



CHAPTER IV RESULTS AND DISCUSSION

4.1 Catalyst Characterization

This section exhibited the catalyst characterization results. The results were determined by using variety characterization techniques, including XRD, BET, TPR, ICP, H₂ pulse chemisorption and TEM. The characteristic of the catalysts in this part will be used to explain the catalytic activity of each prepared catalysts.

4.1.1 X-ray Diffraction Patterns (XRD)

The XRD patterns of Au, Pt and AuPt supported on mordenite zeolite prepared by deposition-precipitation at different metal-loaded ratios, pretreatment conditions, calcination conditions and compared with blank mordenite zeolite are shown in Figures 4.1-4.4. The prepared catalysts after drying at 60°C were called “fresh catalysts”. The fresh catalysts pretreated with H₂ at 400°C were denoted as “reduced catalysts”, while these treated at 500°C were denoted as “calcined catalysts”. All the samples exhibited similar X-ray diffraction patterns indicating the structural intensity of mordenite ($2\theta = 10.8^\circ, 20.6^\circ, 22.0^\circ, 25.4^\circ, 26.7^\circ, 28.0^\circ$ and 32.3°). The structural integrity was demonstrated comparing these peaks with the ones found for mordenite in sodium form. However, the additional peaks observed at 2θ of $38.2^\circ, 44.4^\circ, 64.5^\circ, 82.0^\circ, 9.8^\circ, 39.8^\circ, 46.2^\circ, 69.5^\circ$ and 81.5° were observed corresponding to Au[111], Au[200], Au[220], Au[222], Pt[200], Pt[111], Pt[200], Pt[220] and Pt[311] for CuK α (1.5406 Å) radiation, respectively, for Au, Pt and AuPt/mordenite catalysts. The XRD patterns of Au and Pt peaks indicated the existing metals in the prepared catalysts and the crystallite sizes of the metals were calculated by Scherrer’s equation as shown in Table 4.1. From the results, the peaks of Au and Pt in Au, Pt and Au-Pt/mordenite catalysts were unable to observe due to the particle sizes of Au and Pt were too small to be detected by XRD method. According to Chang *et al.* (1998), the limitation of XRD for reduced gold crystallites corresponds to a particle size smaller than 5 nm. These results were confirmed by the H₂

pulse chemisorption and TEM micrographs afterward. Additionally, the many peaks of mordenite overlapped the peaks of Au and Pt especially at 2θ of 44.4° , 64.5° , and 46.2° . However, the XRD patterns of 1% Au/MOR showed the peak of Au[111] particularly the calcined 1%Au/MOR. Therefore, it confirmed the presence of Au and unaffected structure of mordenite in catalysts. The Pt peaks of 1% Pt/MOR were observed at 39.8° (Pt[111]) and 69.5° (Pt[220]) in different pretreatment conditions but the Pt peaks of the calcined 1%Pt/MOR were sharper than other pretreated catalysts. It was noticed that the prepared catalysts were aggregation of Au and Pt when they were calcined at 500°C for 5 h. From the XRD patterns, the Au metallic phase at $2\theta = 38.2^\circ$ corresponding to Au[111] was observed for Au/MOR catalysts as shown in Figure 4.1. The mean crystallite diameters of Au[111] determined by the Scherrer's equation were found to be 44.7, 71.2, and 118.4 nm for fresh, reduced and calcined Au/MOR catalysts, respectively. It was interesting to observe that the calcined catalyst had the biggest crystallite sizes. The XRD patterns of the Pt metallic phase at $2\theta = 39.8^\circ$, 69.5° , 81.5° corresponding to Pt[111], Pt[220], and Pt[311] were observed for Pt/MOR catalysts as shown in Figure 4.2. The mean crystallite diameters of Pt[111], Pt[220] and Pt[311] determined by the Scherrer's equation were found that the reduced Pt/MOR had the smallest crystallite diameters. It was inferred that the size of Pt particle might be small when it was pretreated with H_2 at 400°C for 1 h. In bimetallic catalysts, they could not observe the Au[111] and Pt[111] which can be explained by the small size of Au and Pt when it pretreated with H_2 at 400°C for 1 h. However, the crystallite diameters of the calcined catalysts had the biggest among the catalyst examined.

Table 4.1 Metal crystallite sizes of the prepared catalysts

Catalyst	Crystallite Size (nm)				
	Au[111]	Au[222]	Pt[111]	Pt[220]	Pt[311]
1% Au/MOR (Fresh)	44.7	No	-	-	-
1% Au/MOR (Reduced)	71.2	44.8	-	-	-
1% Au/MOR (Calcined)	118.4	No	-	-	-
1% (1:1) Au:Pt/MOR (Fresh)	No	112.0	No	102.9	No
1% (1:1) Au:Pt/MOR (Reduced)	No	44.8	No	41.1	88.9
1% (1:1) Au:Pt/MOR (Calcined)	50.9	148.2	No	102.9	147.7
1% (1:5) Au:Pt/MOR (Fresh)	No	112.2	119.0	102.9	147.7
1% (1:5) Au:Pt/MOR (Reduced)	No	22.3	No	No	22.3
1% (1:5) Au:Pt/MOR (Calcined)	No	148.2	119.0	81.9	147.7
1% Pt/MOR (Fresh)	-	-	89.9	No	147.7
1% Pt/MOR (Reduced)	-	-	71.6	41.1	88.9
1% Pt/MOR (Calcined)	-	-	No	136.2	147.7

No = No peaks of Au and Pt were observed for bimetallic catalyst.

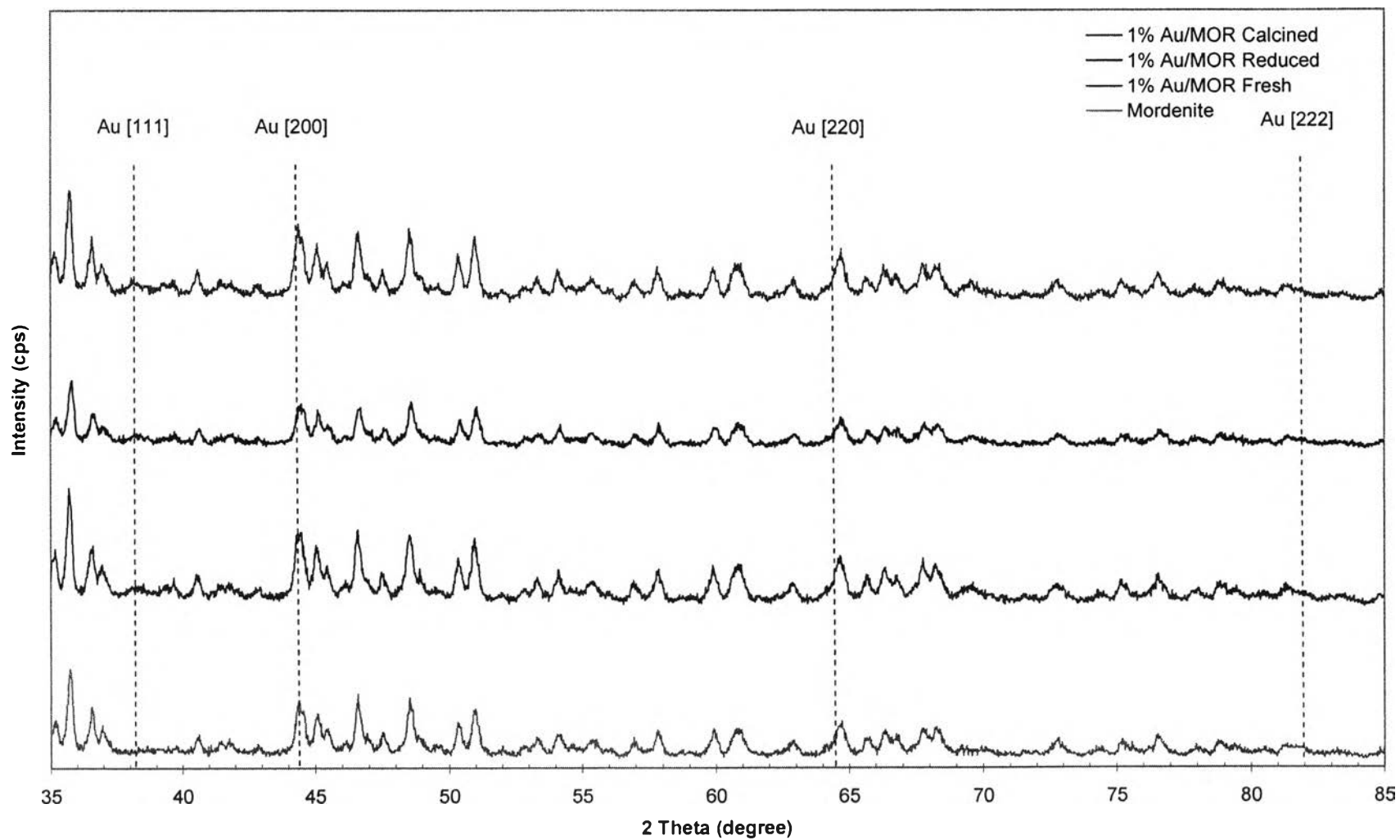


Figure 4.1 XRD patterns of 1%Au/MOR catalyst at different pretreatment conditions.

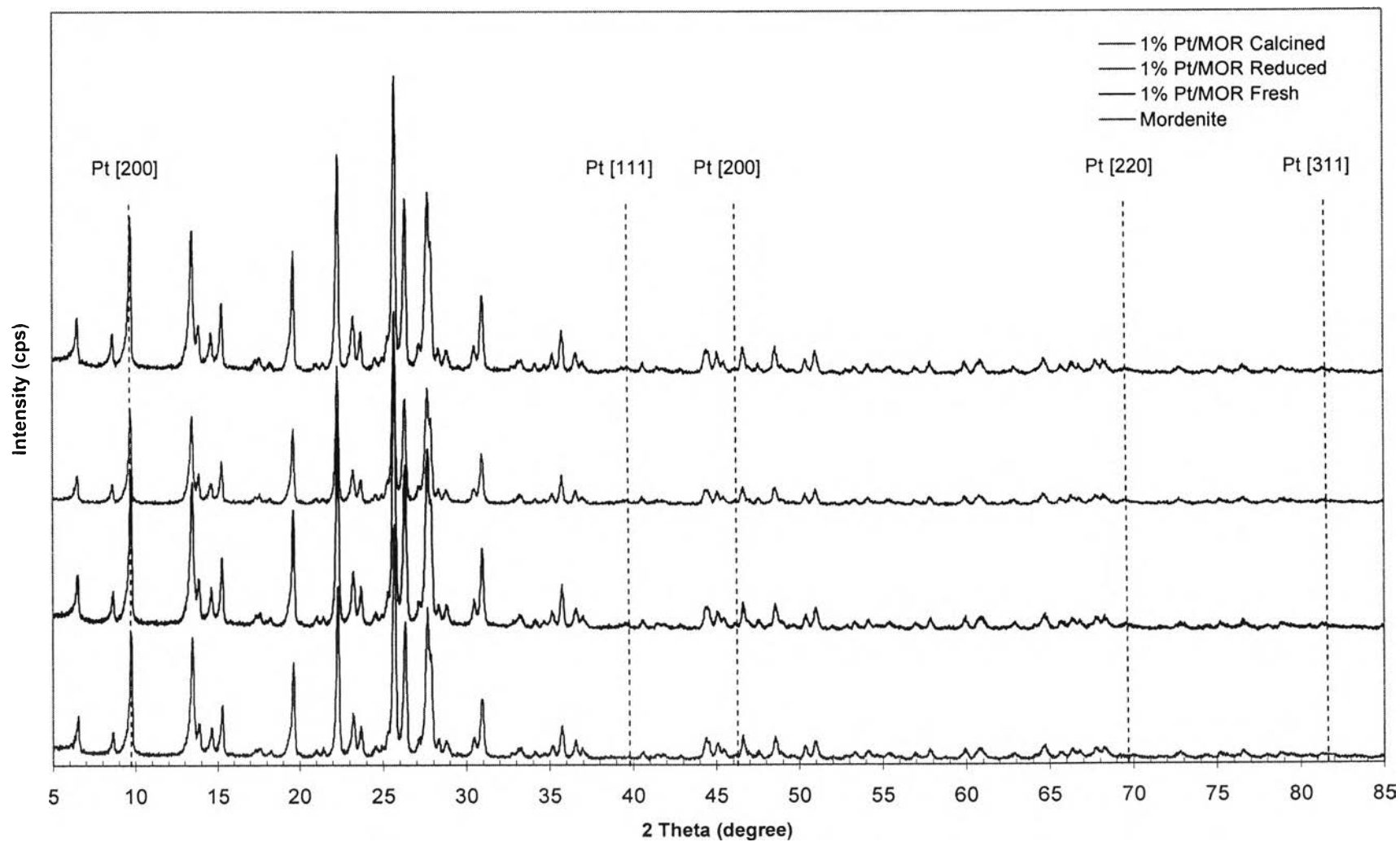


Figure 4.2 XRD patterns of 1% Pt/MOR catalyst at different pretreatment conditions.

