

CHAPTER IV

ACTIVITY STUDY OF METAL LOADED ZEOLITES

4.1 Abstract

Carbon monoxide oxidation (CO oxidation) was used to reduce the amount of CO that is poison to the proton exchange membrane (PEM) fuel cells by using zeolite-A loading gold and platinum, as catalyst. The catalysts were successfully synthesized by using fumed silica, aluminium hydroxide, and various types of alkaline species, namely lithium (Li), sodium (Na), and potassium (K) hydroxides, via sol-gel process and microwave heating technique. After loading with different types of metal via impregnation method, Na-A zeolite loading platinum showed higher CO conversion than gold loaded Na-A zeolite. The highest conversions of platinum and gold loadings were 100 and 26%, respectively. In addition, all of the alkaline-A zeolites showed slightly different conversion for CO oxidation and reached 100% at 240 °C. Moreover, the conversion for PROX reaction was lower than that for the CO oxidation. It reached the highest conversion of 89% at 240 °C and dropped at higher temperature.

Keywords: zeolite, microporous, carbon monoxide oxidation.

4.2 Introduction

Although proton exchange membrane (PEM) fuel cells become an interesting propulsion system of vehicles because of their high power density, compactness, light weight, relatively low emission, extreme quietness, transient response, quick start up, and low operating temperature [6, 14, 24], it is very sensitive to carbon monoxide (CO) occurring in hydrogen stream generated during reforming process. Many scientists have tried to overcome its drawback by using various techniques, and one of them is to use CO oxidation reaction using various types of catalysts, not only to keep the low cost but also to decrease amount of CO to less than 100 ppm.

Transition metals, such as platinum (Pt), rhodium (Rh), ruthenium (Ru), and palladium (Pd), are outstanding choices to catalyze CO oxidation reaction [12]. Pt-containing catalyst was a good choice for preferential oxidation of CO reaction (PROX) since it showed an accomplished CO conversion in a wide temperature range and a high selectivity [18]. PROX reaction is similar to the CO oxidation, except addition of hydrogen in the system. However, Pt-containing catalyst was generally limited to a low temperature [16]. Gold (Au) dispersed on the support was another metal found to be more suitable in the PROX reaction [15, 16], providing a high CO conversion and selectivity at low temperature [10, 21].

Recently, some scientists have paid attention to studying low temperature CO oxidation by using many types of metal loaded support, such as Pt and Au [11, 12]. For example, Pt-supported on Linde type A zeolite (LTA) had better selectivity than Pt-supported on alumina because molecular sieve of zeolite has the highest cation exchange capacity (CEC) [14].

In this work, we thus focused on zeolite-A as a support and Au and Pt as active metals loaded on the support via the impregnation method. The performances of Au and Pt were compared for CO oxidation. Furthermore, synthesis of zeolite-A was conducted by using different alkaline species, namely lithium (Li), sodium (Na), and potassium (K), via sol-gel process and microwave heating technique to compare the catalytic performance for the CO oxidation reaction. Lastly, PROX reaction was also conducted to study the effect of hydrogen in the reaction.

4.3 Experimental

4.3.1 Materials

Fumed silica (SiO_2 , 99.8%, Nippon Aerosil, Japan), aluminium hydroxide ($\text{Al}(\text{OH})_3$, Sigma, USA), lithium hydroxide (LiOH , >99.5%, Fisher Chemicals, UK), sodium hydroxide (NaOH , 99%, RCI Labscan, Thailand), potassium hydroxide (KOH , Sigma-Aldrich, USA), hydrogen gas (H_2), carbon monoxide gas (CO), oxygen gas (O_2), helium gas (He), nitrogen gas (N_2), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Sigma-Aldrich, USA), hexachloroplatinic(IV) acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Merck, Germany) were used with no further purification.

4.3.2 A-type Zeolite Synthesize

4.3.2.1 *Synthesis of Li-A Zeolite*

To synthesize Li-A zeolite, SiO_2 and $\text{Al}(\text{OH})_3$ were mixed with LiOH at the molar ratio of $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ [20]. The mixture was aged for 12 h at room temperature to obtain fully gel formation and brought to hydrothermal treatment using microwave technique for 10 h. The synthesized product was washed using distilled water three times and dried at 60 °C overnight. The obtained white powder product was characterized using SEM and XRD.

4.3.2.2 *Synthesis of Na-A Zeolite*

To synthesize Na-A zeolite, SiO_2 and $\text{Al}(\text{OH})_3$ were mixed with NaOH at the molar ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3:3\text{Na}_2\text{O}:410\text{H}_2\text{O}$ [19]. The mixture was aged for 12 h at room temperature to obtain fully gel formation and brought to hydrothermal treatment using microwave technique for 10 h. The synthesized product was washed using distilled water three times and dried at 60 °C overnight. The obtained white powder product was characterized using SEM and XRD.

