CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

This section shows the catalysts characterization results. The results were obtained from variety characterization techniques, including XRD, BET, H_2 Pulse Chemisorption, ICP, SEM, TEM and TPR. The characteristic of the catalysts in this part will be used to explain the catalytic activity of the prepared catalysts. Additionally, the precursors of synthesized A zeolite (silatrane and alumatrane) and synthesized A zeolite were characterized and discussed in this section.

4.1.1 Precursor Synthesis

The silatrane and alumatrane were synthesized via the Oxide-One-Pot-Synthesis (OOPS) process. 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, that provides only one mass loss transitions at 390°C, which is corresponding to the decomposition of the organic ligand and oxidation of the carbon residue. The silatrane has percent ceramic yield of about 22.4%, which is higher than the theoretical ceramic yield of 18.6% (Sathupunya 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.

4.1.1.2 Alumatrane Characterization

Figure 4.3 shows the TGA thermogram of alumatrane, having two mass loss transitions at The TGA results give two mass loss transitions at 139°C and 393°C with 24.2% ceramic yield corresponding to the structure of $Al(OCHCH_3CH_2)_3N$, which has 23.7% theoretical ceramic yield reported by Sathupunya 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 Sathupunya *et al.,* 2003.
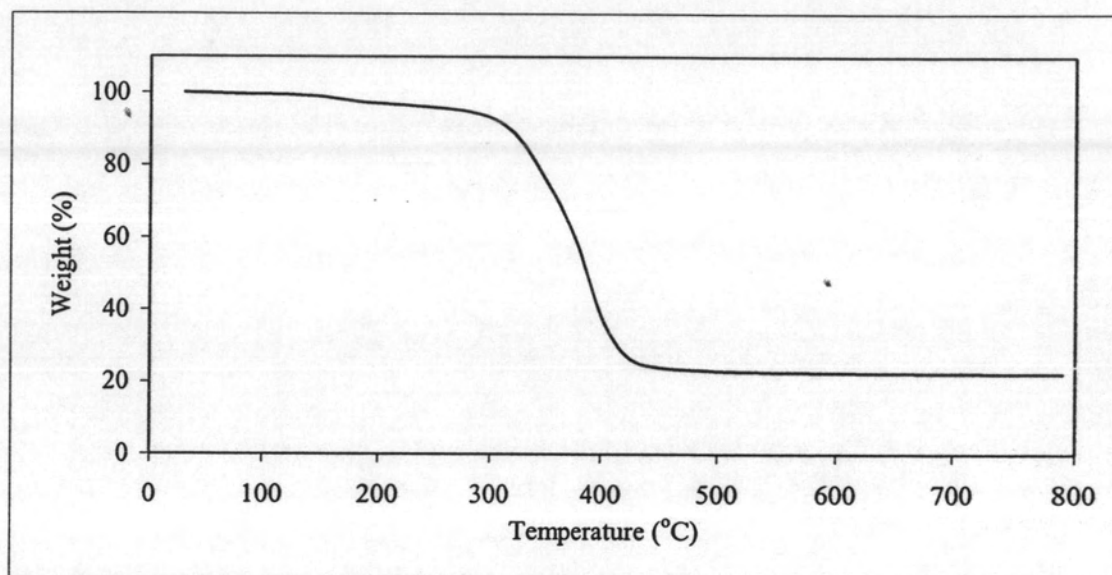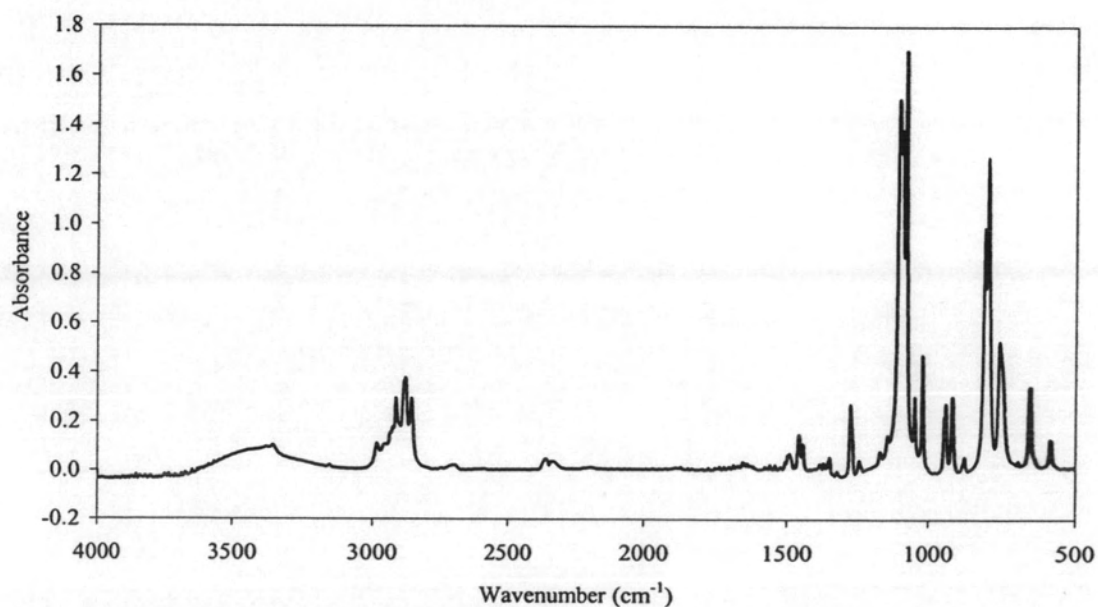

Figure 4.1 The TGA result of silatrane.

Figure 4.2 FTIR spectrum of silatrane.

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

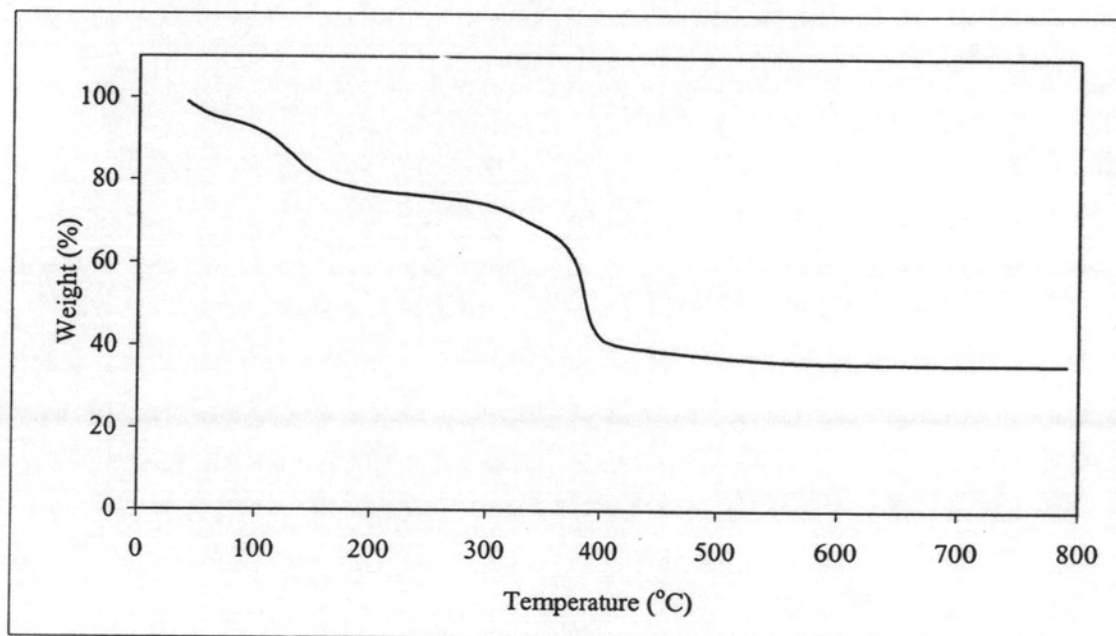| Peak positions (cm^{-1})	Assignments
3100-3700	ν(O–H)
2800-3000	ν(C–H)
1445, 1459, 1500	δ(C–H)
1351	ν(C–N)
1276, 1022	ν(C–O)
1080-1180, 1049	ν(Si–O)
1096	ν(Si–O–C)
700-940	δ(Si–O–C)
580	Si← N

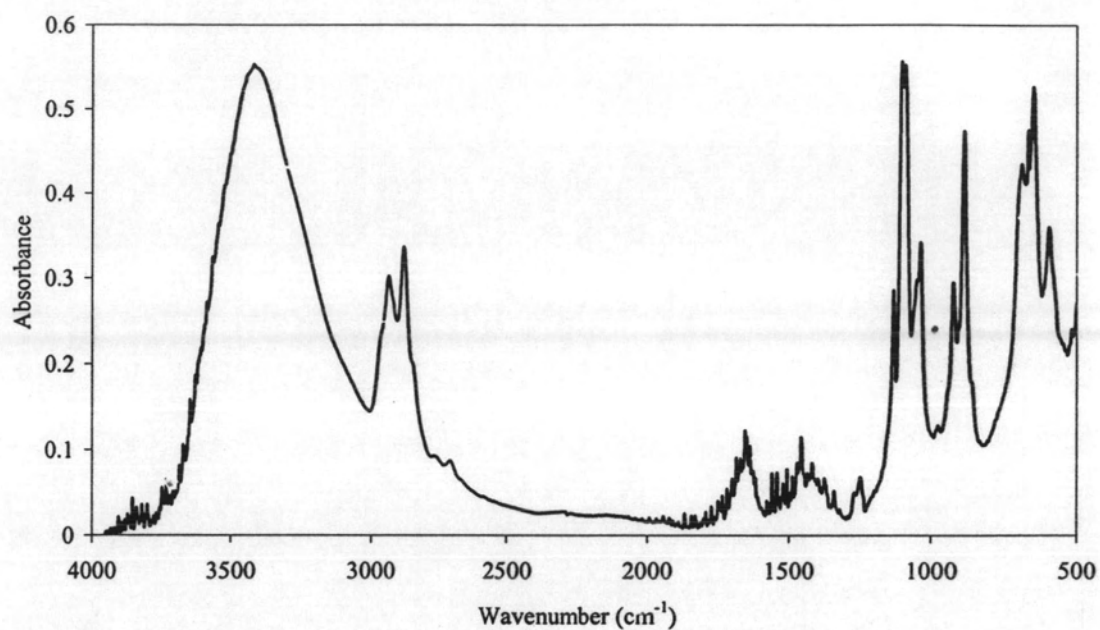**Figure 4.3** The TGA result of alumatrane.

Figure 4.4 FTIR spectrum of alumatrane.

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

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

4.1.2 A-Type Zeolite Synthesis

A-type zeolite can be synthesized via sol-gel process and microwave heating techniques by using silatrane and alumitrane as a precursor. The synthesized A zeolite was characterized by XRD and SEM techniques.