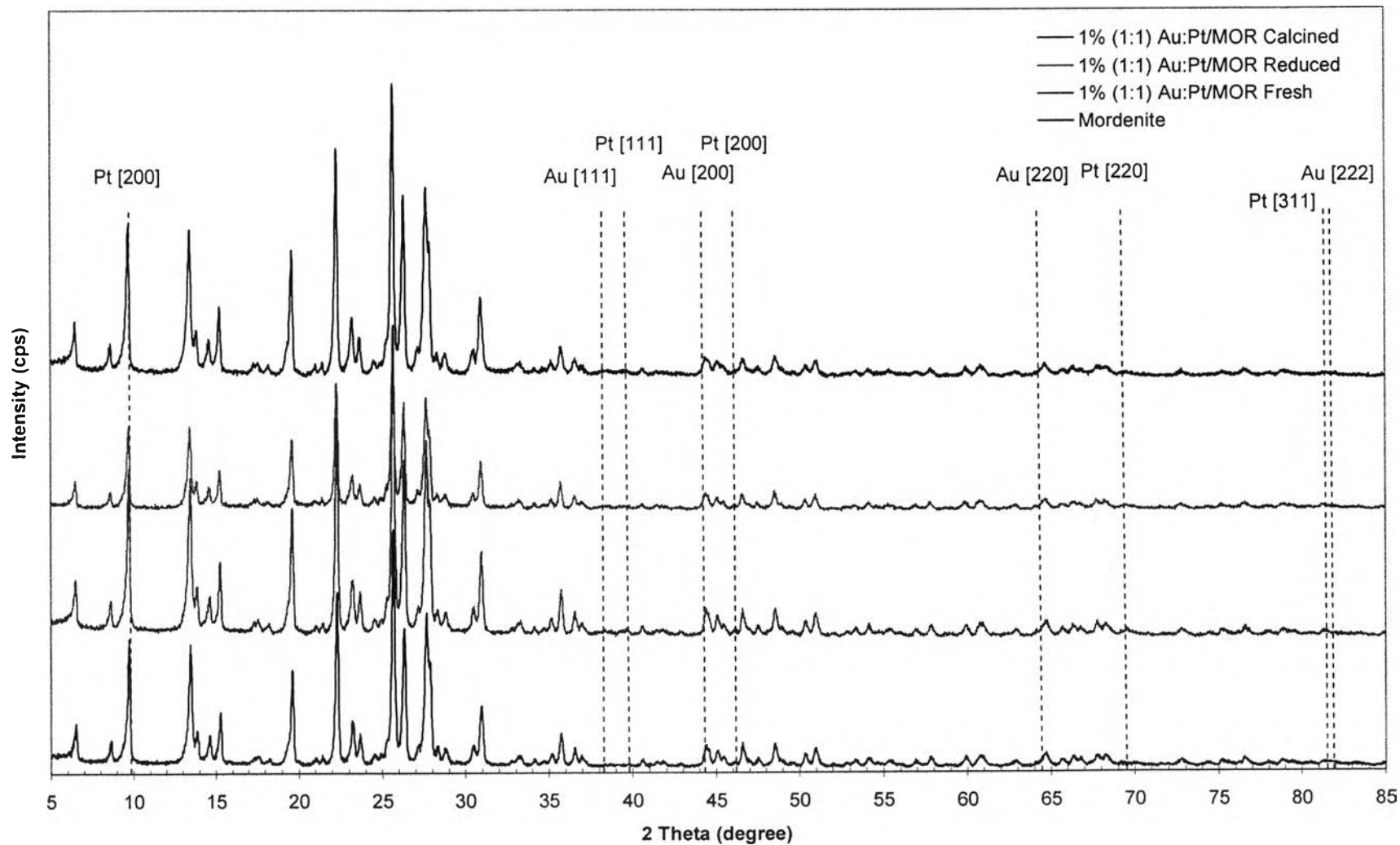


Figure 4.3 XRD patterns of 1% (1:1) Au:Pt/MOR catalyst at different pretreatment conditions.

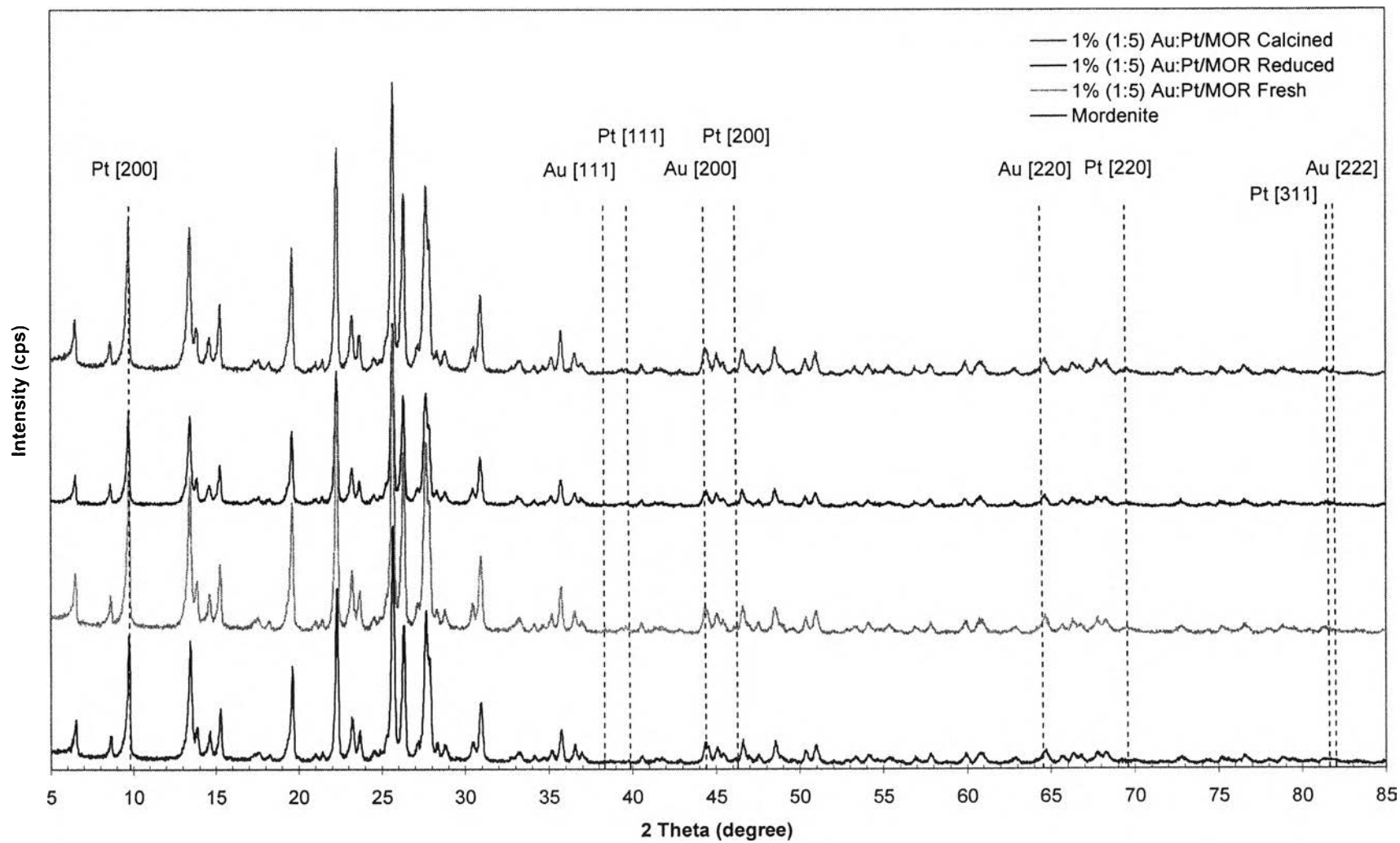


Figure 4.4 XRD patterns of 1% (1:5) Au:Pt/MOR catalyst at different pretreatment conditions.

4.1.2 Surface Area (BET) and Pore Size Measurements

The results of surface area measurements by adsorption of nitrogen at -196°C are shown in Table 4.2. The BET surface area and pore size of the prepared catalysts strongly depended on the metal loading and the initial surface area of catalyst support. The mordenite support had a surface area of $368.48\text{ m}^2/\text{g}$ while the fresh catalysts did not show much difference in the range of $314.59\text{-}348.74\text{ m}^2/\text{g}$. It suggested that the high surface area of the catalysts even after calcination at high temperatures. The calcined catalysts did not present much difference in the range of $301.42\text{-}316.87\text{ m}^2/\text{g}$ except the 1% (1:1) Au:Pt/MOR (calcined), that presented the biggest decrease in surface area ($287.57\text{ m}^2/\text{g}$) as compared to fresh catalyst ($326.11\text{ m}^2/\text{g}$). The specific surface area showed a decrease with increasing the amount of Pt. Moreover, Pt particles retained in the small channels, aggregated at pore mouths of channels and thereby substantially blocked the diffusion of gas molecules (Yuvaraj S. *et al.*, 2004). However, there is no clear difference between the surface areas of Au/MOR, Au-Pt/MOR, and Pt/MOR catalysts. Furthermore, the values of the pore volume of catalysts showed in the range of $0.222\text{-}0.833\text{ cm}^3/\text{g}$ while the mordenite support had a pore volume of $0.965\text{ cm}^3/\text{g}$. It is apparent that the amount of Au and Pt decreased the pore sizes and pore volume of the catalysts due to the metal adhered in internal surface of mordenite zeolite. These results were confirmed by EDX of Au-Pt catalyst. It showed that the Si, Al and O were covered the Au and Pt when the mapping was used to find the metal. Furthermore, the calcination of each catalyst led to decrease the surface area because the metal might form aggregation at 500°C for 5 h and obstruct the small pore of zeolite.

4.1.3 Inductively Coupled Plasma (ICP)

ICP was used to determine the actual content of total metal loading over the mordenite zeolite-supported catalysts. The measured total metal loading of the prepared catalysts is shown in Table 4.2. From the results, the measured values of total metal loading in all prepared catalysts were much lower than the expected values. The disappearance of the metals might be owing to the error during sample preparation step. In addition, the actual total metal loading provided by ICP tech-

nique showed that the surface area of fresh catalysts decreased with increasing the total metal loading.

Table 4.2 Specific surface area, pore size and pore volume of mordenite zeolite (MOR), 1%Au/MOR, 1% (1:1) Au:Pt/MOR, 1% (1:5) Au:Pt/MOR and 1%Pt/MOR

Catalyst	Specific Surface Area (m ² /g)	Pore Size (Å)	Pore Volume (cm ³ /g)	Total Metal Loading %
MOR	363.48	6.560	0.965	-
1%Au/MOR (Fresh)	348.74	5.060	0.553	0.41
1%(1:1) Au:Pt/MOR (Fresh)	326.11	5.039	0.629	0.47
1%(1:5) Au:Pt/MOR(Fresh)	314.59	5.620	0.378	0.51
1%Pt/MOR(Fresh)	315.45	8.807	0.351	0.77
1%Au/MOR (Calcined)	316.87	6.016	0.833	0.41
1%(1:1) Au:Pt/MOR (Calcined)	287.57	7.451	0.222	0.47
1%(1:5) Au:Pt/MOR (Calcined)	311.14	5.960	0.246	0.51
1%Pt/MOR(Calcined)	301.42	5.163	0.248	0.77

4.1.4 Temperature-programmed Reduction (TPR)

Temperature-programmed reduction technique was also used to characterize both the fresh and calcined Au, Pt and Au-Pt catalysts in order to examine the interaction between metals species and supports' surface. The TPR profiles of the prepared catalysts and blank mordenite zeolite catalyst support are revealed in Figure 4.5. It presents one reduction peak in low temperature with a maximum temperature at ~ 50 - 160°C . The reduction peak at $\sim 70^\circ\text{C}$ might be attributed to the reduction of Au and Pt species in on the exterior surface of mordenite. The main reduction of 1%Au/MOR occurred at $\sim 73^\circ\text{C}$ that was similar to the results from Wan *et al.* (2005). The complete reduction of Au (III) into Au (I) is accomplished in the 70 - 150°C range. Consequently, the high-temperature peak represents the reduction of Au (I) in to Au (0). This peak showed maxima at $\sim 320^\circ\text{C}$ in the profiles of Au/MOR fresh and calcined (Figure 4.5 (b) and (c)). In addition, the fresh 1% Au/MOR appeared a broadened peak at 567°C , suggesting that the gold species on the interior surface of zeolite particles. Both fresh and calcined 1%Pt/MOR catalysts showed lower main reduction temperatures than other catalysts, suggesting that the Pt species were reduced easily. The sizes of these species in 1% Pt/MOR were probably smaller than those in others; therefore, these species can be reduced at low temperatures. Additionally, the 1%Pt/MOR had the second reduction peak at high temperatures, the calcined 1%Pt/MOR showed a peak at 510°C and was sharper than the fresh catalyst situated close to 435°C . It is interesting to observe that it corresponds to the reduction of metal precursor from Pt (IV) to Pt (0) and the fresh 1%Pt/MOR was reduced more easily than the calcined catalyst. For fresh bimetallic catalysts, a region of H_2 uptake with maxima at 560°C was observed; however, for the calcined bimetallic catalysts, no significant H_2 uptake was observed. It may be expected that the peak appeared at 560°C was the impurity because of disappearance of these peak after calcination. The reduction peak at $\sim 400^\circ\text{C}$ could be ascribed to the reduction of Pt ions in the fresh bimetallic catalysts. The calcined Au-Pt/mordenite could be seen one peak at $\sim 75^\circ\text{C}$.

