAX) together with chemisorption. They found that when adding Fe oxide into the Pt/$Al_2O_3$ catalyst the Fe oxide would locate on the Pt metal particle and partially covers the Pt metal surface causing decrease in Pt metal active sites. Moreover, the CO did not adsorb on the Fe which means that the surface reaction of CO oxidation did not occur on the Fe oxide surface. However, the Fe oxide could provide more active oxygen to the Pt, resulting in more active for the CO oxidation reaction. In addition, the Fe oxide strongly interacted with the Pt metal and modified the electronic property of the Pt metal. As a result of this modified electronic property, the CO was adsorbed on the Pt longer.

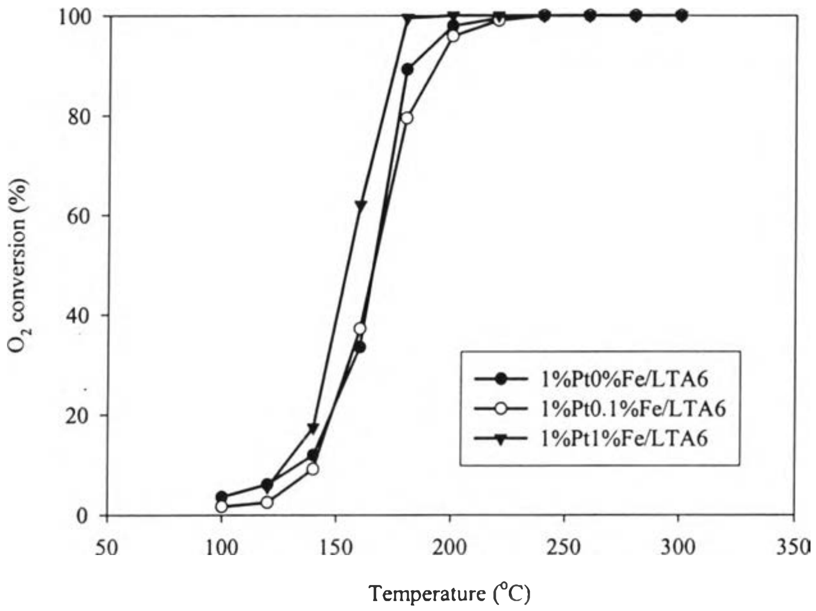

**Figure 4.21** Effect of Fe promoted 1% Pt/LTA6(commercial) on the $O_2$ conversion; 0%Fe (●), 0.1%Fe (○), and 1%Fe (▼). Reactant composition of 1% CO, 1% $O_2$, 40% $H_2$ and He (balance).

There are many possibilities for the explanation of the behavior of our Fe promoted 1%Pt/LTA6 catalyst. Based on the work of Lui *et al.*, (2002), it might be that the Fe sat on the Pt metal particle and covered some surface of the Pt metal particle and reduced the number of Pt active sites. Unlike the Fe promoted

$Pt/Al_2O_3$ in work of Lui *et al.*, the Fe in our work did not supply additional oxygen to the Pt metal, therefore, instead of promoting the reaction the Fe retarded the performance of the 1%Pt/LTA6. Another possibility might be that unlike $Pt/Al_2O_3$, the Fe did not sit on the Pt metal particle at all. The Fe just located on the LTA support, as a consequence, it could not supply oxygen to the Pt metal. On the other hand, it blocked some pore of the support and caused a reduction in the performance of the 1%Pt/LTA6 catalyst. To investigate the causes of this behavior of the Fe promoted 1%Pt/LTA6 catalyst further study is required.

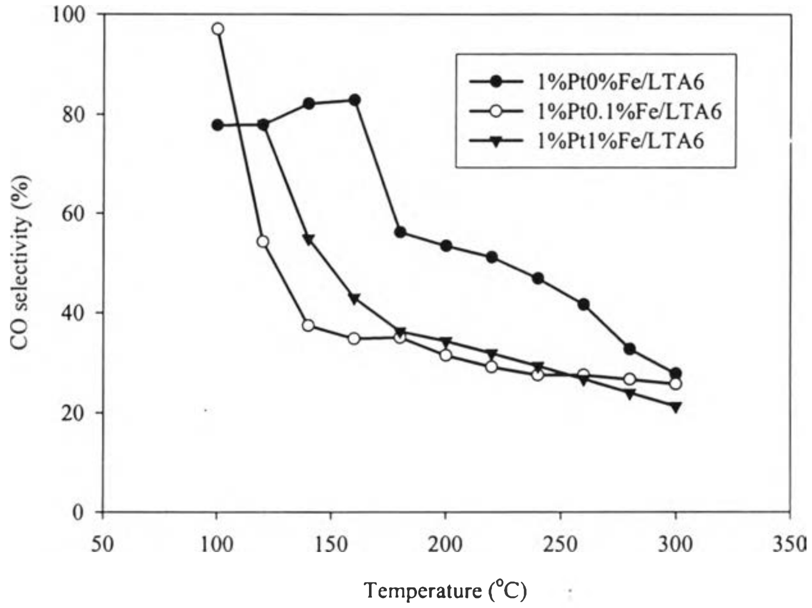

**Figure 4.22** Effect of Fe promoted 1% Pt/LTA6(commercial) on the CO selectivity; 0%Fe (●), 0.1%Fe (○), and 1%Fe (▼). Reactant composition of 1% CO, 1% $O_2$, 40% $H_2$ and He (balance).

4.2.6 Durability Testing

To investigate the durability of the Pt/LTA catalyst, the 1%Pt/LTA6 was tested for 12 hrs continually. The reaction was conducted with 1%CO, 1%$O_2$, and 40%$H_2$ at 200 °C, which is the maximum CO conversion temperature of the 1%Pt/LTA6 catalyst. The data was recorded every 10 mins. No deactivation was observed, as shown in Figure 4.23. This suggests that the Pt/LTA catalyst has a good durability for the selective CO oxidation reaction.

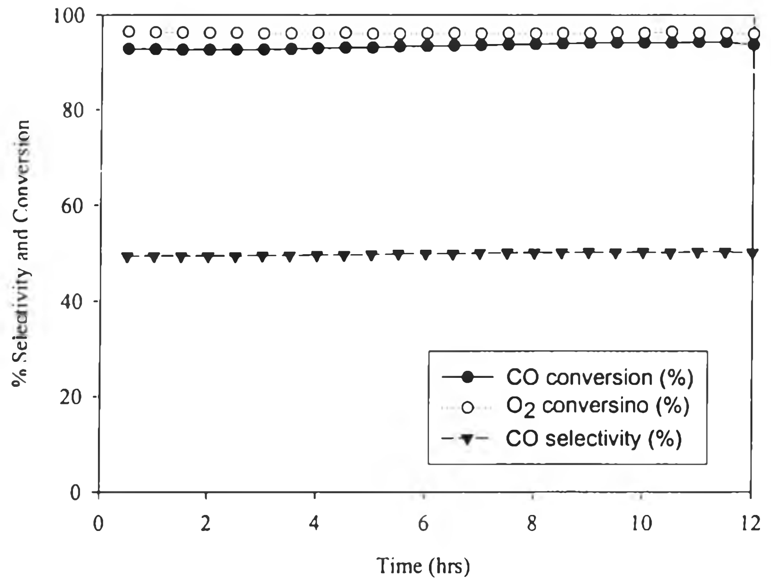

**Figure 4.23** Durability testing, the CO oxidation was performed at 200 °C under atmospheric pressure; CO conversion (●), $O_2$ conversion (○), and CO selectivity (▼). Reactant composition of 1% CO, 1% $O_2$, 40% $H_2$ and He (balance).