4.1.2.1 X-ray Diffraction Patterns

Figure 4.5 presents the XRD patterns of commercial A zeolite and synthesized A zeolite. As before, Sathupunya *et al.*, (2003), reported the synthesized A zeolite were matched to with the Linde (A-LTA) structure having PDF# 39–0222 and $Na_{96}Al_{96}$-$Si_{96}O_{384}.216H_2O$, Si:Al:Na=1:1:1. Additionally, Figure 4.5 shows XRD pattern of the synthesized A zeolite. Its XRD pattern has many sharp peaks and perfected with a commercial A zeolite.
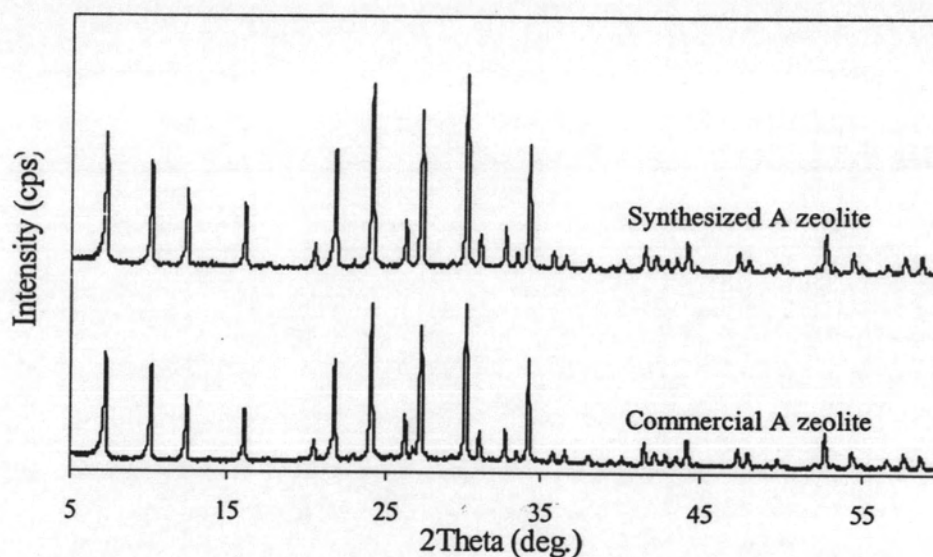

Figure 4.5 XRD patterns of commercial A zeolite and synthesized A zeolite.

4.1.2.2 Scanning Electron Microscope (SEM)

The SEM micrographs were employed to observe the morphology in microscale of the synthesized A zeolite and commercial A zeolite. There was a big difference between two A zeolites as illustrated in Figures 4.6-4.7. The synthesized A zeolite shows a better homogeneous morphology than the commercial zeolite which almost all crystalline product was formed. From this result leads to the hypothesis that is the zeolite morphology might affect to the catalytic activity of preferential CO oxidation reaction.
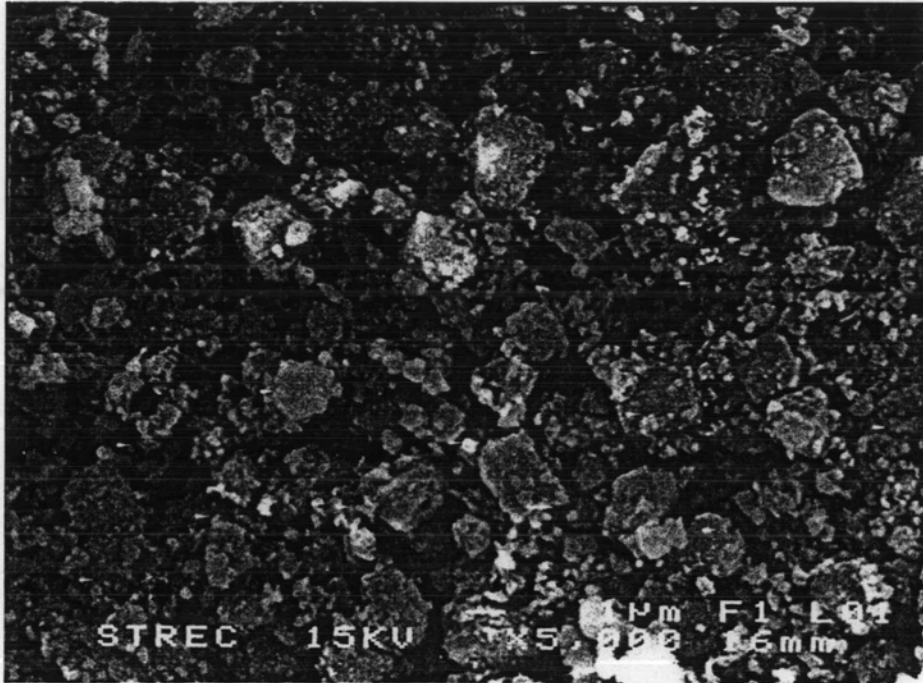
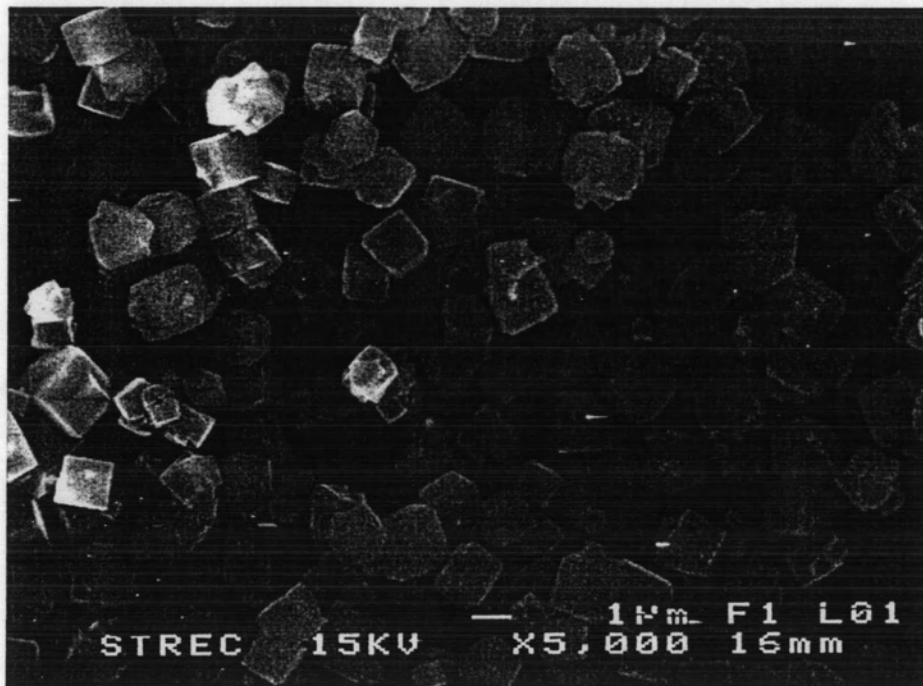**Figure 4.6** SEM micrograph of the commercial A zeolite.

Figure 4.7 SEM micrograph of the synthesized A zeolite.

4.1.3 Prepared Catalyst Characterization

Many catalyst characterization techniques were utilized to explain the differences in the activity and selectivity of each prepared catalyst.

4.1.3.1 X-ray Diffraction Patterns

All XRD patterns of AuPt/A zeolite catalysts prepared by incipient wetness impregnation method at different sequential order of metal loading and zeolite A were illustrated in Figure 4.8. If Au is firstly loaded on the A zeolite followed by Pt loading, they will be denoted as Pt-Au/A zeolite. However, if Pt is firstly loaded on the A zeolite followed by Au loading, they will be denoted as Au-Pt/A zeolite. For co-impregnation, they will be denoted as AuPt/A zeolite. The XRD patterns of Au and Pt peaks indicate the existing metals in the prepared catalysts and the crystallite size of metals were calculated by Scherrer Equation as summarized in Table 4.3. The XRD patterns of all samples were almost the same but peak intensity of all samples have a little difference. Those additional peaks observed at 2θ of 38.2 and 39.8° were corresponding to Au(111) and Pt(111) for CuKα (1.5406 Å) radiation, respectively. This result indicates that the metal particles of Au and Pt are not mixed to alloy form, hence, Au-Pt alloys are not present. Since the peak for the alloy would be shifted towards small angles. Even the position of each metal peak shifted, it may be resulted from Au atom in lattice of Au metal was took place with partially Pt atom or the metals on the catalyst support formed mixed particles; the number of Pt atoms surrounded by Au; as proposed by Riahi *et al.* (2002). The Pt peak of AuPt/ A zeolite was sharper than another prepared catalyst. However, the Au peak of Au-Pt/A zeolite was sharper than another prepared catalyst. It was observed that the average metal crystallite sizes were not much different among the prepared catalysts. In addition, the amounts of total metal loading of all catalysts are almost the same, as confirmed by the ICP results. From those results, the sequential order of metal loading did not show a significant effect on the catalytic activities of each catalyst. Additionally, the same metal crystallite sizes might lead to the same metal dispersion, resulting in not much different catalytic activities between Pt-Au/A zeolite, Au-Pt/A zeolite and AuPt/A zeolite catalysts.
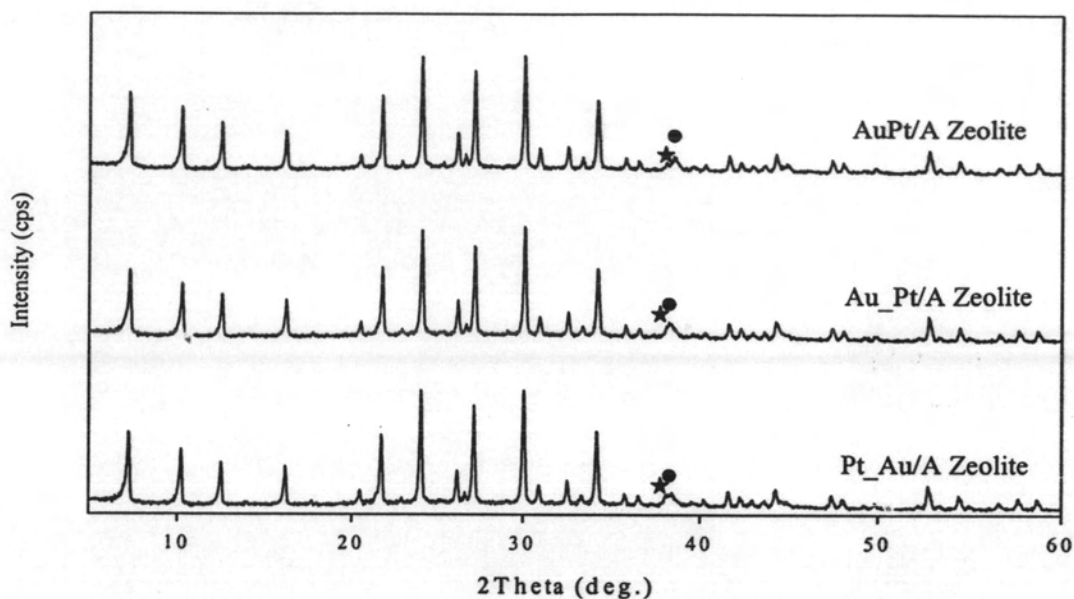
Figure 4.8 XRD patterns of AuPt supported on commercial A zeolite at different sequential order of metal-loading: (★) Au; (●) Pt.