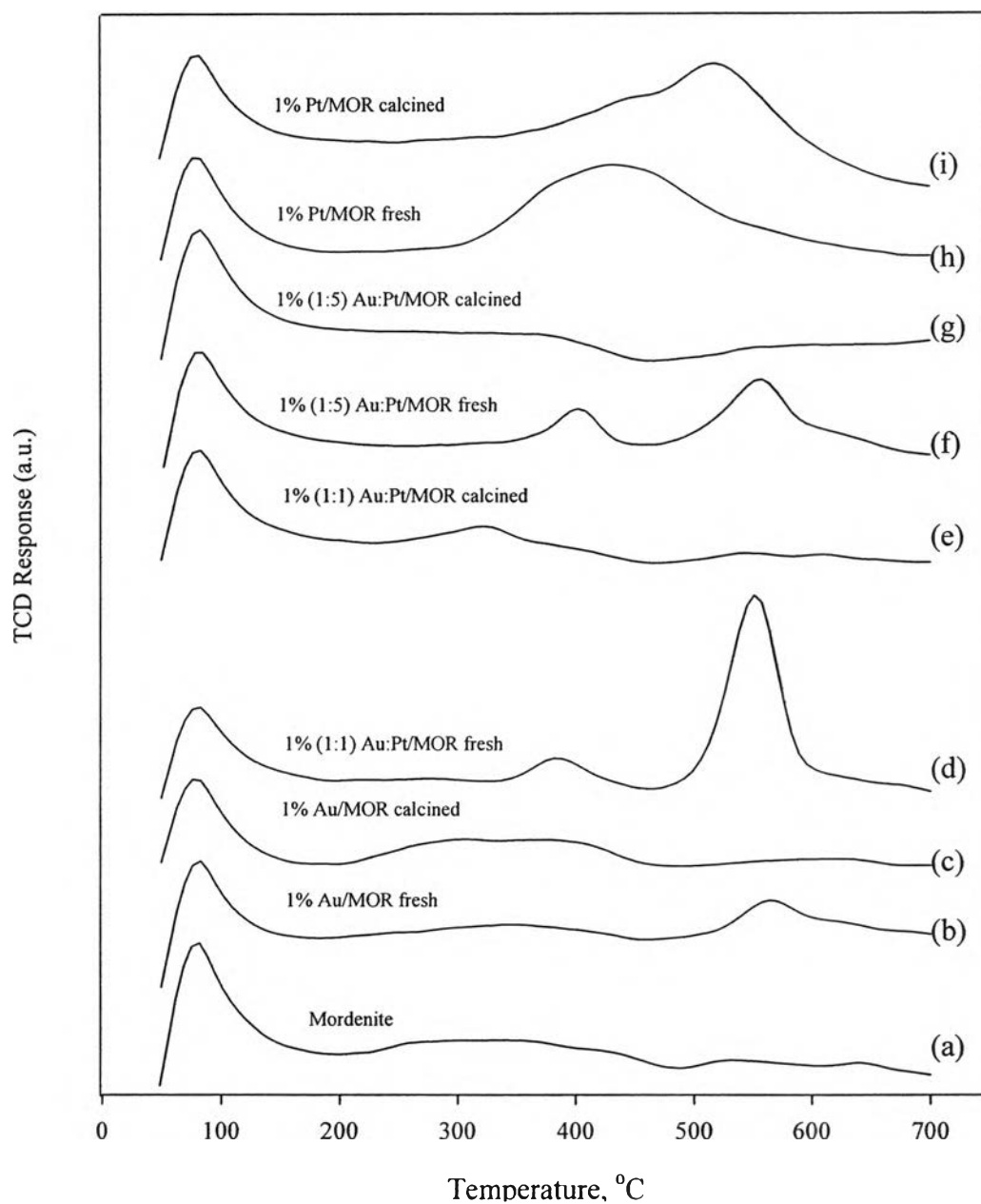


Figure 4.5 Temperature-programmed reduction profiles of the prepared catalysts: (a) mordenite zeolite, (b) fresh 1%Au/MOR, (c) calcined 1%Au/MOR, (d) fresh 1% (1:1) Au:Pt/MOR, (e) calcined 1% (1:1) Au:Pt/MOR, (f) fresh 1% (1:5) Au:Pt/MOR, (g) calcined 1% (1:5) Au:Pt/MOR, (h) fresh 1%Pt/MOR and (i) calcined 1%Pt/MOR.

4.1.5 H₂ Pulse Chemisorptions

A summary of chemisorption uptakes for each catalyst is shown in Table 4.3. H₂ is used as the adsorbate gas to study chemisorption on metal. The metal dispersions were calculated by H₂ chemisorption data assuming an adsorption stoichiometry of one hydrogen atom per surface metal atom. From the results, when the Au-Pt/mordenite and Pt/mordenite prepared by deposition-precipitation, a higher dispersion of Au and Pt can be obtained. Dispersions of about 55% and 29% were obtained for 1% Pt/MOR and 1% (1:5) Au:Pt/MOR, respectively. It is interesting to observe that the bimetallic catalyst (1% (1:5) Au:Pt/MOR) showed much lower dispersion as well as larger particle size than the monometallic catalyst (1%Pt/MOR) having a crystallite size of approximately 1.846 nm. It was inferred that the 1% (1:5) Au:Pt/MOR catalyst might form the aggregation state of the metals Pt and Au which lead to large particle size.

Table 4.3 The degree of metal dispersion and mean particle diameter of 1% (1:5) Au:Pt/MOR and 1%Pt/MOR catalysts

Catalyst	Metal Dispersion (%)	Mean Particle Diameter (nm)
1%(1:1) Au:Pt/MOR(Fresh)	1.705	59.715
1%(1:5) Au:Pt/MOR(Fresh)	29.042	3.506
1%Pt/MOR(Fresh)	55.149	1.846

4.1.6 Transmission Electron Micrograph (TEM)

Transmission electron micrographs of the 1%Pt/mordenite and 1% (1:5) Au:Pt/mordenite catalysts (Figure 4.6-4.7) show that the nanoparticles in both catalysts were well dispersed on the support and had similar morphology, with most metal particles were smaller than 10 nm. These results were confirmed by H₂ pulse chemisorption of 1% (1:5) Au:Pt/mordenite and 1%Pt/mordenite catalysts having average particle of approximately 3.506 nm and 1.846 nm for 1% (1:5)

Au:Pt/mordenite and for 1%Pt/mordenite, respectively. The 1% (1:5) Au:Pt/MOR had a larger size than %Pt/mordenite because Au and Pt might form alloy. The interaction between Pt and Au was explored at the nanometer scale by means of EDX. With the electron beam converged to nanometer size, X-ray photons emitted from the local area could be detected in the microscope. As shown in Figure 4.8, Pt L edges appear as small shoulders at the low-energy side of the Au L edges. The EDX spectrum of 1% (1:5) Au:Pt/mordenite zeolite had the peak of Au and Pt in individual single particle. It indicated that the examined single particle did not segregate of Au or Pt.

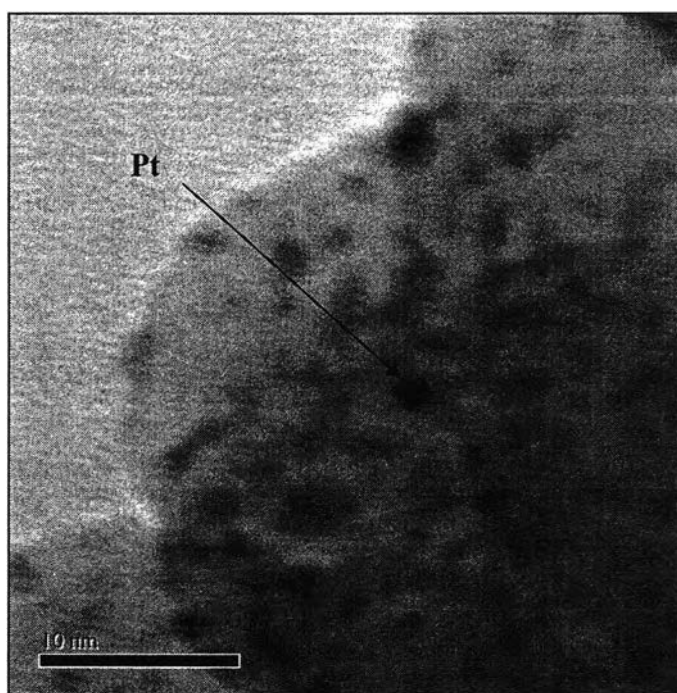


Figure 4.6 TEM micrograph of 1% Pt/mordenite zeolite.

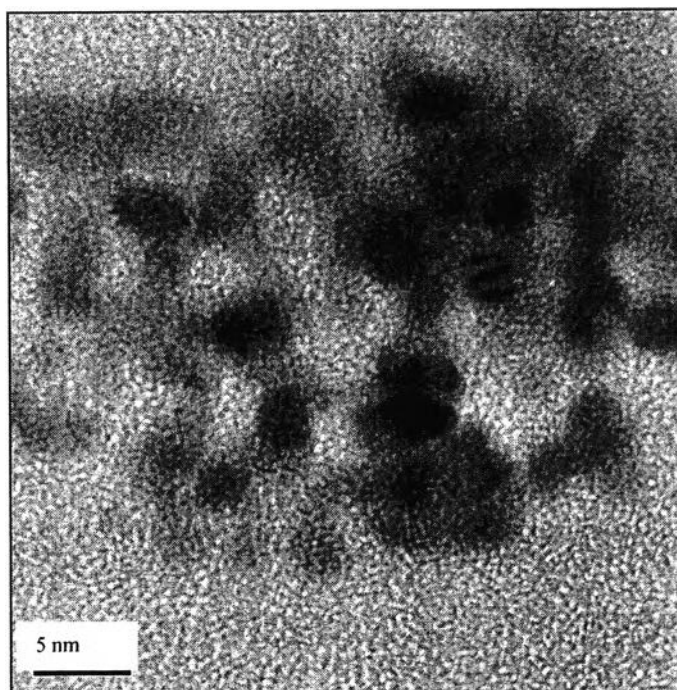


Figure 4.7 TEM micrograph of 1% (1:5) Au:Pt/mordenite zeolite.