4.3.2.3 *Synthesis of K-A Zeolite*

To synthesize K-A zeolite, SiO_2 and $\text{Al}(\text{OH})_3$ were mixed with KOH at the molar ratio of $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$ [18]. The mixture was aged for 12 h at room temperature to obtain fully gel formation and brought to hydrothermal treatment using microwave technique for 10 h. The synthesized

product was washed using distilled water three times and dried at 60 °C overnight. The obtained white powder product was characterized using SEM and XRD.

4.3.3 Catalyst Preparation

All catalysts were prepared by the impregnation method, using A-type zeolites as supports [12]. Aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, containing 1wt% gold, and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, containing 1wt% platinum, were impregnated onto the synthesized zeolite supports. All catalysts were dried in the air at 110 °C overnight and calcined at 500 °C for 5 h. Prior to each catalyst measurement, the catalyst was grounded and sieved to an 80–120 mesh size. The loaded gold and platinum contents were determined by AAS.

4.3.4 Catalyst Characterization

The crystallinity of zeolite supports and metal loaded supports were analyzed using Rigaku X-ray diffraction (XRD) system equipped with a RINT- 2200 wide angle goniometer using CuK_α radiation (1.5406 Å) and a generator voltage and current of 40 kV and 30 mA, respectively. Hitachi, TM3000 scanning electron microscope (SEM) provides the support morphology. The metal content was determined by Varian, Spectra AA 300 atomic adsorption spectrophotometer (AAS). Transmission electron microscopy (TEM) images were taken with JEOL, JEM-2010.

4.3.5 Activity Measurement

All catalytic activity measurement for CO oxidation was performed in a fix-bed U-tube micro-reactor with 100 mg of the catalyst [12]. The catalyst activity was investigated in a temperature range of 100°–350°C. The inlet gas contained 1% CO, 1% O₂, balance in He, with a total rate of 50 mL/min under atmospheric pressure. The outlet gasses from the reactor were analyzed by an on-line GC equipped with a packed carbosphere and TPD detector.

4.4 Results and Discussion

4.4.1 Characterization of Zeolites

According to XRD result of synthesized Li-A zeolite (Figure 4.1), each position of XRD pattern is matched with those from Sathupunya's work for Li-A zeolite (EDI type) [21]. Therefore, it can indicate that Li-A zeolite typed EDI was successfully synthesized. However, after calcination at 550°C, all peaks were disappeared and the material became amorphous even at the temperature of 270 °C [21]. From XRD results (Figure 4.2), Na-A zeolite was completely synthesized via sol-gal process and microwave heating technique using silica, aluminium hydroxide, and sodium hydroxide as main resources [20]. After calcination at 550°C, the pattern still maintained and the peak intensity was higher due to the removal of the impurities at high temperature. For K-A zeolite (Figure 4.3), XRD spectra of both uncalcined and calcined K-A zeolite show the same peak pattern of that reported elsewhere [19]. Thus, it can be confirmed that the K-A zeolite was successfully synthesized in this research. Moreover, the peak intensity slightly increased after calcination because the impurities were eliminated at high temperature.

From SEM micrographs of zeolite A with different types of cation, crystal morphology of Li-A zeolite looks like orthorhombic, having different lengths of each side. The crystal size varies from 0.5 to 1.5 μm (Figure 4.4 (a)). Due to the smallest size of lithium ion, as compared to the others, it has less steric hindrance in zeolite formation, making it is easy to form various sizes of particles [21]. For Na-A zeolite (Figure 4.4 (b)), crystal morphology is an cubic shape with homogeneity. The size of crystals is approximate 0.5 μm that is quite small. The SEM image of K-A zeolite (Figure 4.4 (c)) is a bundle-like crystal and its particle size is about 12 μm that is much bigger than the others.

4.4.2 Characterization of Catalysts

In accordance with XRD result of Na-A zeolite loading gold calcined at 500 °C (Figure 4.5), all of the peaks appear at the same position as those for the unloaded Na-A zeolite calcined at 550 °C. It does not seem to have any extra peaks of gold at 38.10° (Au (111)), and 44.37° (Au (200)) after loading with gold. It can be

implied that the gold particles prepared by the impregnation method have a good distribution on the surface. Besides, the particle size of the loaded gold might be too smaller to be detected by this technique [15, 16]. XRD pattern of Na-A zeolite loading platinum calcined at 500 °C (Figure 4.6) shows the similar peak position to the pure Na-A zeolite calcined at 550 °C. The characteristic peaks of the platinum at 39.8° and 46.4°, corresponding to Pt(1 1 1) and PtO were not clearly noticed. It means that loaded platinum using the impregnation method was successfully distributed on the surface of Na-A zeolite or the particle size was not large enough to be detected by the XRD technique [14]. For Li-A zeolite loading platinum (Figure 4.7), the characteristic peaks at 39.8° and 46.4° of the platinum in platinum loading Li-A zeolite calcined at 500 °C were not observed. It can be interpreted that the loaded platinum has a good dispersion on the surface of Li-A zeolite or it cannot be measured by the XRD technique due to too small size. In addition, both pure (calcined at 550 °C) and platinum loaded Li-A zeolite showed amorphous due to too high calcination temperature, as discussed previously. For XRD spectra of platinum loaded K-A zeolite (Figure 4.8), in the XRD spectrum of platinum loading K-A zeolite calcined at 500 °C were the same as those in the unloaded one calcined at 550 °C. However, in this case, there were some additional peaks at about 39° and 46°, referring to the characteristic peaks of Pt(1 1 1) and PtO, respectively. As a result, it could be concluded that platinum was aggregated, implying a bad dispersion.