Table 4.3 The metal crystallite sizes of the prepared catalysts

Catalysts	Au Crystallite Size (nm)	Pt Crystallite Size (nm)
(1:1.5)Pt-Au/4A zeolite	71.3	71.5
(1:1.5)Au-Pt/4A zeolite	71.2	71.3
(1:1.5)AuPt/4A zeolite	71.2	71.3

4.1.3.2 Scanning Electron Micrograph

The SEM micrographs were employed in order to observe the morphology in microscale of the Au-Pt/A zeolite prepared catalysts. There was a big difference between two prepared catalysts as illustrated in Figures 4.9-4.10. The AuPt/synthesized A zeolite shows a better homogeneous morphology and the particle size was smaller than the AuPt/ commercial A zeolite. The Au and Pt metal particles can not be observed and indicated from these results.
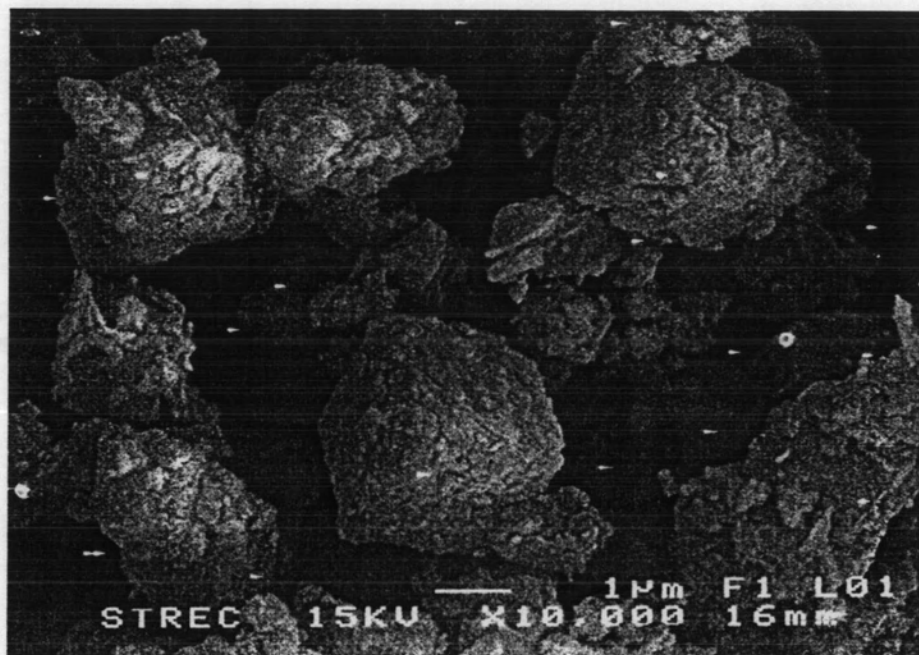
Figure 4.9 SEM micrograph of 1% (1:2)AuPt/commercial A zeolite.

Figure 4.10 SEM micrograph of 1% (1:2)AuPt/synthesized A zeolite

4.1.3.3 Transmission Electron Micrograph

The Au and Pt crystallite sizes of the 1% (1:2)AuPt/commercial 4A zeolite catalysts could be clearly observed in TEM micrograph as shown in Figure 4.11 (a-b). Metal particles are seen as dark contrasts on the surface of zeolite particles. The presence of metals on the zeolite catalyst support was confirmed by energy dispersive spectroscopy (EDS). It can be observed that the average diameters of the Pt particles are much smaller than the diameter of Au particles. Crystallite sizes of Au were about 200 nm while crystallite sizes of Pt were almost uniform in size 100 nm and quite homogeneous in size. The observations agreed well with the fact that the Pt crystallite size was 71.3 nm, calculated from the half-width of the main peak Pt(111) according to Scherrer's Equation. The driving force for growing large Au particles on the support surface may increase form the hydroxyl group on the surface of Au particles because the hydrogen bond on the hydroxyl group can raise strong hydrophilic interaction among Au particles. Consequently, the condensation of water from hydroxyl groups between the particles causes the sintering on the support surface. In addition, Au metal particles weakly interact with the Pt metal particles so that Au metal did not form an alloy with Pt metal because two metals appear to be severely phase separated. Subsequently, Chandler B. D. *et al.* (1999) reported that the co-impregnation of Au with Pt from chloride salts yielded catalysts with little or no interaction between the two metals. At a higher metal loading, agglomeration of metal particles is observed both on the Au and Pt. As can be seen, the Au metal has a little interaction with the zeolite catalyst support because of the Au^{+3} ion is a metal cation which is a easy to reduce resulting in the Au is surely the most difficult metal to disperse and to anchor in zeolite. But if we use the acidic zeolite, which favors the dispersion of the metal and the thermal stability, lead to an increase the catalytic activities, reported by Riahi *et al.* (2002). Additionally, the small size of the Au particles and the stability of all the nanoparticles are described by the anchoring of the metal on the Brønsted acid sites of the zeolite catalyst supports.
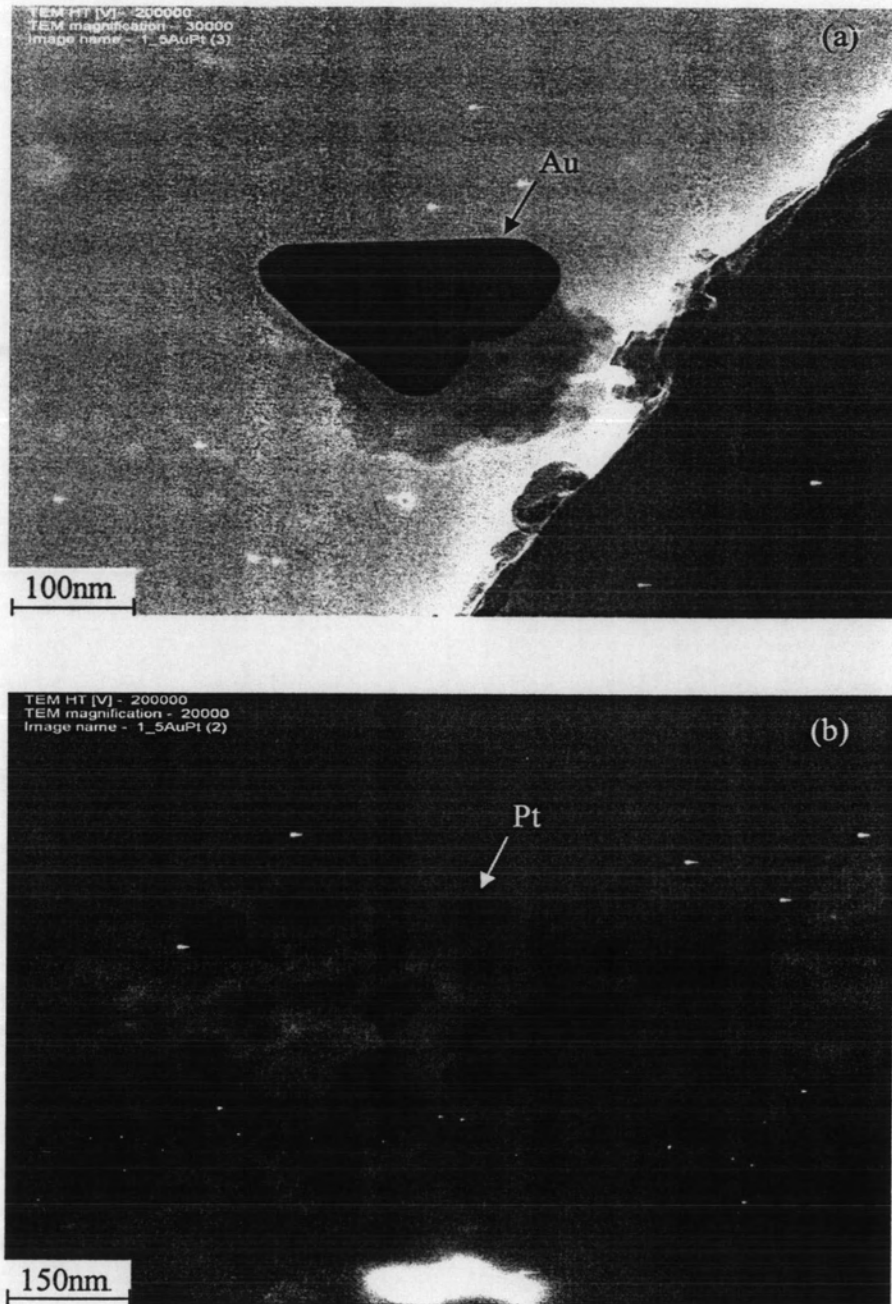
Figure 4.11 TEM micrographs of 1% (1:2)AuPt/commercial A zeolite: (a) Au metal and (b) Pt metal.

4.1.3.4 Inductively Coupled Plasma

ICP was employed to determine the content of Au and Pt metals of the A zeolite supported catalysts. The measured loading of Au and Pt with different ratios (1:0, 1:1, 1:1.5 and 1:2) is shown in Table 4.4. This table shows the comparison between the expected values and the actual values of metals contents in all prepared catalysts. From these results, the measured percentage of Au and Pt loading in the prepared catalysts were much lower than the expected values. The disappearance of metals might be due to the error during preparation step. Additionally, the measured percentage loading of Au and Pt with different sequential order of metal loading are also shown in Table 4.3. From ICP results, the sequential order of metal loading did not show the significant effect on the catalytic activities of each catalyst as XRD results because the actual ratio and the actual total metal loading of each prepared catalyst are almost the same.

Table 4.4 The measured percentages loading of 1% metal with different Au to Pt ratio supported on 4A zeolite catalysts.

Catalysts	Actual ratio (Au:Pt)	Actual total metal loading (%)
1%Au/4A zeolite	1:0	0.81
1%(1:1)AuPt/4A zeolite	1:0.8	0.90
1%(1:1.5)AuPt/4A zeolite	1:1.3	0.65
1%(1:2)AuPt/4A zeolite	1:2	1.20
1%(1:2)AuPt/synthesized	1:1.5	1.00
1%(1:1)Au-Pt/4A zeolite	1:0.6	0.73
1%(1:1)Pt-Au/4A zeolite	1:0.7	0.75

4.1.3.5 Surface Area Measurement (BET)

Surface area of the prepared catalysts is summarized in Table 4.5. The surface area was strongly dependent on the metal loading and the initial surface area of catalyst support. The BET surface area showed a decrease with increasing the percentage of metal loading. The synthesized A zeolite has a surface area more than the commercial A zeolite. These suggest that the particle size of the synthesized A zeolite was smaller than the commercial A zeolite. Additionally, the surface area of 1% Pt/4A zeolite decrease with adding the Au to the catalysts. These results were confirmed by the TEM micrographs of the AuPt catalyst that the diameter of the Au particle was much bigger than the Pt particle so that the presences of Au in Pt/4A zeolite catalyst lead to decrease the surface area. However, the surface area of each catalyst has no correlation with the catalytic activities but the actual total metal loading provided by ICP technique shows that the surface area increased with decreasing the total metal loading. However, additional study is needed to quantify this relationship.