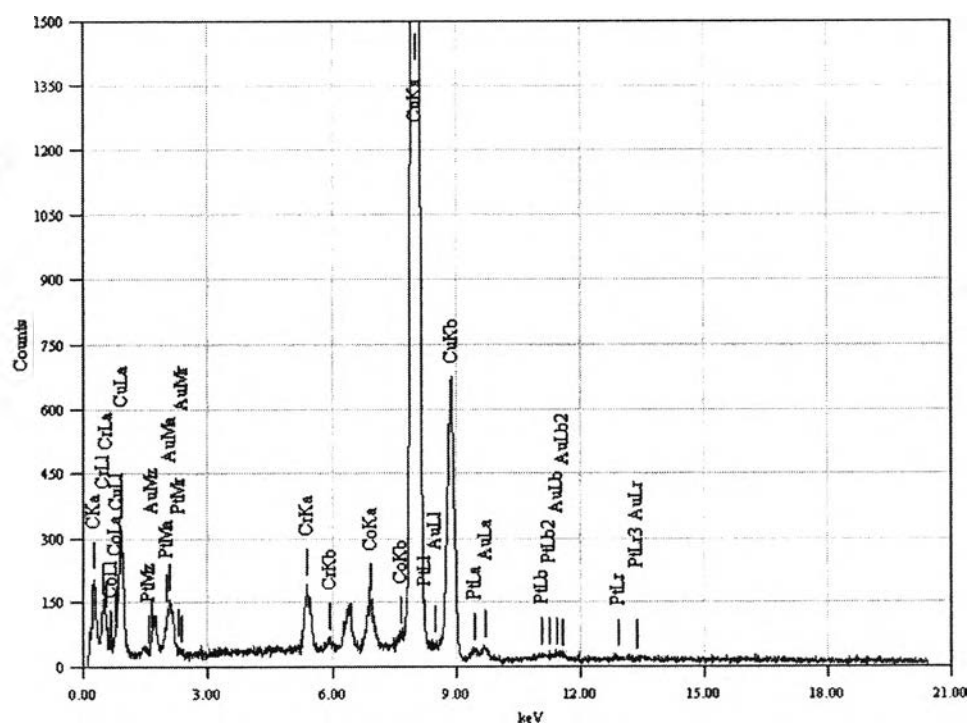


Figure 4.8 The EDX spectrum for individual single particle from 1% (1:5) Au:Pt/mordenite zeolite.

4.2 Catalytic Activity

The catalytic activity tests were carried out in a fixed bed U-tube micro-reactor with an inside diameter of 6 mm by packing with 100 mg catalyst of 80-120 mesh inside. The activity was investigated at varied temperature in the range of 50-330°C under atmospheric pressure.

4.2.1 Effect of Metal-loaded Ratio

The CO conversion and selectively versus temperature curves obtained over different mordenite supported Au, Pt and Au-Pt catalysts at 1% total metal loading are shown in Figure 4.9. The Au:Pt ratios were varied at 1:0, 1:1, 1:5 and 0:1. The Pt supported on mordenite zeolite gave the highest CO conversion (100%) and selectivity (69.77%). For all catalysts, the higher CO conversion was obtained at high temperatures but the higher CO selectivity was obtained at low temperatures. Au catalyst is inert for catalytic applications, however, it is more active for selective CO oxidation, and more for CO oxidation than for H₂ oxidation (Okumura *et al.*, 2002). According to Au gave high selectivity at low temperatures, so that the maximum selectivity of the bimetallic 1% (1:1) Au:Pt/MOR showed at lower temperature than 1% (1:5) Au:Pt/MOR. From the results, when the small amount of Pt was added to Au/MOR, the CO conversion was higher and the temperature at the maximum CO conversion of 1% Au:Pt/MOR was shifted to lower temperature according to the ratio of Pt. In comparison, the monometallic Au sample exhibited the lowest activity among all samples examination and completed conversion over the monometallic Pt sample was reached at approximately 210°C. The bimetallic Au-Pt samples exhibited the activity between monometallic Pt and Au samples. The behavior of the bimetallic Au-Pt supported on mordenite was opposite to what was observed over CeO₂ (Monyanon *et al.*, 2006). The bimetallic catalyst (PtAu/CeO₂) were more active than monometallic catalysts (Pt/CeO₂ and Au/CeO₂) for PROX of CO. Additionally, the performance of the bimetallic Au-Pt supported on mordenite was also inconsistent with the bimetallic Au-Pt supported on A zeolite. Naknam *et al.*, (2006) reported that 1% AuPt/A zeolite gave the best performance because the pres-

ence of Au on the Pt/A catalyst improved the both the CO conversion and selectivity. From the ICP result of 1%Au/MOR, the amount of Au deposited on the support was low. It was inferred that the catalyst had low active sites, so this catalyst provided a low CO conversion. On the other hand, the 1%Pt/MOR has high amount of Pt deposited on the support since this catalyst had high active sites. In addition, the Pt particle had small sizes of approximately 1.8-2 nm, so the high surface led to the high interaction area. The presence of a small particle size increased the metal-support interfacial area, increasing the effectiveness of the mechanism of carbon removal from the metallic surface, which takes place at the metal-support interfacial perimeter (Matos *et al.*, 2005).

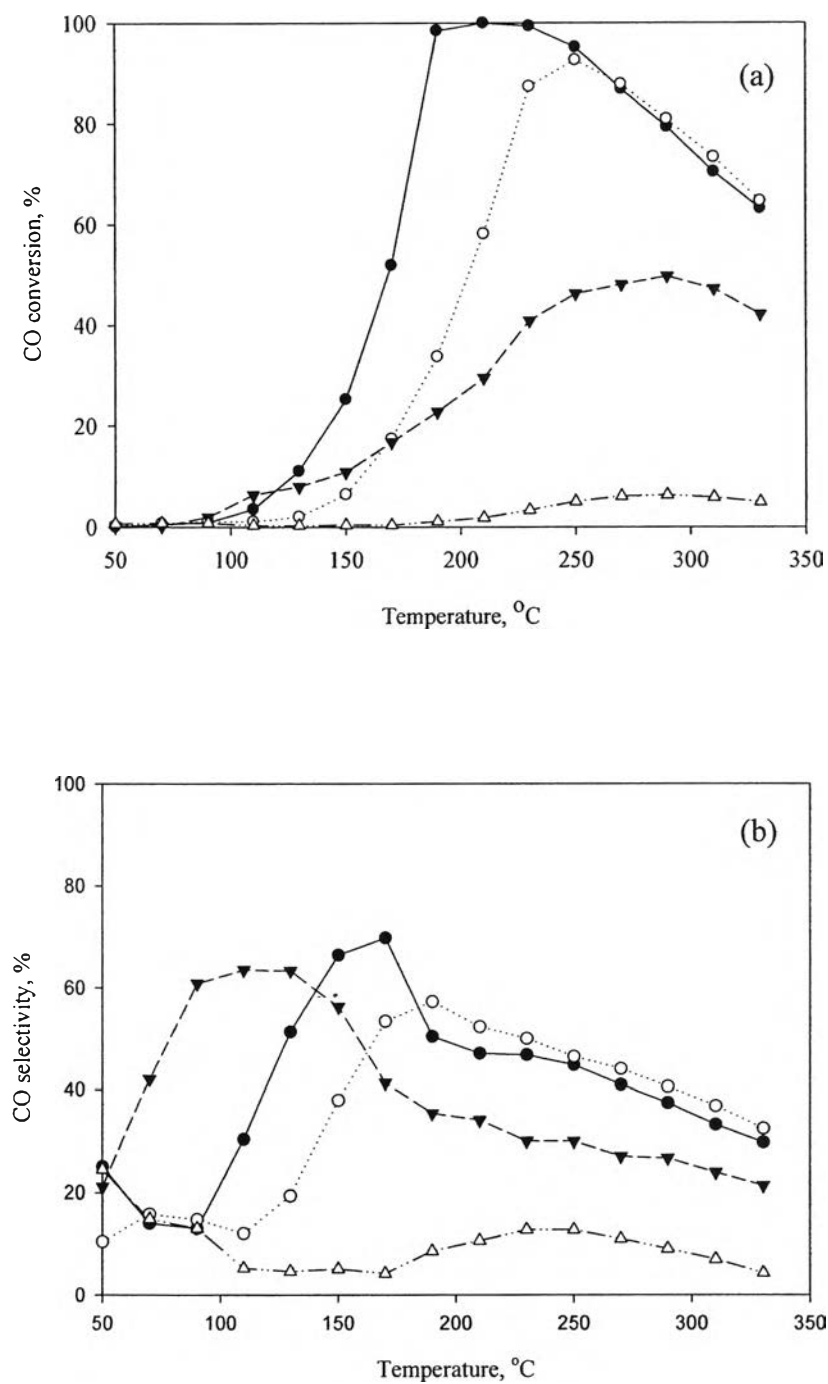


Figure 4.9 Dependencies of the CO conversion (a) and the CO selectivity (b) of mordenite supported catalysts: (Δ) 1% Au/MOR, (\blacktriangledown) 1% (1:1) Au:Pt/MOR, (\bigcirc) 1% (1:5) Au:Pt/MOR, and (\bullet) 1% Pt/MOR.

4.2.2 Effect of Catalyst Pretreatment

Supported Au, Pt and Au-Pt catalysts prepared by deposition-precipitation were studied with different pretreatment conditions as shown in Figures 4.10-4.13. All catalysts were pretreated with different conditions; non-pretreatment, H₂ at 400°C, O₂ at 200°C and He at 110°C for 1 h.

As shown in Figure 4.10, the 1% Au/MOR pretreated with H₂, O₂ and He gave yield more active than non-pretreatment. The non-pretreatment of this catalyst gave the lowest CO conversion and lowest CO selectivity. It was able to observe that He pretreatment gave the highest CO selectivity of 47.10% at ~100°C. In summary, The CO conversion of 1%Au/MOR of all pretreatments did not exceed 20%. The reaction results presented that this catalyst is inactive. It is plausible that this is a consequence of the complete absence of Au and the pretreatment conditions could not activate the uncalcined sample.

For 1% (1:1) Au:Pt/MOR as shown in Figure 4.11, it is likely that O₂ and He induced the growth of Au species because the pretreatment in H₂ atmosphere and non-pretreatment did not cause appreciable growth of Au particles. It can be seen that the CO conversion profile of the oxidizing pretreatment was similar to the inert pretreatment. These catalysts of the oxidizing pretreatment and the inert pretreatment showed higher CO conversion than the reducing pretreatment and non-pretreatment. When the pretreatment condition was converted to O₂ and He, the maximum CO conversion was shifted to lower temperature (~230°C). In the selectivity profile, He pretreatment gave the highest CO selectivity of 99.51% at low temperatures, while the selectivity profile of oxidizing pretreatment was similar to the non-pretreatment. It is interesting to observe that the selectivity of pretreatment in H₂, O₂ and non-pretreatment were not much different in the temperature range of 170- 330°C, while the selectivity of the reducing pretreatment gave the lowest selectivity.

For 1% (1:5) Au:Pt/MOR as shown in Figure 4.12, the CO conversion of all pretreatments was maximized in range of 210-250°C and then slightly decreased with increasing temperature. The catalysts pretreated with H₂ atmosphere gave the highest CO conversion at low temperatures, while the catalysts of non-pretreatment gave the highest CO conversion at high temperatures. The maximum CO conversion of 1% (1:5) Au:Pt/MOR was 90.05% of non-pretreatment at 250°C.

The temperature at the maximum CO conversion was shifted to 230°C when pretreated in O₂ atmosphere. In addition, The H₂ pretreatment showed the highest CO selectivity of 93.58% at low temperatures but increasing temperature dramatically minimized the CO selectivity. The selectivity of non-pretreatment, oxidizing pretreatment and inert pretreatment increased dramatically at low temperatures, while decreased slightly at high temperatures. However, all pretreatments of catalysts showed a similar trend in the temperature range of 190-330°C.

In Figure 4.13, CO was completely converted to CO₂ by 1% Pt supported on mordenite zeolite with all pretreatments in the temperature range 190-230°C. The temperature at the maximum CO conversion of O₂ pretreated catalyst was 210°C, while the temperature at the maximum CO conversion of H₂ pretreatment was shifted to 170°C. The CO conversion of O₂ pretreatment and H₂ pretreatment followed the same trend as in the temperature range of 50- 130°C rose considerably. However, the CO conversion declined moderately at high temperatures. At the low temperatures, the CO selectivity of O₂ pretreatment and H₂ pretreatment decreased rapidly while the CO selectivity of He pretreatment and non-pretreatment increased dramatically. However, the CO selectivity of all pretreatment did not show much different in the range of 190-330°C. The selectivity of all pretreatment showed in the range of 47.1-49.9%. This suggested that only a slight difference in the value of selectivity was observed.

Among Au-Pt/MOR catalysts, 1% Pt supported on mordenite zeolite with H₂ pretreatment gave the best performance due to the CO conversion of 100% and the CO selectivity of 48.14% was obtained at the low temperature (170 °C). However, 1% Pt/MOR with non-pretreatment and He pretreatment gave the wider range of temperature at the maximum CO conversion.

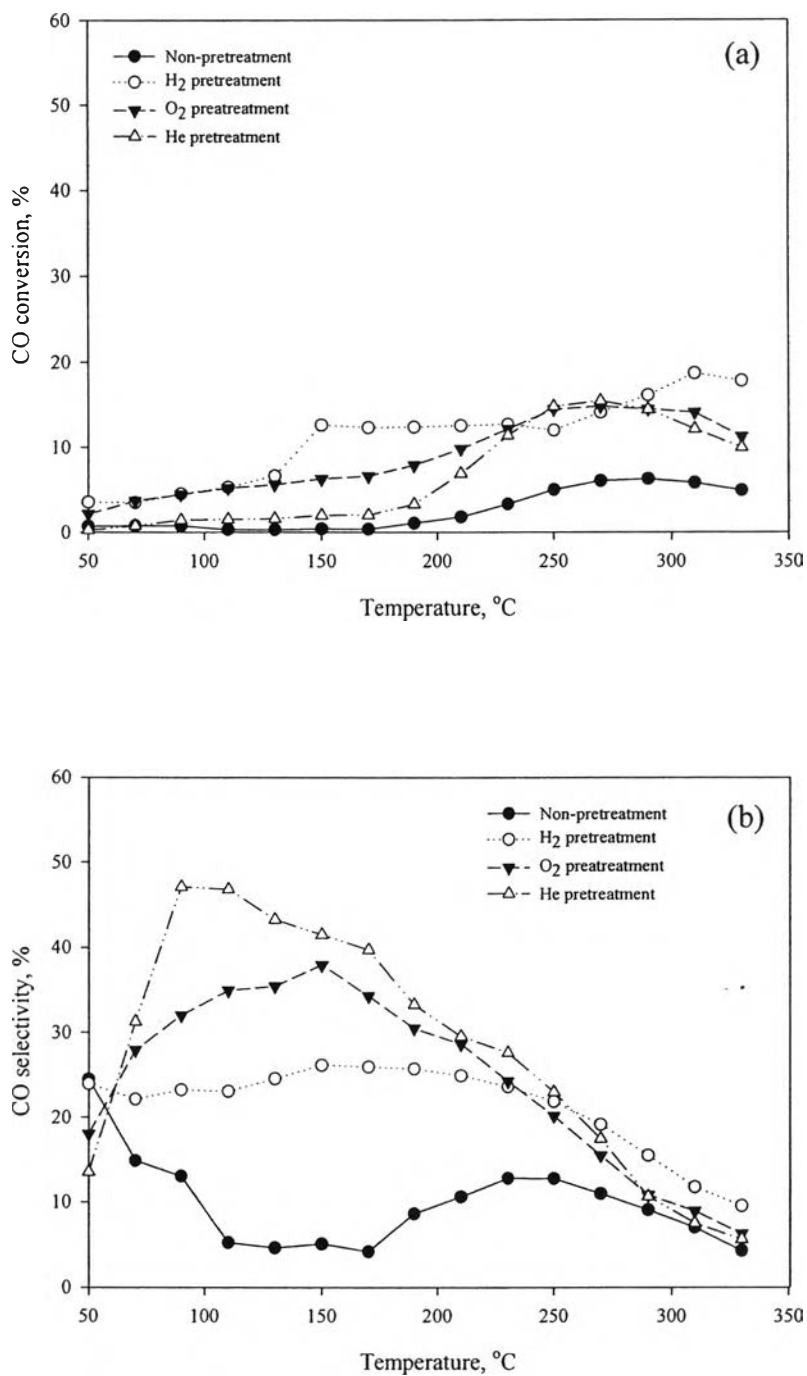


Figure 4.10 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% Au/mordenite zeolite catalyst: (●) Non-pretreatment, (○) H₂ pretreatment at 400°C for 1 h, (▼) O₂ pretreatment at 200°C for 1 h, (Δ) He pretreatment at 110°C for 1 h.

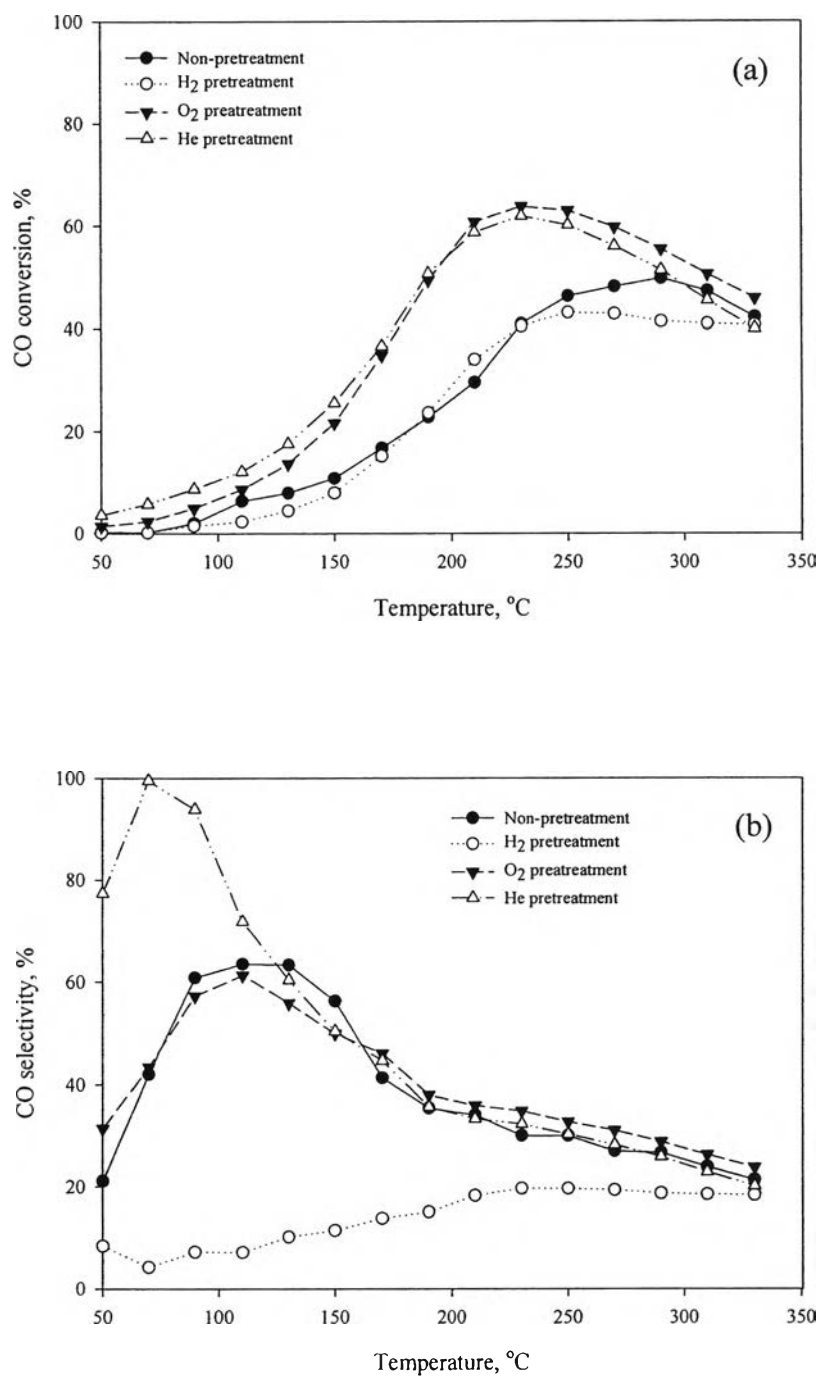


Figure 4.11 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% (1:1) Au:Pt/mordenite zeolite catalyst: (●) Non-pretreatment, (○) H₂ pretreatment at 400°C for 1 h, (▼) O₂ pretreatment at 200°C for 1 h, (Δ) He pretreatment at 110°C for 1 h.

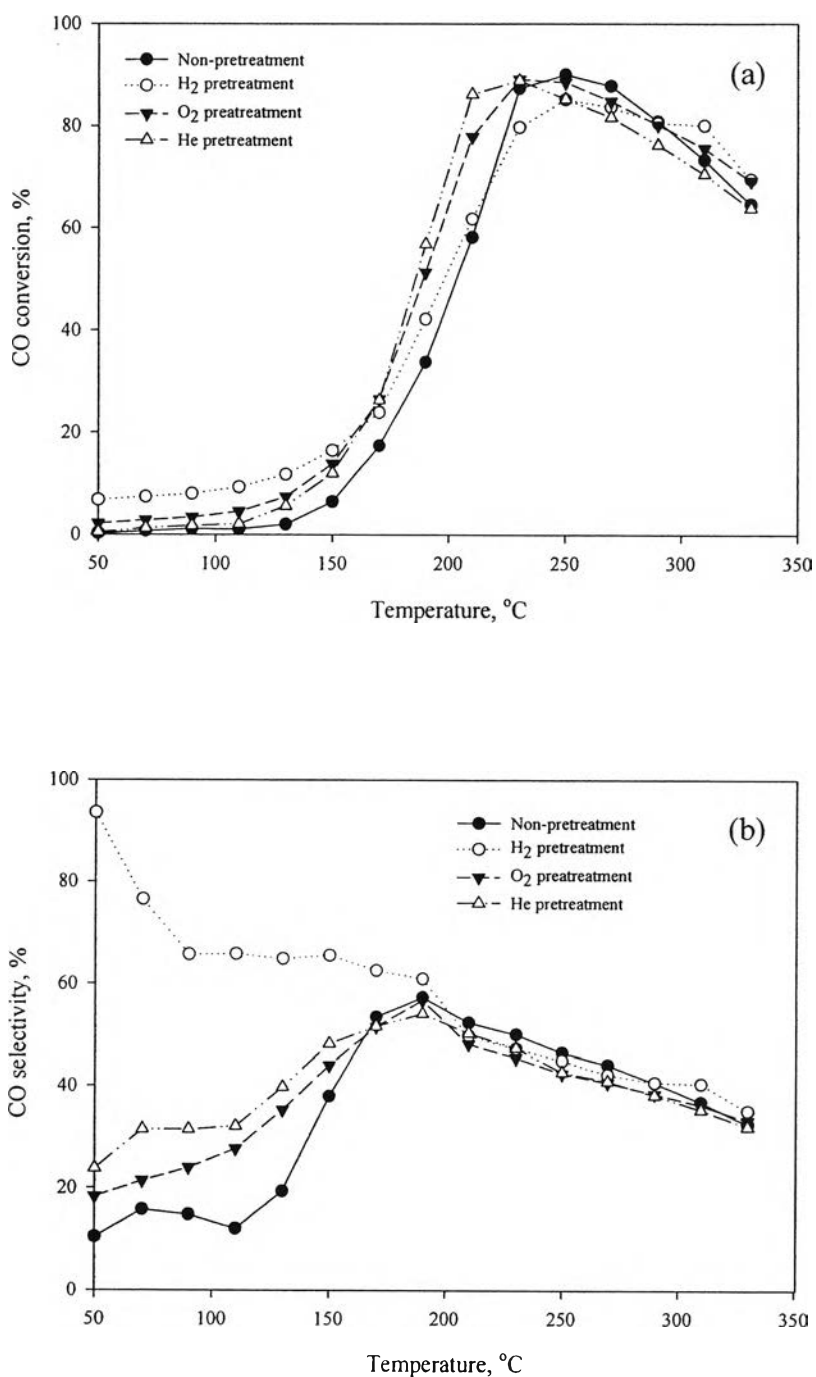


Figure 4.12 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% (1:5) Au:Pt/mordenite zeolite catalyst: (●) Non-pretreatment, (○) H₂ pretreatment at 400°C for 1 h, (▼) O₂ pretreatment at 200°C for 1 h, (△) He pretreatment at 110°C for 1 h.