4.1.3.6 H_2 Pulse Chemisorption

H_2 is used as the adsorbate gas to study chemisorption on metals because H_2 adsorption occurs by dissociation into two H atoms with a 1:1 H:metal atom relationship. The metal dispersion can be calculated from pulse chemisorption results. Degree of metal dispersion and mean particle diameter of the prepared catalysts is given in Table 4.5. The catalytic activities of all prepared catalysts depended strongly on the metal crystallite size. Higher dispersion values equate to a more efficient metal atom usage for catalytic reaction. The 1% (1:2)AuPt/4A zeolite has higher metal dispersion which is 26.73% than 21.34% metal dispersion of 1% Pt/4A zeolite. As before, when the small amount of Au was added to Pt/A zeolite catalyst caused to the particle size of Pt metal was decreased, resulted in the 1% (1:2)AuPt/4A zeolite showed a highly dispersed metal on the catalyst support which provide optimal CO conversion and CO selectivity at relatively low temperature. Additionally, the catalyst performances depend on many variables such as the support, the total metal loading, the crystallite size of metal.

Table 4.5 BET surface area, degree of metal dispersion, mean particle diameter and the metal crystallite size calculated by Scherrer Equation from X-ray diffraction technique of the prepared catalysts.

Catalyst	BET surface area (m^2/g)	Metal dispersion (%)	Mean particle diameter (nm)	Metal crystallite size (nm)	
				Au(111)	Pt(111)
1% Pt/4A zeolite	1623	21.34	4.77	-	59.9
1% (1:1)AuPt/4A zeolite	833	44.05	2.31	44.7	51.1
1% (1:1.5)AuPt/4A zeolite	1242	23.95	4.25	71.2	71.3
1% (1:2)AuPt/4A zeolite	606	26.73	3.81	51.0	71.3
1% (1:2)AuPt/synthesized	1425	-	-	25.6	25.7
1% (1:2)AuPt/3A zeolite	-	12.12	8.40	71.2	59.9
1% (1:2)AuPt/5A zeolite	1048	48.80	2.09	89.4	-

4.1.3.7 Temperature Programmed Reduction

Temperature programmed reduction experiments were performed on the prepared catalyst in order to investigate the reactivity of the zeolite catalyst support upon metals addition. The experimental TPR profiles of the prepared catalyst and of the pure zeolite catalyst support are shown in Figure 4.12. In these Figure, it presents a peak in low temperature region below 100°C and a peak in high temperature above 930°C, assigned to the reduction of bulk 4A zeolite, which is not influenced by the presences of Au and Pt. In the TPR profile of Au/4A zeolite catalyst, two peaks in correspondence of two peaks of the pure support at 650°C and 800°C are observed but the reduction temperature of Au/4A zeolite was shifted around 20°C to lower temperature. This indicates that it is easier to reduce resulting in easier apply for the oxidation-reduction catalytic reaction than 4A zeolite. Moreover, TPR profiles of Pt/4A zeolite and AuPt/4A zeolite, it can be seen that one peak appears at 115°C which corresponds to the reduction of the metal precursor from Pt^{4+} to Pt^0. For the bimetallic AuPt catalyst, the H_2 consumption at 80°C was

sharply decreased and the shoulder peak at 650°C which corresponds to the reduction peak of the pure 4A zeolite catalyst support can not be observed. However, the reduction temperature was dropped to around 720°C, which were about 20°C lower than the 4A zeolite. Additionally, two reduction peaks of Pt/4A zeolite in correspondence of two peaks of the pure support at 650°C and 800°C can not be observed.
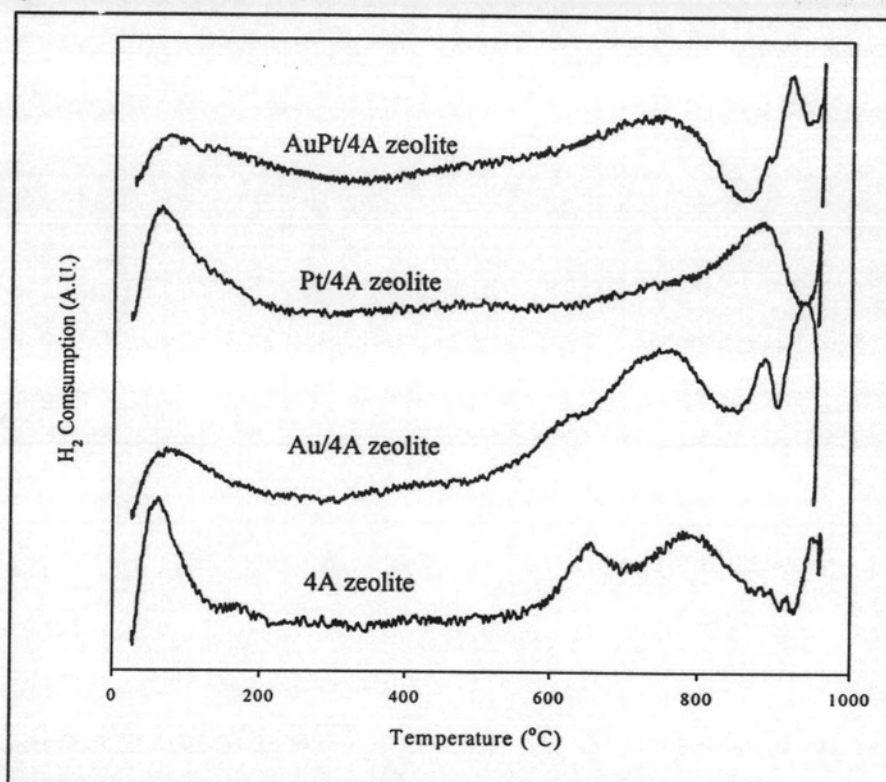

Figure 4.12 Temperature programmed reduction profiles of the prepared catalysts.

4.2 Activity Testing

This section shows the catalytic activity results of the prepared catalysts. The catalytic activity tests were carried out in the fixed bed U-tube micro-reactor by packing with 100 mg catalyst of 80-120 mesh inside. The activity was investigated at varied temperature in the range of 50 to 310°C at atmospheric pressure.

4.2.1   Effect of Au on Pt/A Zeolite Performance

Figure 4.13 (a-c) shows the results of preferential CO oxidation catalyzed by Pt/A zeolite and AuPt/A zeolite catalysts as a function of temperature. The CO conversion profile of AuPt/A zeolite was similar to Pt/A zeolite. However, CO was completely converted to CO_2 by the Pt/A zeolite at around 220°C. The catalytic activity of Pt/A zeolite was improved slightly in the presence of Au. The temperature at the maximum CO conversion of AuPt/A zeolite was shifted approximately 50°C to lower temperature that it gave the maximum temperature at around 170°C, suggesting that CO adsorption on Au is much weaker than Pt (Schubert et al., 1999 and Kandoi et al., 2004). CO can weakly adsorb on Au and easily desorbs off the surface. The adsorbed CO is generally observed only at low temperatures. Au has fully occupied d-orbitals and exhibit weak coordination ability toward CO. As a result of that adsorption, the temperature at the maximum CO conversion of AuPt/A zeolite catalyst was shifted to lower temperature. In addition, both catalysts showed similar characteristic of selectivity at high temperatures. At low temperatures, the AuPt/A zeolite catalyst provided 100% of CO selectivity while the Pt/A zeolite provided CO selectivity at 65%. Moreover, the O_2 conversion of both catalysts increased with increasing temperature but the rate of O_2 consumption of the AuPt/A zeolite catalyst higher than the Pt/A zeolite catalyst. Otherwise, the O_2 conversion of AuPt/A zeolite catalyst reached 100% at the same temperature of 210°C. Additionally, Zhang et al., (2003), they conducted the experiment of selective oxidation of CO in H_2-rich gas over Pt-Au/ZnO catalyst prepared via co-precipitation method. They found that when small amount of Pt (1%) were added to 1.5% Au/ZnO, its stability was improved and this catalyst provided a high CO conversion about 95% at 80°C. Those differences are the results of different catalysts preparation method, which lead to the difference in the metal dispersion, the metal particle size and different amount of metal loading.
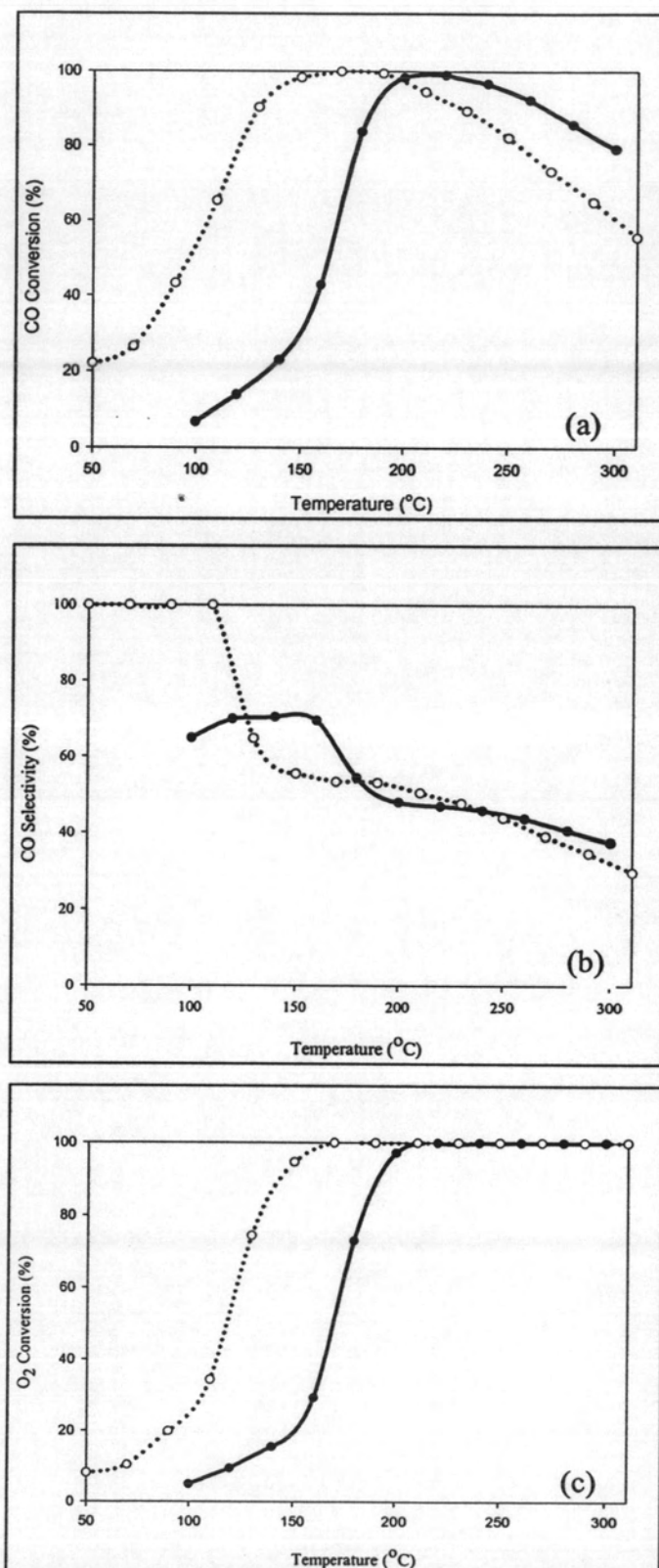
Figure 4.13 The catalytic activities of Pt/A zeolite (●) and AuPt/A zeolite (○) catalysts : (a) CO conversion, (b) CO selectivity and (c) O_2 conversion.

4.2.2 Effect of Sequential Metal-Loaded

The sequential order of metal loading did not show the significant effect on both CO conversion and O_2 conversions as shown in Figure 4.14. The maximum CO conversion took place at temperature around 190°C. However, the sequential order of metal loading showed the significant effect on the CO selectivity at low temperatures. It can be seen that a higher CO selectivity was obtained at low temperatures for all tested catalysts; however, with the sequential order of metal loading did not have significant effect on the CO selectivity at high temperatures (170-310°C). At low temperatures, the CO selectivity of Pt-Au/A zeolite catalyst was lower than the Au-Pt/A zeolite and AuPt/A zeolite catalysts around 5-10%. All catalysts showed similar characteristic of O_2 consumption at all over the tested temperature range which the O_2 conversions of all catalysts reached 100% at the same temperature of 210°C. These results can be explained by the same of average metal crystallite size obtained from XRD characterization (Table 4.3) which gave almost the same metal dispersion and total metal loading obtained from ICP technique. This suggests that if either Au or Pt was initially loaded in the sequential metal loading or co-impregnation was used, it does not affect on the metal coverage over each other because the crystallite of both metals was observed on the XRD patterns. On the other hands, two metals have weak or no interaction, confirmed by the TEM technique, because two metals appear to be severely phase separated. But also two metals may provide their unique catalytic properties cause to these catalysts show the comparable performance.
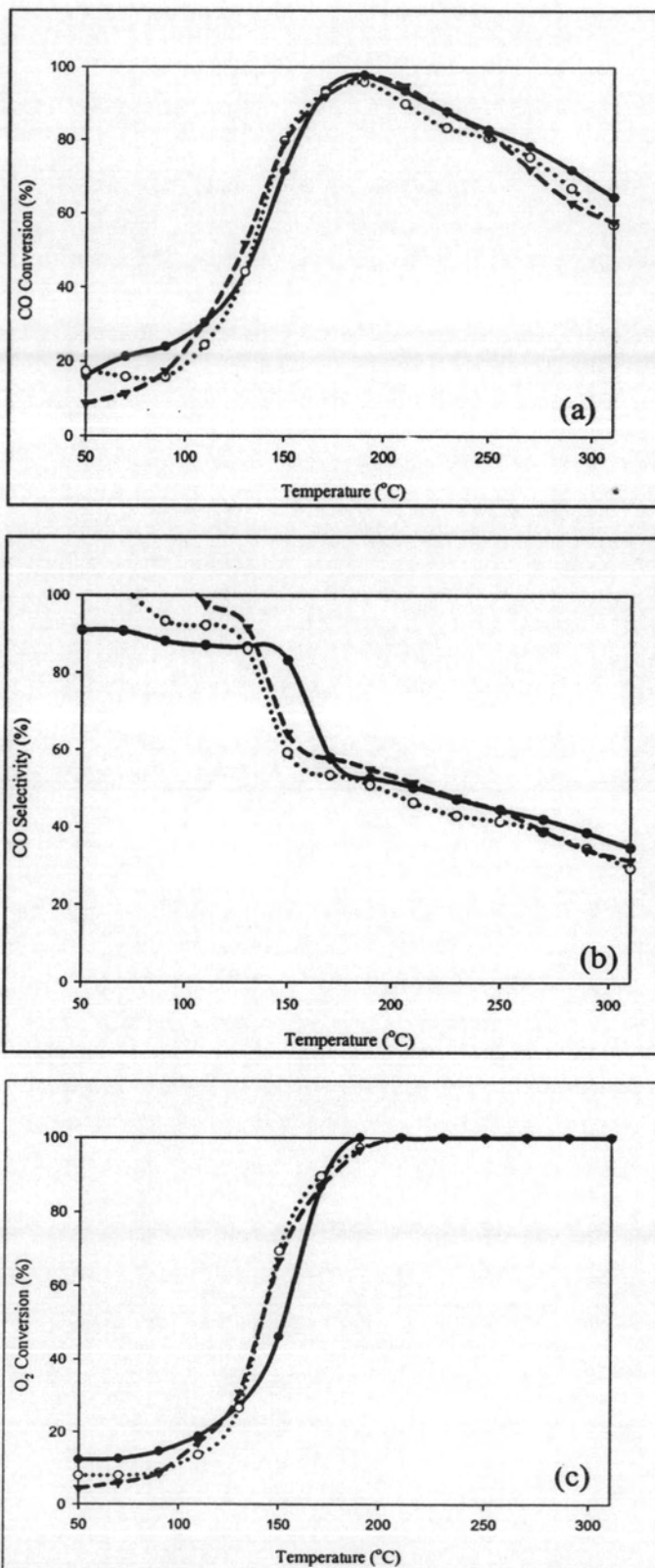
Figure 4.14 The catalytic activities of Pt-Au (●), AuPt (○) and Au-Pt (▼)supported on A zeolite catalysts : (a) CO conversion, (b) CO selectivity and (c) O₂ conversion.

4.2.3 Effect of Metal-Loaded Ratio

To improve the activity of the AuPt/A zeolite catalyst, the effect of the addition of Au to the Pt/A zeolite was investigated. The AuPt/A zeolite catalysts were prepared by co-impregnation method. The Au:Pt ratios were varied at 1:1.0, 1:1.5 and 1:2.0. As shown in Figure 4.15, the presence of Au on the Pt supported on A zeolite improved both the CO conversion and CO selectivity. The AuPt/A zeolite catalyst containing the Au to Pt ratio of 1:2 gave the highest CO conversion (100%) and selectivity. Moreover, the temperature at maximum CO conversion was also shifted to lower temperatures. Zhang *et al.,* (2003) conducted the experiment of preferential oxidation of CO in hydrogen rich gas over Pt-Au/ZnO catalyst, they found that the catalytic activity increased with increasing content of Pt and the optimum content of Pt in the catalyst was 1.0 wt.% which this catalyst provided a high CO conversion about 95% at 80°C. Those differences are the results of different amounts of metal loading, different catalyst preparation method and catalyst support. After that, Wang *et al.,* (2005), they reported that only Au supported on ZnO can oxidize CO to CO_2 at reaction temperature of 40-120°C but CO selectivity decreased slightly when the reaction temperature beyond 80°C. However, little addition of Pt to Au/ZnO catalyst can improve the selectivity but Pt catalyst could not sufficiently remove CO from H_2-rich at mild reaction temperature. In addition, O_2 conversion profiles of all prepared catalysts showed the same trend, and the O_2 consumption was in order of 1:2.0 > 1:1.0 > 1:1.5.
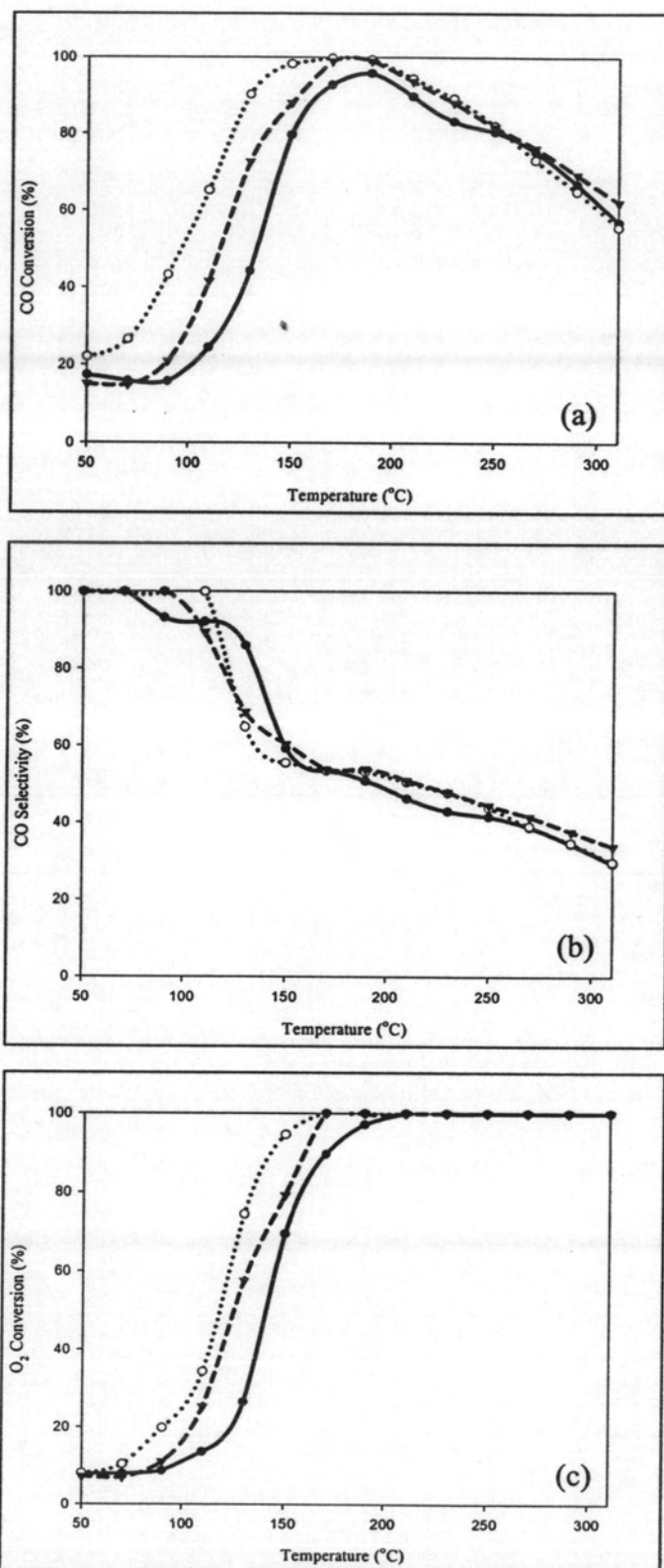
Figure 4.15 The catalytic activities of AuPt/A zeolite at varied Au:Pt ratios; 1:1 (▼), 1:1.5 (●) and 1:2 (○) supported on A zeolite catalysts: (a) CO conversion; (b) CO selectivity; and, (c) O₂ conversion.