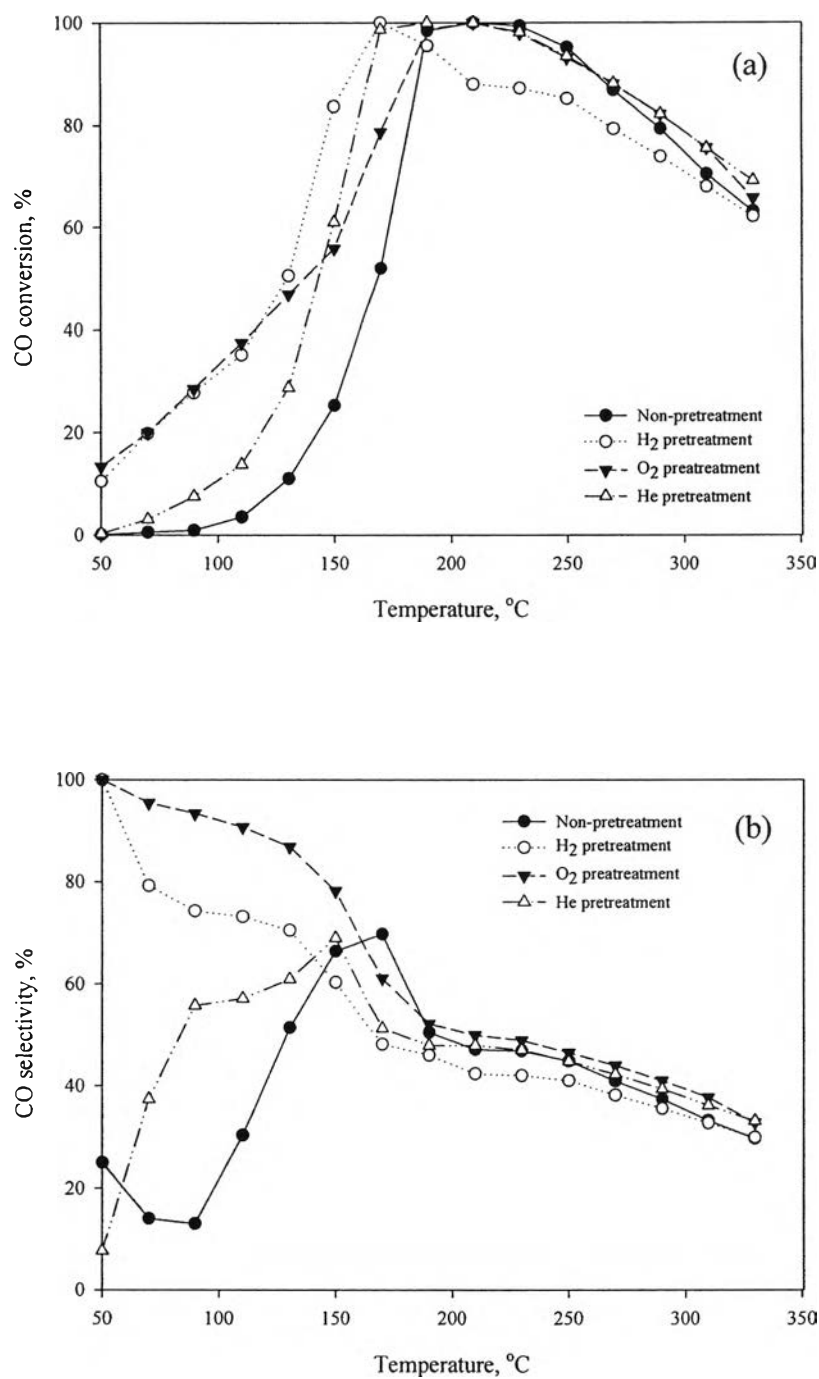


Figure 4.13 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% Pt/mordenite zeolite catalyst: (●) Non-pretreatment, (○) H₂ pretreatment at 400°C for 1 h, (▼) O₂ pretreatment at 200°C for 1 h, (△) He pretreatment at 110°C for 1 h.

4.2.3 Effect of Calcination

To investigate the influence of the calcination conditions, the activity of uncalcined and calcined samples is measured. In the calcination conditions, the samples were calcined in air at 500°C for 1 h. Both uncalcined and calcined catalysts were pretreated with H₂ at 400°C for 1 h or with O₂ at 200°C for 1 h.

The reaction was performed with uncalcined and calcined Au/MOR under the same condition at the temperature range of 50-330°C as shown in Figure 4.14. It was found that the CO conversion of uncalcined catalyst was ~12-15%. Whereas, the conversion of calcined catalysts was ~21-25%, which was higher than the uncalcined sample. After calcinations at 500°C, the calcined Au/mordenite was metallic form (from XRD results) and it was more active than the uncalcined one. For the catalysts pretreated with H₂, the CO conversion of uncalcined catalysts were higher than calcined catalysts at low temperatures, while the CO conversion of uncalcined catalysts were lower than calcined catalysts at high temperatures. The selectivity of catalysts pretreated with O₂ and H₂ in the temperature range of 210-330°C declined considerably. It is inferred that the Au/MOR catalysts at high temperatures gave low CO selectivity due to at high temperature H₂ oxidation was able to occur easier than CO oxidation (Marino *et. al.*, 2005).

Surprisingly, the uncalcined catalyst 1% (1:1) Au:Pt/MOR pretreated with O₂ was more active than the uncalcined catalyst when treated with H₂ as shown in Figure 4.15. The failure of H₂ reduction at 400°C to activate Au-Pt/mordenite indicates that production of metallic Au is not the only requirement for an active catalyst. In comparison of the uncalcined and calcined 1% (1:1) Au:Pt/MOR pretreated with H₂ showed that the CO conversion did not show much different in the temperature range of 50-330°C, while the calcined catalyst gave higher selective than uncalcined catalyst. However, the uncalcined catalyst pretreated with O₂ displayed the highest selectivity all the temperature range of interest. To summary, the uncalcination and oxidizing pretreatment of 1% (1:1) Au:Pt/MOR gave high CO conversion of 63.76% and high selectivity of 34.82% at 230°C.

Similarly, the uncalcined Au-Pt/mordenite catalysts were more active in this reaction than the calcined catalysts. Figure 4.16 shows the CO conversions and selectivity with uncalcined and calcined 1% (1:5) Au:Pt/MOR. The maximum

CO conversions were in the order of 1% (1:5) Au:Pt/MOR uncalcination and O₂ pretreatment > uncalcination and H₂ pretreatment > calcination and O₂ pretreatment > calcination and H₂ pretreatment. Additionally, the temperature at the maximum conversion of uncalcined catalysts pretreated with O₂ was shifted from 230°C to lower temperature than the calcined catalysts pretreated with O₂. The uncalcined 1% (1:5) Au:Pt/MOR pretreated with O₂ achieved the maximum CO conversion at around 89%. From the selectivity profile as shown in Figure 4.16 (b), all catalysts showed different characteristic of selectivity at temperature lower than 200°C. The selectivity of calcined catalyst pretreated with O₂ has the high value at low temperatures and decreased slightly at high temperatures. On the other hand, the selectivity of uncalcined catalyst pretreated with O₂ was approximately constant, it slightly fluctuate between 44-61% in the temperature range of 50-250°C.

The difference of CO conversion and selectivity between uncalcined and calcined of 1% Pt/MOR is illustrated in Figure 4.17. CO was completely converted to CO₂ by the uncalcined catalyst pretreated with H₂ and O₂. The temperature at the maximum CO conversion of uncalcined catalyst pretreated with O₂ was at 210°C, whereas the uncalcined catalyst pretreated with H₂ gave the temperature at the maximum CO conversion shifted 40°C to lower temperature. On the contrary, the CO conversion of calcined catalyst could not achieve 100% CO conversion. The CO conversion profile of calcined catalyst pretreated with O₂ was similar to the uncalcined catalyst pretreated with O₂; however, the maximum CO conversion of the calcined catalyst pretreated with O₂ was about 99% at 210°C. Moreover, the maximum CO conversion of catalyst pretreated with H₂ was dropped 4% when the catalyst was calcined at 500°C for 1 h and the temperature at the maximum CO conversion was also shifted 40°C to higher temperature. For CO selectivity, all catalysts showed similarly selectivity. It decreased significantly at low temperatures and decreased slightly at high temperatures.

The catalytic activity of calcined and uncalcined catalysts pretreated with H₂ and O₂ was difference for Au-Pt/MOR catalysts. The calcination has a positive effect on the CO conversion of 1% Au/MOR at high temperatures. By contrast, the bimetallic Au-Pt/MOR and 1%Pt/MOR was negatively affected by calcination 500°C for 1 h.

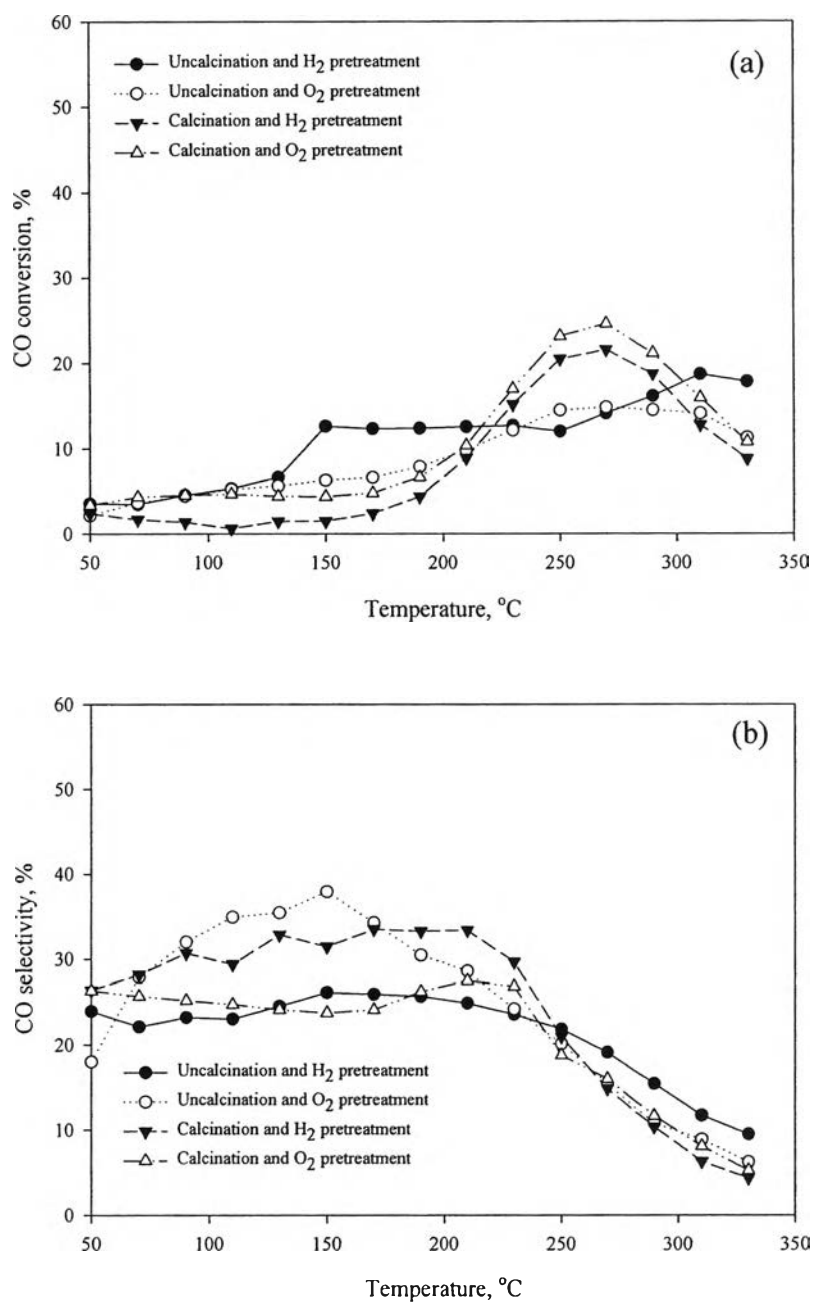


Figure 4.14 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% Au/mordenite zeolite: (●) uncalcined and H₂ pretreatment at 400°C for 1 h, (○) uncalcined and O₂ pretreatment at 200°C for 1 h (▼) calcined and H₂ pretreatment at 400°C for 1 h, (△) calcined and O₂ pretreatment at 200°C for 1 h.

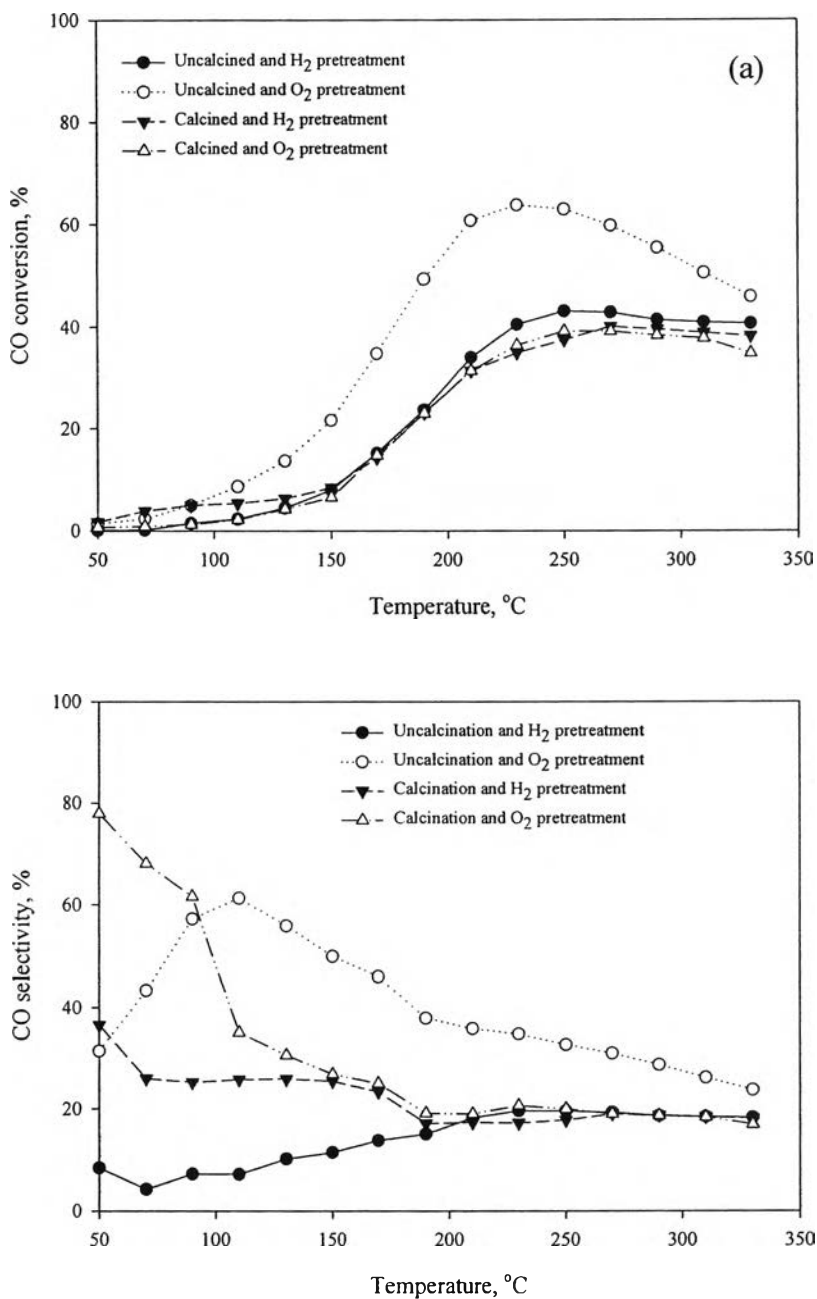


Figure 4.15 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% (1:1) Au:Pt/mordenite zeolite: (●) uncalcined and H₂ pretreatment at 400°C for 1 h, (○) uncalcined and O₂ pretreatment at 200°C for 1 h (▼) calcined and H₂ pretreatment at 400°C for 1 h, (△) calcined and O₂ pretreatment at 200°C for 1 h.

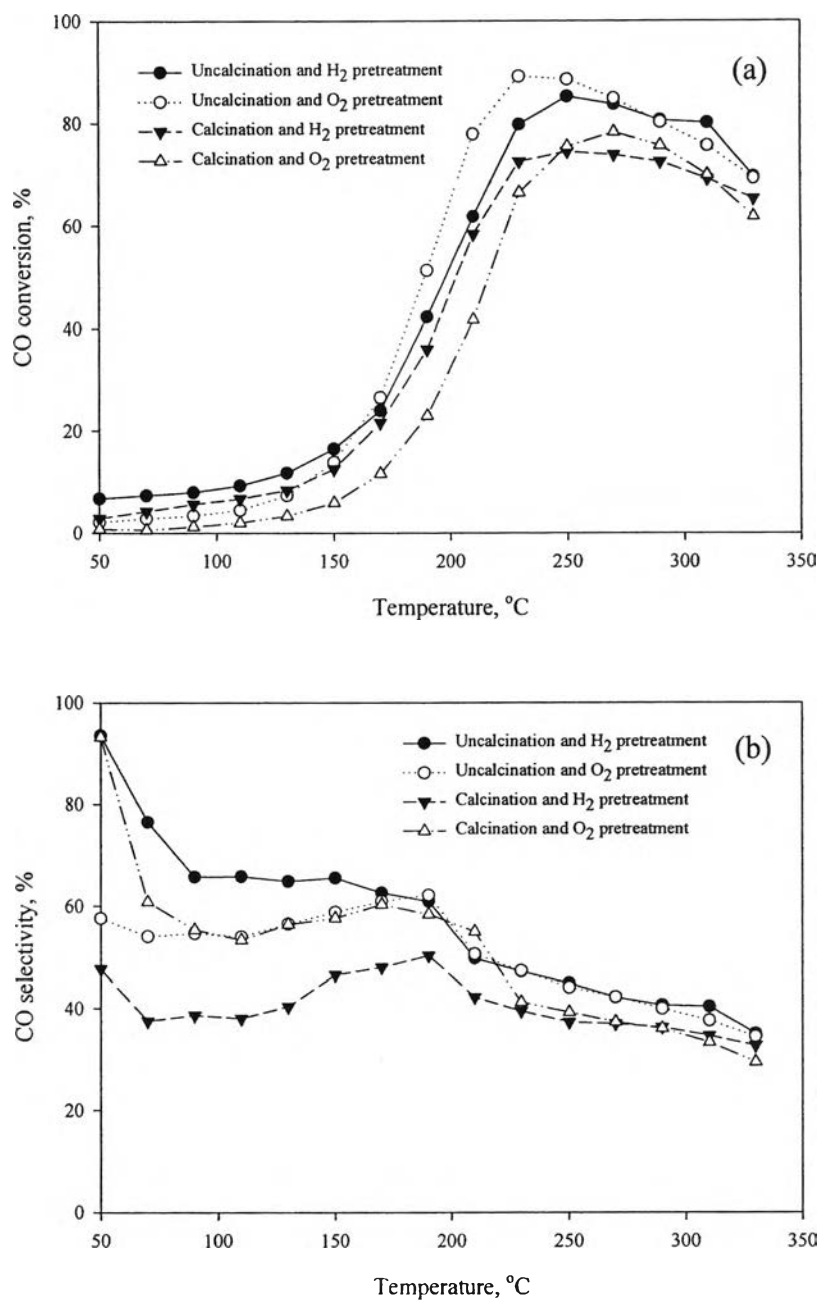


Figure 4.16 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% (1:5) Au:Pt/mordenite zeolite: (●) uncalcined and H₂ pretreatment at 400°C for 1 h, (○) uncalcined and O₂ pretreatment at 200°C for 1 h (▼) calcined and H₂ pretreatment at 400°C for 1 h, (△) calcined and O₂ pretreatment at 200°C for 1 h.

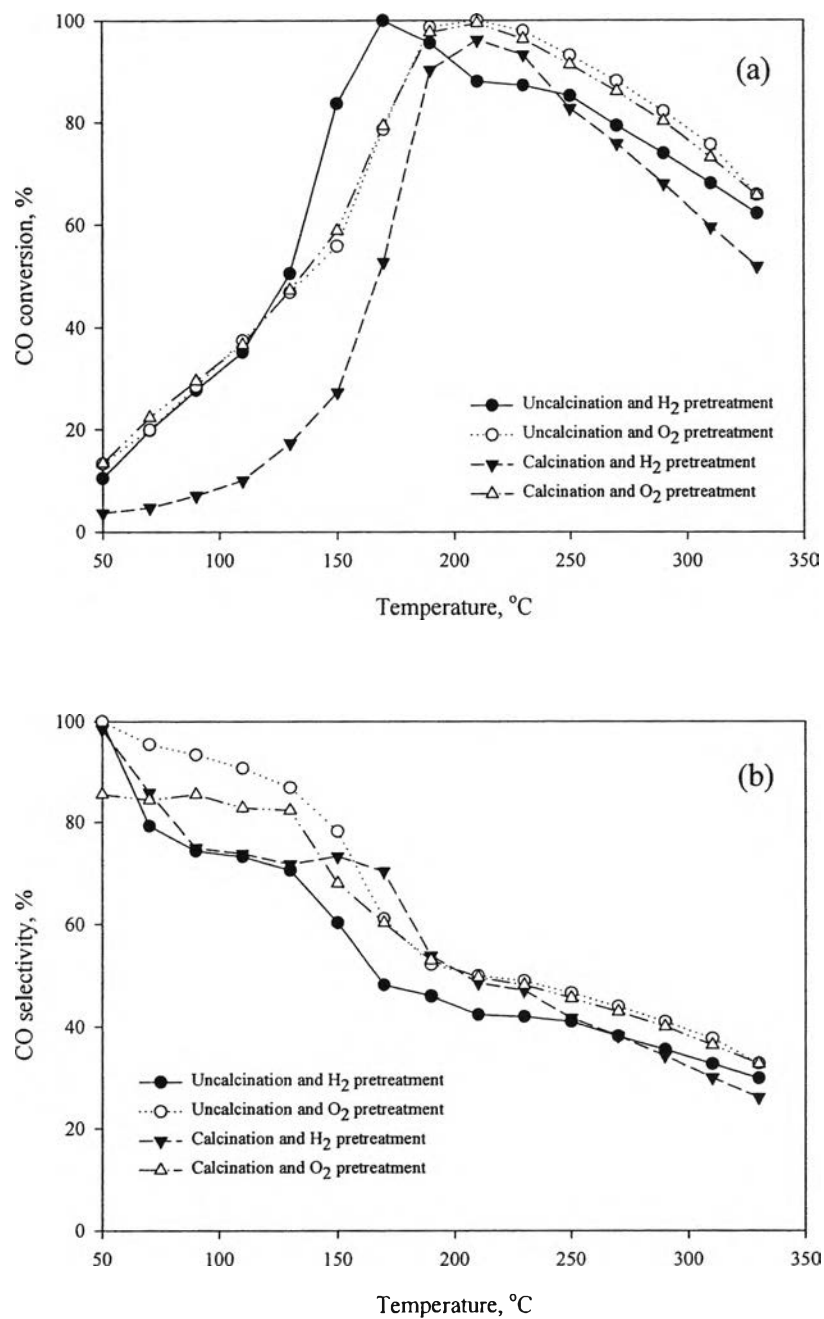


Figure 4.17 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% Pt/mordenite zeolite: (●) uncalcined and H₂ pretreatment at 400°C for 1 h, (○) uncalcined and O₂ pretreatment at 200°C for 1 h (▼) calcined and H₂ pretreatment at 400°C for 1 h, (△) calcined and O₂ pretreatment at 200°C for 1 h.

4.2.4 Stability Testing

Long-term test with the unclined 1% Pt/mordenite catalyst pretreated with H₂ were conducted to evaluate the catalyst stability under PROX reaction conditions. The feed gas mixture contained 40% H₂, 1% CO and 1% O₂ balanced in He. The reaction was run for 12 hours at 170°C. Figure 4.18 shows that there was no loss of CO conversion or CO selectivity over the time period tested. This is an indication that this catalyst exhibited a stable catalytic performance during 12 hours of testing time.

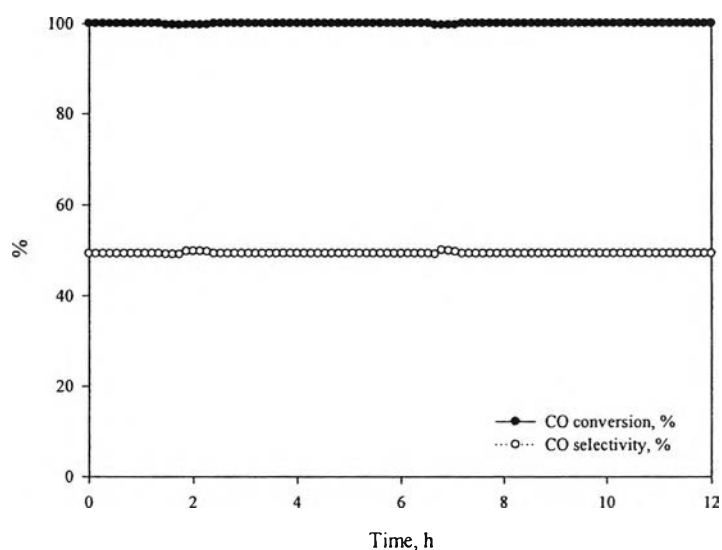


Figure 4.18 Stability testing of 1% Pt/mordenite at 170°C under atmospheric pressure; (●) CO conversion and (○) CO selectivity.

4.2.5 Bench-scale Fuel Processor Testing

After the catalytic testing for the preferential CO oxidation was investigated, the proper catalysts of the catalytic performance in bench-scale experiments were studied. The optimum condition from lab-scale was applied for PROX unit in fuel processing system for a hydrogen production of 50 l/day, utilizing natural gas as a hydrogen feedstock. The experimental conditions between the lab-scale and bench-scale experiments are presented in Table 4.4. In bench-scale experiments, reactant gases were controlled by three mass controllers for natural gas, He and O₂, respectively. The liquid feed of water was controlled by a syringe pump. The reactants were fed through a series of steam reformer (SR), high-temperature water-gas shift (HT-WGS), low-temperature water-gas shift (LT-WGS) and PROX reactors. Additionally, Table 4.5 presents the comparison of the gas composition before and after reaction in PROX unit between the lab scale and bench-scale experiments. The gas composition of bench-scale was collected at 8 hrs time on stream.