4.2.4 Effect of Catalyst Pretreatment

The catalytic activities of 1% (1:2)AuPt/A zeolite catalyst pretreated differently versus temperature are shown in Figure 4.16 (a-c). Two pretreatment conditions, which are He at 110°C and H_2 at 400°C for 1 hour were performed for this catalyst. It can be observed that He pretreatment achieved higher maximum CO conversion and higher CO selectivity. The selectivity was maximized at low temperatures and then dramatically decreased with increasing temperature. The He pretreatment was necessary to remove adsorbed species on the catalyst surface. However, H_2 pretreatment of this catalyst affected the temperature at maximum CO conversion was shifted 40°C to lower temperature and the CO selectivity at the maximum CO conversion was lower than the He pretreated catalyst around 5%. After this part, pure He pretreatment at 110°C for 1 hour was selected as the appropriate pretreatment condition for this method.
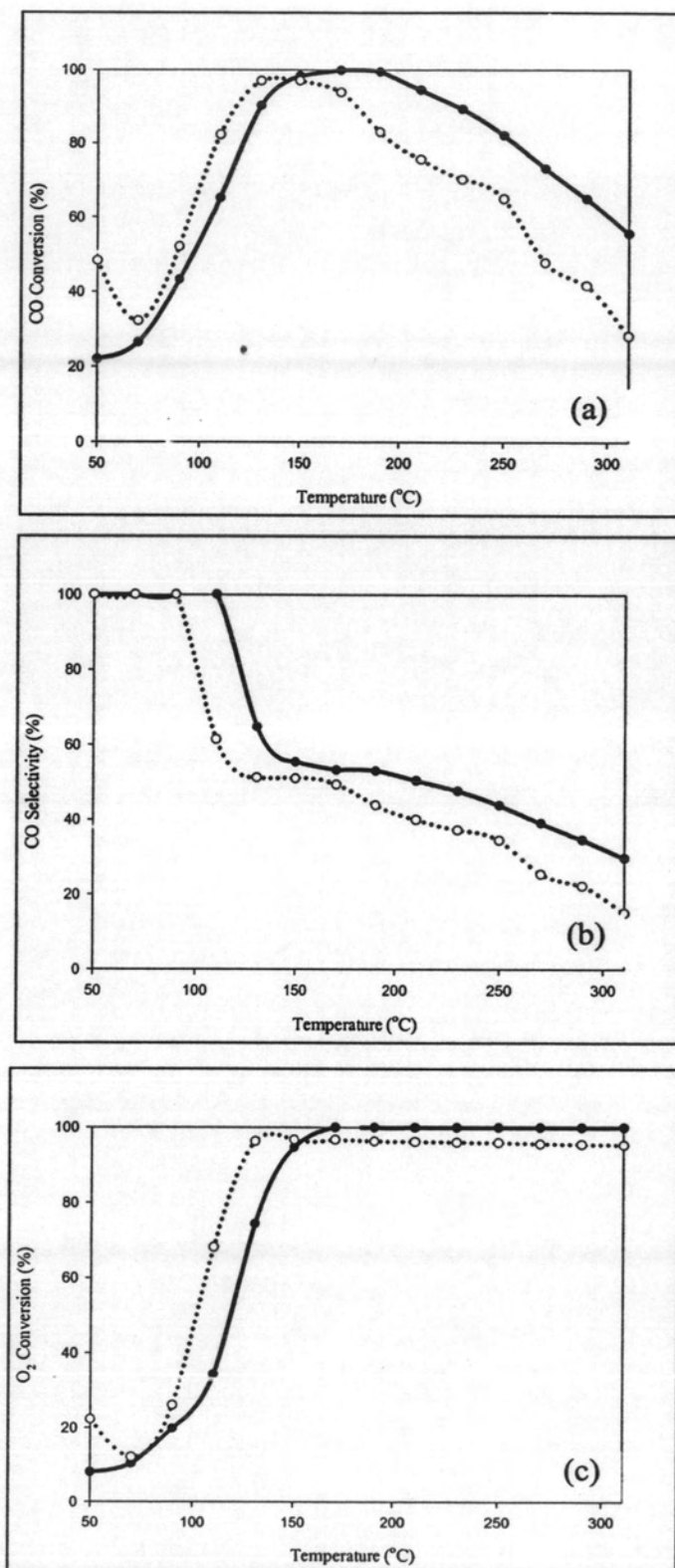
Figure 4.16 Effect of pretreatment condition on 1% (1:2)AuPt/A zeolite catalyst:
(●) He pretreatment, (○) H₂ pretreatment: (a) CO conversion, (b) CO selectivity and
(c) O₂ conversion.

4.2.5 Effect of Catalyst Support

Figure 4.17 (a-c) shows the CO conversions, CO selectivity and O_2 conversions of 1% (1:2)AuPt supported on various types of A zeolite which are commercial A zeolite and synthesized A zeolite. The maximum CO conversions were in the order of AuPt/commercial A zeolite > AuPt/synthesized A zeolite (Figure 4.17-a). In addition, the temperature at which the maximum CO conversion of AuPt/synthesized A zeolite was shifted 60°C to higher temperature. The CO was completely converted to CO_2 by the AuPt/commercial A zeolite at 190°C while the AuPt/synthesized A zeolite gave a maximum temperature at about 250°C. In contrast, the AuPt/synthesized A zeolite achieves the maximum CO conversion at around 78%. This result might be explained by the differences of morphology in micro-scale that obtained from SEM technique (Figures 4.9-4.10). As can be seen, the AuPt/synthesized A zeolite shows a better homogeneous morphology and its particle size was smaller than the AuPt/ commercial A zeolite. From this result, the synthesized A zeolite catalyst support facilitated the metal dispersion to the deeper of the pore of A zeolite. From this reason, the AuPt/synthesized A zeolite catalyst gave the higher temperature at the maximum CO conversion. The AuPt/commercial A zeolite catalyst also provided the CO selectivity higher than the AuPt/synthesized A zeolite at low temperatures. Additionally, the O_2 consumption rate of the AuPt/commercial A zeolite was fasted up that it reached 100% at the lower temperature of 190°C while the AuPt/synthesized A zeolite reached 100% of O_2 conversion at 270°C. The experiment results indicated clearly that the performances of Au catalyst were greatly improved by using commercial A zeolite catalyst support. The results mentioned previously make a good agreement with Nimsuk's results (2005) indicating that the Pt/commercial A zeolite achieved a maximum CO conversion and provided a higher CO selectivity at lower temperatures than the Pt/synthesized A zeolite.
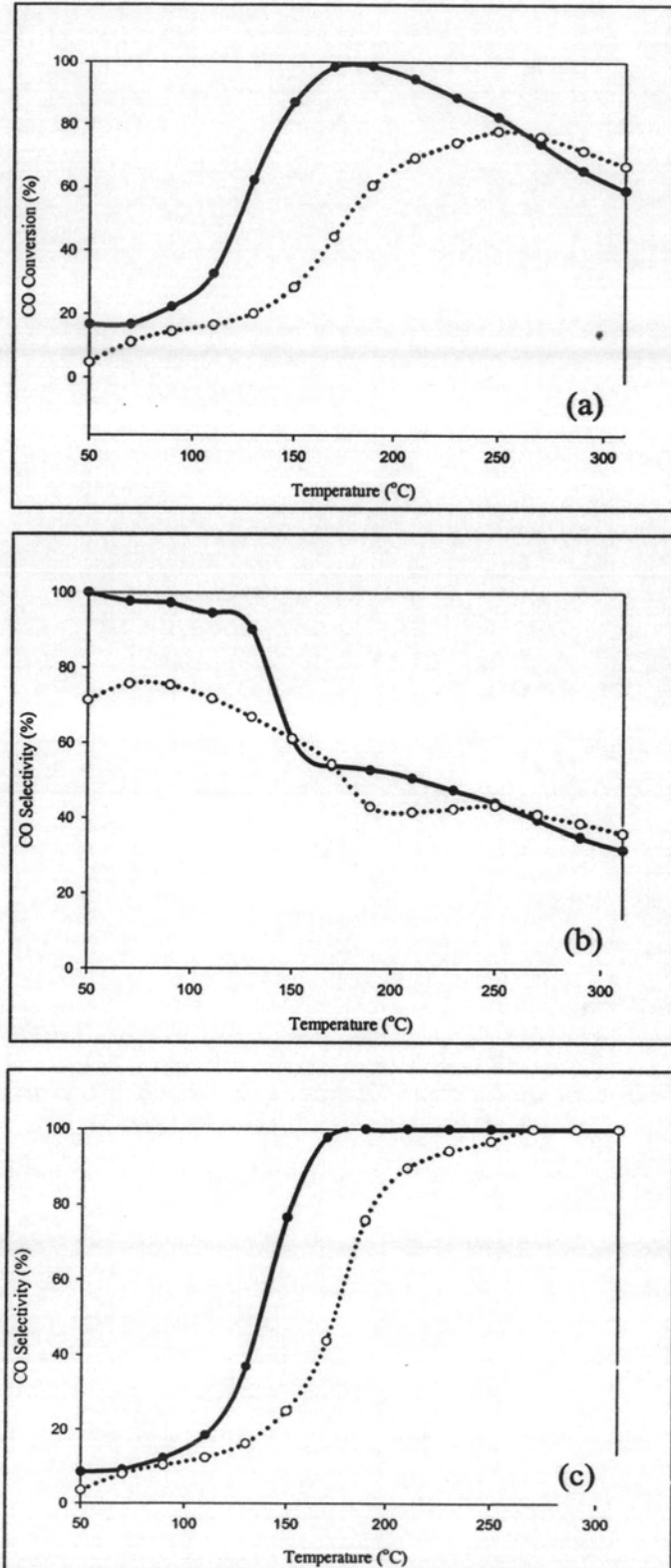
Figure 4.17 Effect of catalyst support on 1% (1:2)AuPt catalyst: (●) commercial A zeolite, (○) synthesized A zeolite: (a) CO conversion, (b) CO selectivity and (c) O_2 conversion.

4.2.6 Effect of Pore-Size Aperture

Figure 4.18 (a-c) shows the CO conversions, CO selectivities and O_2 conversions of 1% (1:2)AuPt supported on various types of A zeolite. The CO conversions were in the order of AuPt/4A ~ AuPt/5A > AuPt/3A (Figure 4.18-a). In addition, the temperature at the maximum CO conversion of AuPt/3A was shifted to around 60°C higher. The CO was completely converted to CO_2 by the AuPt/5A zeolite at 190°C while the AuPt/4A zeolite gave a maximum temperature at about 170°C. In contrast, the AuPt/3A zeolite could not achieve 100% CO conversion. In addition, the AuPt/3A zeolite achieves a lower CO selectivity at low temperatures, but at high temperatures it achieves a higher CO selectivity than AuPt/4A zeolite and AuPt/5A zeolite. It can be seen that the difference in O_2 conversion profiles the difference in CO conversion. By contrast, Rosso *et al.,* (2004), they conducted the experiment of preferential CO oxidation over Pt supported on several types of A zeolites which the catalyst was prepared via the wet impregnation method. They found that the 1% Pt/3A zeolite catalyst showed the best performance: it gave the complete CO conversion in a wide temperature range, showing the highest selectivity (32%) for CO oxidation with minimal involvement in side reactions, such as H_2 oxidation and RWGS reaction. But the optimum temperature that provided the maximum CO conversion was a high temperature of around 260°C. Based on those results, it can be concluded that the presence of Au metal to Pt/A zeolite catalyst was improved the CO selectivity at low temperatures and the maximum CO conversion temperature was approximately shifted 70°C to lower temperature compared to 1%Pt/3A zeolite catalyst. Those differences are the results of different catalysts preparation method, which lead to the differences in the metal dispersion and in the interaction between metal and catalyst support.
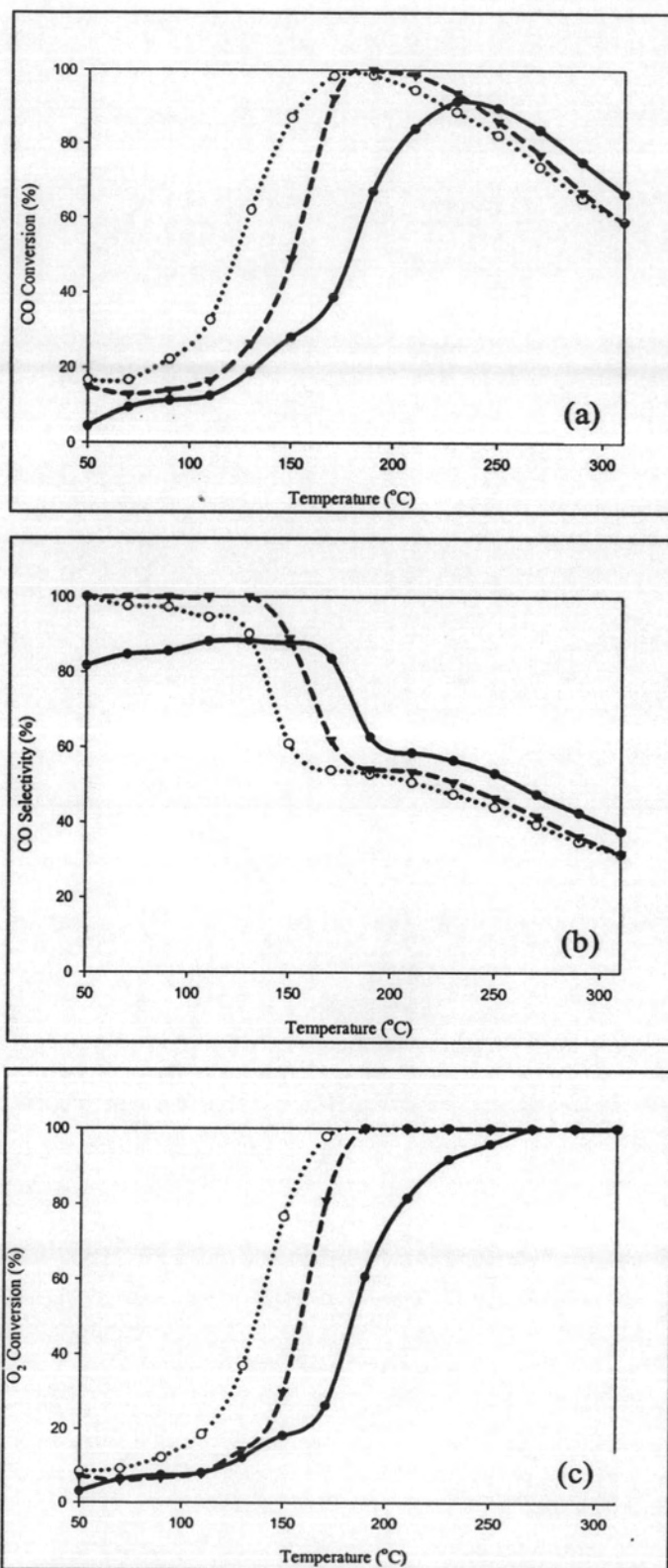
Figure 4.18 The catalytic activities of 1% (1:2)AuPt/various zeolite A: 3A zeolite(●), 4A zeolite(○) and 5A zeolite(▼): (a) CO conversion, (b) CO selectivity, and (c) O_2 conversion.

4.2.7 Effect of CO_2 on Catalytic Performance

The effect of the CO_2 presence in the feed stream on the catalytic performance of the 1% (1:2)AuPt/A zeolite catalyst was investigated. Because of the realistic methanol steam reformate contains up to 25% CO_2 and reverse water gas shift reactors contain about 20-25% CO_2. Therefore, it is essential to investigate the influence of CO_2 on the preferential CO oxidation reaction in simulated reformate which was maintained under more realistic conditions. The catalytic activities of the catalyst were tested with a reactant gas composition of 10%CO_2, 1%CO, 1%O_2 and 40%H_2 balanced in He. As shown in Figure 4.19 (a-c), the presence of CO_2 did not have significant effect on the CO conversion at high temperatures (230-310°C). At low temperatures, the presence of CO_2 has a negative effect on the CO conversion in the temperature range of 110-210°C. Moreover, the presence of CO_2 did not have significant effect on the CO selectivity profile in the range of the tested temperature. Additionally, the difference in O_2 conversion parallels the difference in CO conversion for the presence and the absence of CO_2 in feed stream. In the work of Schubert et al., (2004), they conducted the experiment of the influence of CO_2 and H_2O on the selective CO oxidation over Au/α-Fe_2O_3. It can be concluded that the addition of CO_2 reduces the CO oxidation rate and selectivity, which was attributed to co-adsorption of CO_2 on the Au particles or at the gold–metal oxide interface. Furthermore, deactivation is accelerated due to increased carbonate formation on the catalyst surface. The CO_2 also suppressed the CO conversion and CO selectivity at high temperature of Pt/Al_2O_3, reported by Manasilp and Gulari (2002). This suggests that the interface between support and metal active sites contain mobile O_2 which is blocked by CO_2 adsorbing on the same sites. In contrast, CO_2 can improve the CO selectivity at low temperature which the assumption may be RWGS reaction limiting the CO oxidation at high temperatures causes the CO selectivity was dramatically dropped.
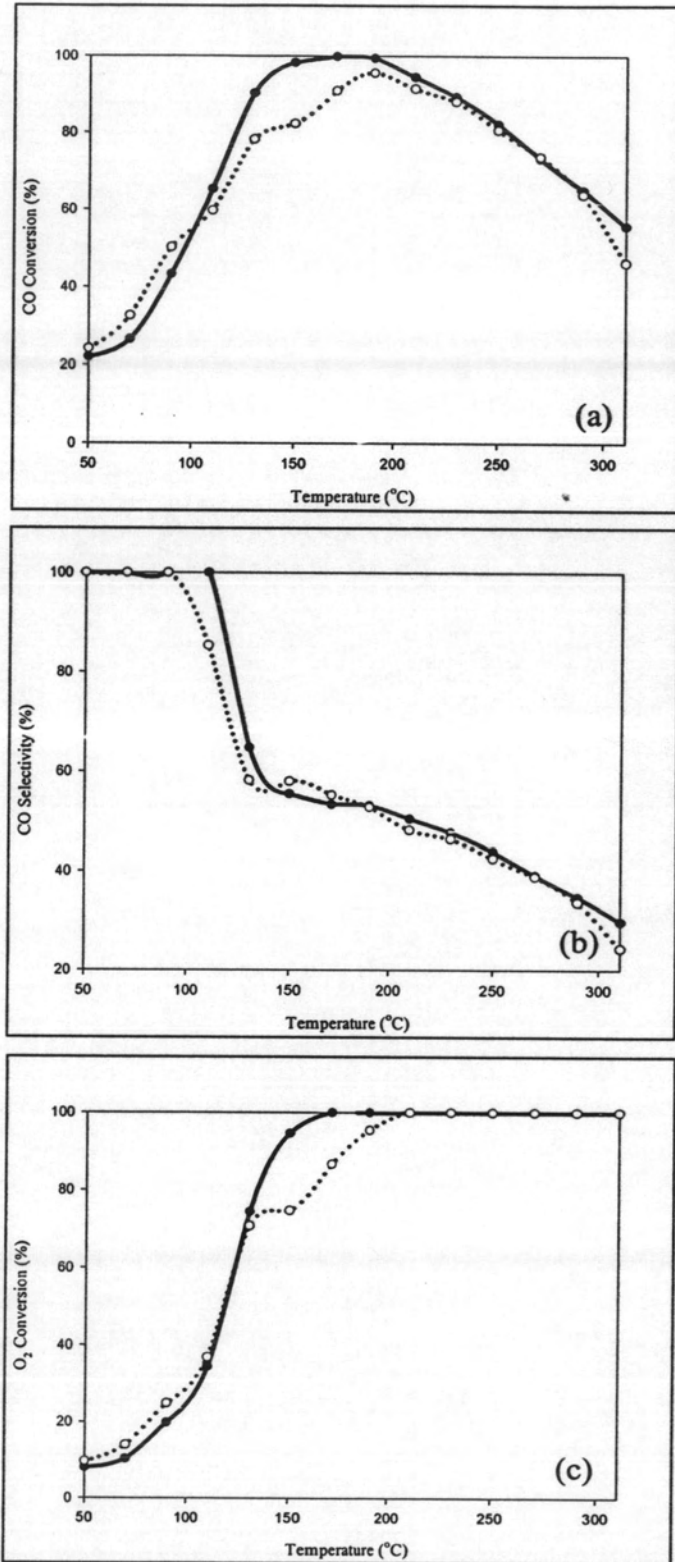
Figure 4.19 Effect of CO_2 on the catalytic activities of 1% (1:2)AuPt/A zeolite catalyst; 0%CO_2 (●) and 10%CO_2 (○): (a) CO conversion, (b) CO selectivity, and (c) O_2 conversion.