Table 4.4 Comparison of the experimental conditions between lab-scale and bench-scale experiments for 1%Pt/MOR catalyst

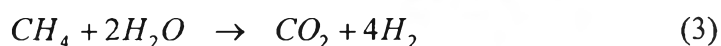
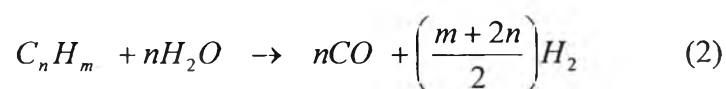
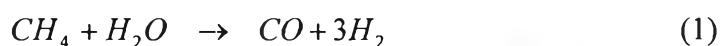
Conditions	Lab-scale Experiment	Bench-scale Experiment
Catalyst pretreatment	non	non
Weight of catalyst (g)	0.1	0.7
Temperature (°C)	200	200
Inlet flow rate (ml min ⁻¹)	50	110
GHSV (ml h ⁻¹ g _{cat} ⁻¹) at dry basis	30,000	9,429
Diameter of reactor	6 mm	10 mm
Particle size of catalyst	250-425 μm	0.85-1.50 mm

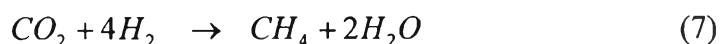
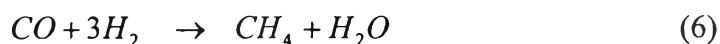
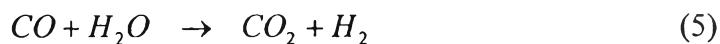
Table 4.5 The gas composition of lab-scale and bench scale experiment

Gas Composition	Lab-scale Experiment		Bench-scale Experiment (at 8 hrs)	
	Before	After	Before	After
H ₂	40%	39.8%	60.6%	57.1%
CO	1%	0%	0.2%	334.8 ppm
O ₂	1%	0%	1.1%	0.7%
CO ₂	0%	1%	18.1%	18.0%
CH ₄	-	-	3.1%	2.8%

The lab-scale results over Pt and Au supported on mordenite zeolite catalysts indicated that the catalysts based on Pt were more active than Au catalyst; therefore, the Pt/MOR catalyst was applied in the PROX unit in a fuel processing system. From studied pretreatment and calcinations of Pt/MOR, these results did not show much different the catalytic activity. The temperature at maximum CO conversion showed in the range of 170-210°C as well as CO conversion and selectivity gave in the range of 96.2-100% and 47.1-49.9%, respectively. However, the uncalcined Pt/MOR catalysts of all pretreatment conditions gave 100% CO conversion. The non-pretreated and uncalcined Pt/MOR catalyst was selected for the PROX unit because it was easy to prepare in the bench-scale experiment. As consequence of these studies, the operational conditions for the developed PROX catalyst were derived in order to reduce the CO concentration in the gas mixture after LT-WGS unit.

A fuel processor was a complex system. There were many reactions that could possibly happen although only four of them were independent. For the SR alone, the possible reactions are as follows:





When a steady condition was reached at around 700°C, SR in Equations (1), (2) and (3) were predominant while the thermal cracking (Equation (4)) or WGS (Equation (5)) or methanation (Equations (6) and (7)) reactions could be either ignored or their reverse reactions were pronounced. In the HT-WGS and LT-WGS units, the WGS reaction would primarily take place to reduce the CO level below 0.5-1%. CO would further be eliminated to below 1000 ppm by PROX unit in this work. In Figure 4.18, the stream gas composition along with time-on-stream at the output of fuel processor was 55.9-58.0% of H₂, 15.2-17.4% of CO₂, 2.5-2.9 of CH₄ and 229-883 ppm of CO concentration. Figure 4.19 shows the CO conversion and selectivity for 8 h long-term test. The CO conversion and selectivity showed in the range of 75.0-92.6% and 28.2-37.2%, respectively. It was observed that the catalytic activities of PROX catalysts in bench-scale experiment were dropped down from the results in lab-scale. This suggests that the decreasing catalytic activity depended on many factors such as H₂O and CO₂ concentrations in the gas mixture before PROX unit. Not only CO₂ was produced from SR, HT-WGS and LT-WGS, but also H₂O vapor was remained in the gas stream and it was produced by H₂ oxidation. In general the catalytic activity of zeolite is liable to be depressed in the presence of water vapor. However, Igarashi *et al.* (1997) reported that the degradation of the activity by H₂O should be negligible over Pt/Mordenite when 20% H₂O was added to the gas stream. In previous work, Naknum *et al.* (2007) found that the adding of 10% H₂O in feed stream did not reduce the catalytic activity of 1% (1:2) AuPt/A zeolite. In contrast, Manasilp and Gulari (2002), reported that the presence of H₂O increases the formation of hydroxyl groups on the catalyst support, with make water a better oxidant than oxygen and increases the oxidation rate of CO and H₂. In addition, there might be reverse water-gas shift reaction limiting the CO oxidation at high tempera-

tures in the presence of CO_2 . To determine the extent of reverse water-gas shift reaction, the stream after LT-WGS unit composed $\sim 17\text{-}19\%$ CO_2 and $\sim 58\text{-}61\%$ H_2 .

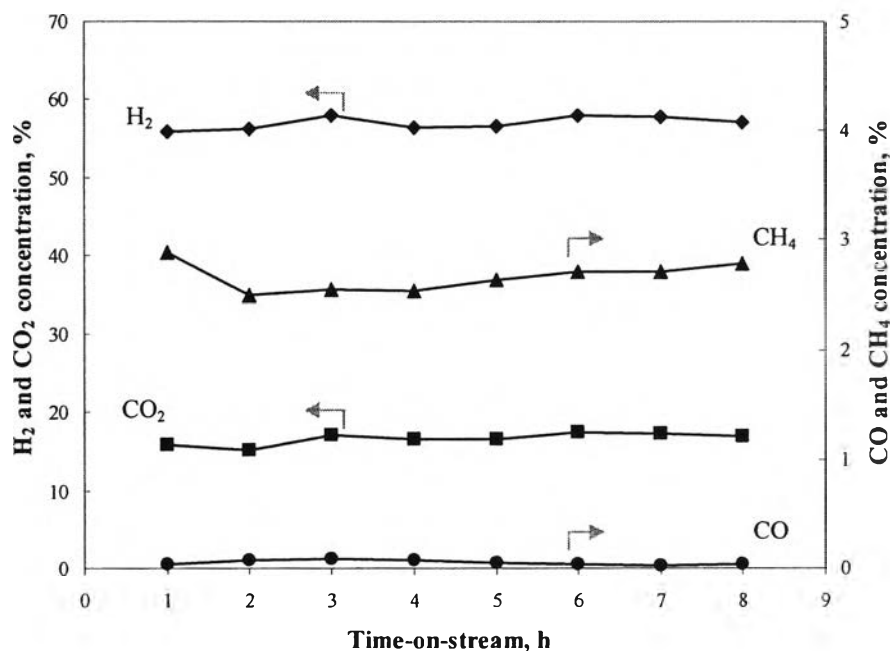


Figure 4.19 Reformate concentration profiles after PROX unit of fuel processor system over 1% Pt/Mordenite along with time-on-stream.

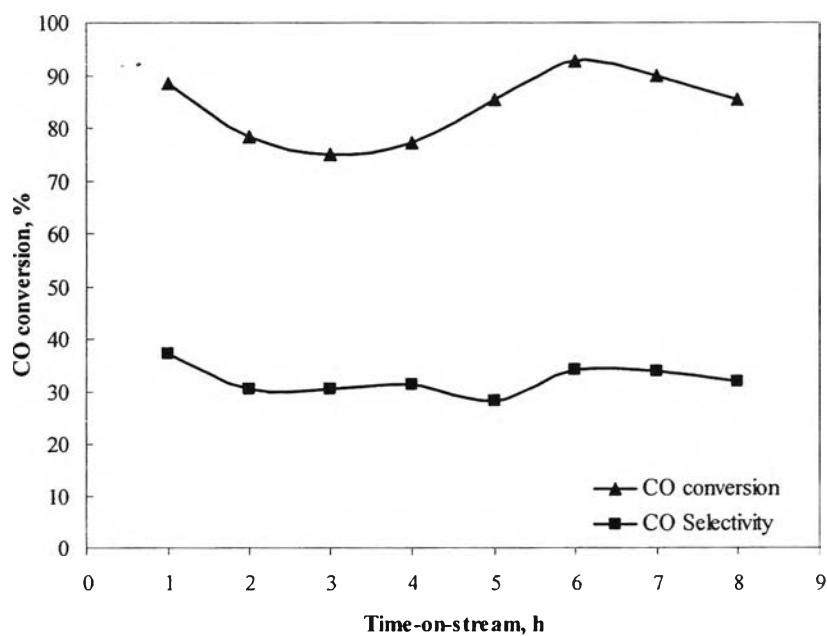


Figure 4.20 Dependencies of the CO conversion (a) and the CO selectivity (b) of 1% Pt/Mordenite from PROX unit of fuel processor system along with time-on-stream.

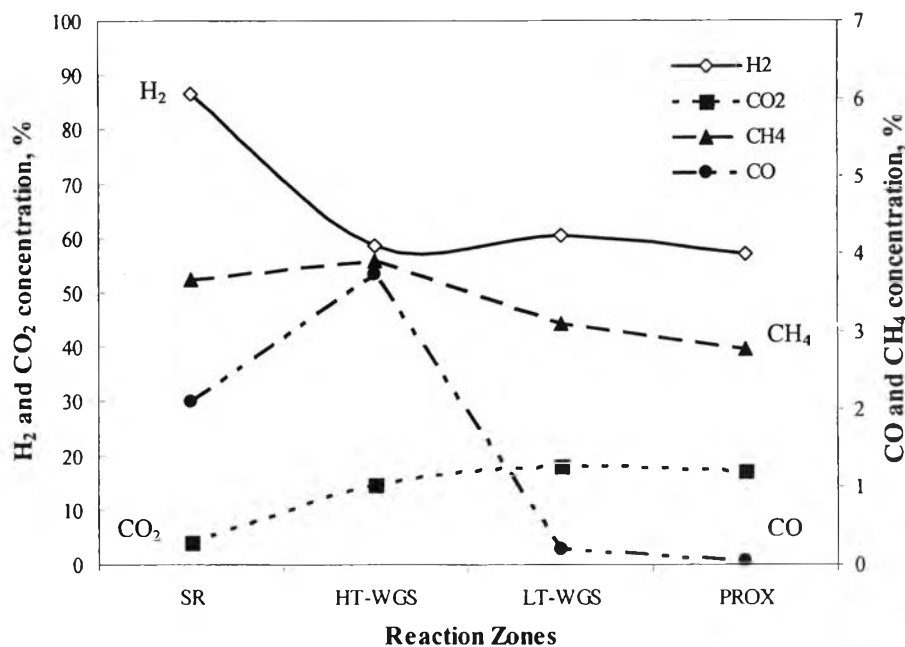


Figure 4.21 Reformate concentration profile as a function of reaction zones at 8 hrs.

After starting-up 8 hrs, the performance of each reaction zone was explored by the concentration of gas mixture after each reaction zone. As shown in Figure 4.20, at SR section where operation temperature was generally as high as 700°C, the natural gas was fully reformed into CO, CO₂ and H₂ although small amount of CH₄ could still remain in stream. Because the reaction temperature was so high, all reactions were presumed to approach their equilibriums. At HT-WGS zone, only to the expected reaction of WGS was believed to happen. Although, CO concentration increased from 2.1 to 3.7%, while H₂ concentration decreased from 86.7 to 58.7%. This suggested that the WGS zone occurred other reactions. However, in LT-WGS CO could be massively suppressed from above 3.7 to 0.2% by making good use of the high WGS reaction rate at low temperature, with a H₂ concentration increasing from 58.7 to 60.6%. The PROX zone reduced CO concentration to 334 ppm, however, the H₂ concentration lessened a lot because of the parasitic consumption as well as He dilution. Therefore, it was essential to promote CO selective oxidation reaction with as little parasitic hydrogen consumption as possible. Additionally, the designing two-stage PROX reactor (Srinivas and Gulari, 2006) and developing H₂O, CO₂ resistant catalysts (Snytnikov *et. al.*, 2003) for PROX were quite helpful.