4.2.8 Effect of H_2O Vapor on Catalytic Performance

The effect of the H_2O vapor presence in the feed stream on the catalytic performance of the 1% (1:2)AuPt/A zeolite catalyst was investigated. Because of the realistic methanol steam reformate contains up to 10-15% H_2O and it was produced by H_2 oxidation. Therefore, it is essential to investigate the influence of H_2O on the preferential CO oxidation reaction with maintained under more realistic gas composition. The catalytic activities of the catalyst were tested with a reactant gas composition of 10%H_2O, 1%CO, 1%O_2 and 40%H_2 balanced in He. As shown in Figure 4.20 (a-c), the presence of H_2O vapors did not have significant effect on the CO conversion and the presence of H_2O vapor had a positive effect on the CO selectivity at high temperatures. The CO selectivity increased about 5% from 50% to 55% at 190°C. Otherwise, the O_2 consumption rate was reduced by the presence of H_2O vapor. In the work of Schubert et al., (2004), they conducted the experiment of the influence of CO_2 and H_2O on the selective CO oxidation over $Au/\alpha\text{-}Fe_2O_3$. It can be concluded that the addition of H_2O results in positive effects that increases the selectivity by suppressing the competing H_2 oxidation reaction, including promoting the WGS reaction. As a result, more CO is converted to CO_2 at high temperatures causes an increase in CO selectivity. Additionally, the presence of H_2O increases the forming of hydroxyl group on the catalyst support that adsorption of water is a better oxidant than oxygen and increase the oxidation rate of CO and H_2, reported by Manasilp and Gulari, (2002). From this result, it can be confirmed by the reducing of O_2 consumption. On the other hand, Calla and Davis (2005) reported the influence of H_2O vapor in the CO oxidation reaction over Au/Al_2O_3. They found that the presence of H_2O in feed stream significantly increased the rate of CO oxidation. Because of the activation energy of CO oxidation was reduced by H_2O. By contrast, Nimsuk, (2004), they investigated the effect of H_2O vapor on the selective CO oxidation over Pt/A zeolite catalyst. They reported that the presence of H_2O vapor had a negative effect on the performance of the catalyst. Based on those results, it can be concluded that when the small amount of Au was added to Pt/A zeolite catalyst resulting in the activities of the 1% (1:2)AuPt/A zeolite did not show much difference between the presence and the absence of H_2O vapor in the feed stream.
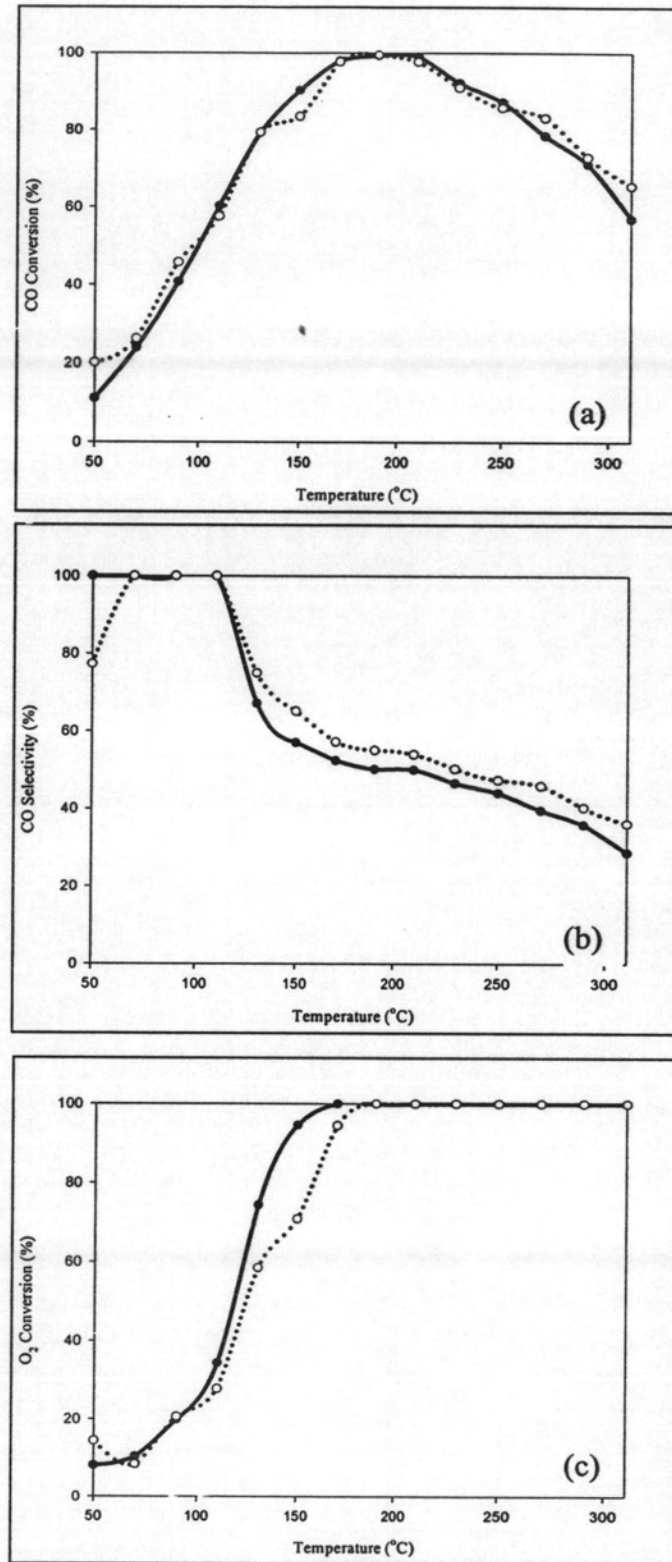
Figure 4.20 Effect of H$_2$O on the catalytic activities of 1% (1:2)AuPt/A zeolite catalyst; 0%H$_2$O (●) and 10%H$_2$O (○): (a) CO conversion, (b) CO selectivity, and (c) O$_2$ conversion.

4.2.9 Effect of Combination of CO_2 and H_2O on Catalytic Performance

The effect of combination of CO_2 and H_2O presence in the feed stream on the catalytic performance of the 1% (1:2)AuPt/A zeolite catalyst was investigated. Because of the realistic methanol steam reformate contains up to 25%CO_2 and 10-15% H_2O. Therefore, it is essential to investigate the influence of CO_2 and H_2O on the preferential CO oxidation reaction in order to evaluate whether the high activity and selectivity observed in simulated reformate are also maintained under more realistic conditions. From the CO conversion profiles from Figure 4.21-a, the presence of CO_2 and H_2O in feed stream had a negative effect on the CO conversion profile of the 1% (1:2)AuPt/A zeolite catalyst. The maximum CO conversion was shifted approximately 10°C to higher temperature. However, the CO selectivity of the catalyst was not significantly impacted by the presence of CO_2 and H_2O in feed stream. Otherwise, the O_2 consumption rate was slowed down but it reached 100% at the same temperature of 190°C. The results of previous studies can be summarized as follows. Avgouropoulos *et al.* (2002), they investigated the influence of CO_2 and H_2O on the activities in the preferential CO oxidation reaction over a $Au/\alpha\text{-}Fe_2O_3$ catalyst. They reported that the presence of CO_2 and H_2O in feed stream further reduced the CO conversion, but increased the CO selectivity. Besides, they reported that the $Pt/\gamma\text{-}Al_2O_3$ shows the most resistance than $Au/\alpha\text{-}Fe_2O_3$ and $CuO\text{-}CeO_2$ towards deactivation. In the same year, Manasilp and Gulari, (2002), studied the the influence of combined CO_2 and H_2O on the preferential CO oxidation over 2% Pt/Al_2O_3 catalyst. They showed that the combination of CO_2 and H_2O sharply increased the CO conversion and the temperature at the maximum CO conversion was shifted 20°C to lower temperature. By contrast, Nimsuk, (2004), they investigated the effect of combination of CO_2 and H_2O vapor on the preferential CO oxidation over Pt/A zeolite catalyst. They reported that the presence CO_2 together with H_2O the CO conversion was significantly reduced. This suggests that the H_2O has stronger influence to the catalytic performance of the Pt/A zeolite catalyst than the CO_2. Based on those results, it can be concluded that the presence of Au in the Pt/A zeolite catalyst can reduce the influence of CO_2 and H_2O.
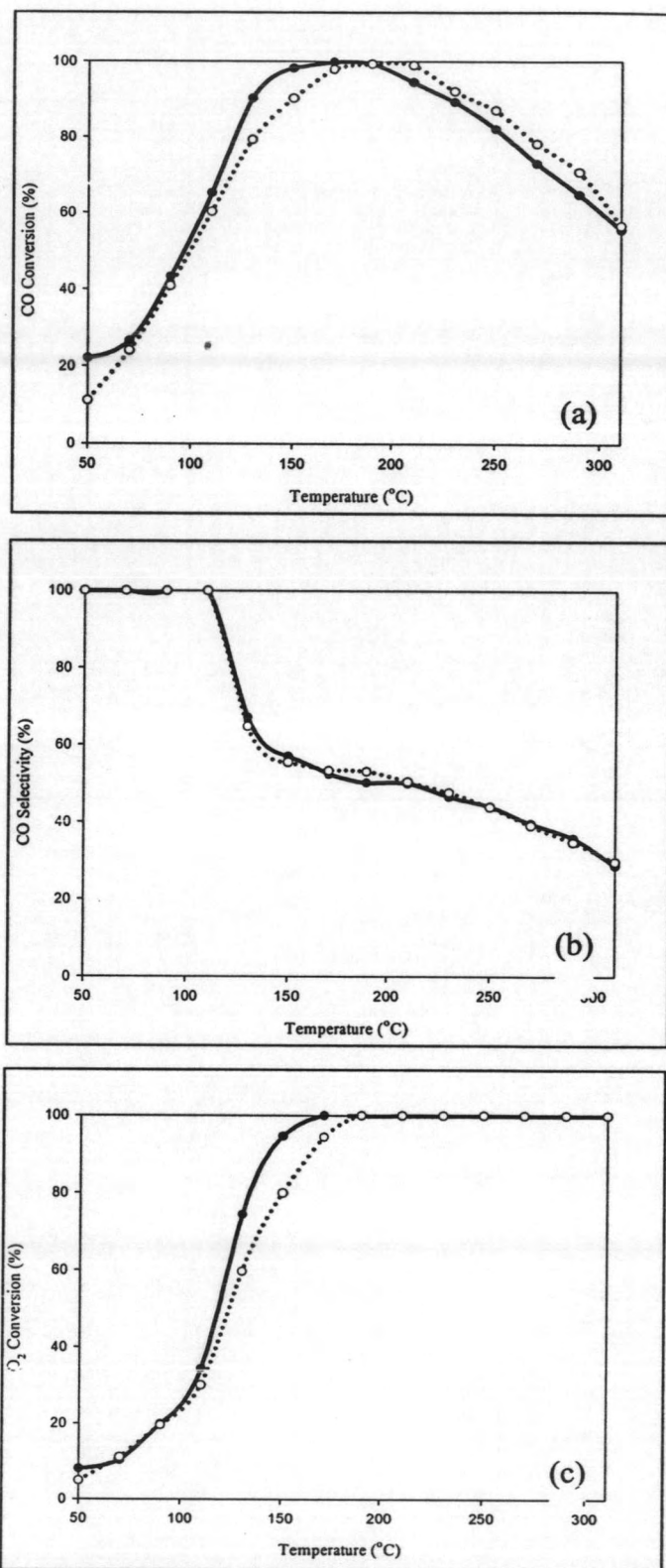
Figure 4.21 Effect of combination of CO_2 and H_2O on the catalytic activities of 1% (1:2)AuPt/A zeolite catalyst; 0%CO_2+0%H_2O (●) and 10%CO_2+10%H_2O (○): (a) CO conversion, (b) CO selectivity, and (c) O_2 conversion.

4.2.10 Durability Testing

The catalytic activity of the 1% (1:2)AuPt/A zeolite was tested at constant temperature for 12 hours in order to observe the stability with time on stream as shown in Figure 4.22. The preferential CO oxidation reaction was performed in the reactant gas with 40%H_2, 1%CO and 1%O_2 balanced in He at 170°C, which is the maximum CO conversion temperature of this catalyst. As can be seen, this catalyst exhibited a stable catalytic performance during 12 hours of testing time.
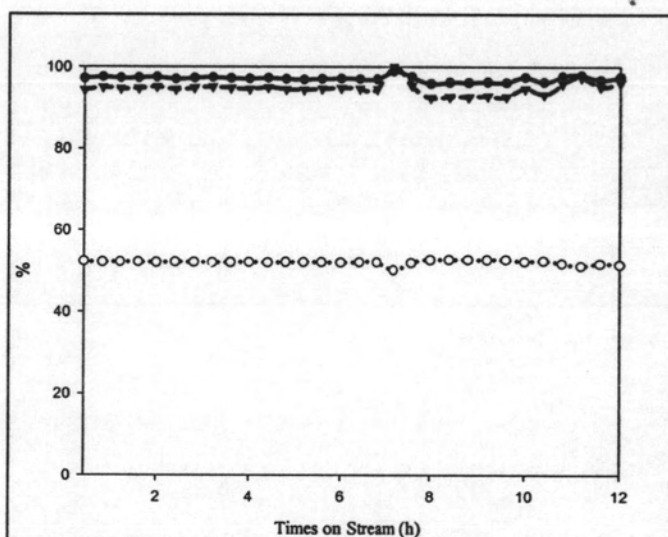

Figure 4.22 Durability testing of 1% (1:2)AuPt/A zeolite at 170°C under atmospheric pressure; CO conversion (●), O_2 conversion (▼), and CO selectivity (○).