TEM micrographs of platinum loading Na-A zeolite show that platinum was loaded only on external surface because of the small pore size of Na-A zeolite, 4Å, and the platinum complex ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) is too large to penetrate into the pores. The platinum size is about 20–30 nm (or 2–3 Å), which is quite small, consistent to the XRD result not able to detect the platinum peaks.

In the preparation of catalysts, platinum and gold were loaded onto Na-A zeolite at 1 wt% by the impregnation method. However, the amounts of platinum and gold loadings analyzed by AAS were the same (0.73%). The mass loss of the metal precursors might occur during the catalyst preparation. Table 4.1 shows the content of platinum loaded onto different zeolite-A containing different cations. Li-A zeolite contains the lowest Pt content when comparing with the others due to

the destruction of the zeolite structure after calcination, as previously shown in the XRD spectrum. Li-A zeolite became amorphous, decreasing the metal loading [25]. Na-A zeolite, on the other hand, presented the highest amount of Pt content probably due to the smallest size of the particles, giving higher surface area for Pt to be loaded. K-A zeolite, having a bundle size referring to lower surface area, thus, contained a lower Pt content than Na-A zeolite.

4.4.3 Activity Measurement

4.4.3.1 *Carbon Monoxide Oxidation Reaction*

Comparing between Pt and Au loading Na-A zeolite containing the same content of metal for CO oxidation, it was found that zeolite loaded with Au resulted in much lower conversion than zeolite loaded with Pt. The highest conversion obtained from Au/Na-A zeolite was about 26% at 350 °C while that obtained from Pt/Na-A zeolite reached 100% at 240 °C and kept constant afterward. It is worth noticing that the conversion using Au/Na-A zeolite tended to rise as temperature. Therefore, considering the %conversion and the operating temperature, it can be stated that Pt was a choice as a catalyst to study further for CO oxidation.

Comparing different cations in the support, it was shown that all of the zeolites provided slightly different conversion rate. Moreover, all zeolites also reached 100% conversion at the same temperature of 240 °C and maintained complete conversion at higher temperature. These results could indicate that various cations in the zeolite support had no significant effect on the CO oxidation.

4.4.3.2 *Preferential Oxidation of Carbon Monoxide Oxidation Reaction*

To study the influence of hydrogen (H₂) in the reaction, PROX reaction was conducted using zeolite containing Pt as a catalyst. As can be seen from Figure 4.12, the PROX reaction, containing H₂ in the system, provides a higher CO conversion than the CO oxidation at the temperature range of 140°–220 °C, however, the highest conversion (89% conversion) was lower at 240 °C, and dropped off at higher temperature due to the competing reaction of O₂ and H₂, instead of O₂ and CO, as shown in eq. 4.1 and 4.2 [12, 23].



4.5 Conclusions

Zeolites-A with different types of cation namely lithium, sodium, and potassium ions was successfully synthesized via sol-gel process and microwave technique using fumed silica, aluminium hydroxide, lithium, sodium, and potassium hydroxide, as silica, alumina, and hydrolytic agents, respectively. After loading different types of metal, such as gold and platinum, via impregnation method, platinum loaded Na-A zeolite showed higher CO conversion for CO oxidation than gold loaded Na-A zeolite. The highest conversion of platinum loading was 100% at 240 °C while gold loading was only 26% at 350 °C. Moreover, the cation type showed slightly different conversion for the CO oxidation and reached 100% at 240 °C. For PROX reaction, the conversion was lower and reached the highest conversion of 89% at 240 °C.

4.6 Acknowledgments

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4.7 References

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Table 4.1 Platinum loading by using different types of support

Types of support	Metal loading (wt%)
Li-A zeolite	0.27
Na-A zeolite	0.73
K-A zeolite	0.40

Table 4.2 % crystallinity of zeolites *

Types of support	Uncalcined	calcined	Loaded Pt	Loaded Au
Li-A zeolite	100.00	5.76	5.74	-
Na-A zeolite	17.72	100.00	40.99	40.87
K-A zeolite	94.23	100.00	92.96	-

$$* \text{ \%crystallinity} = \frac{\text{Intensity of sample peak}}{\text{Intensity of reference peak}} \times 100$$

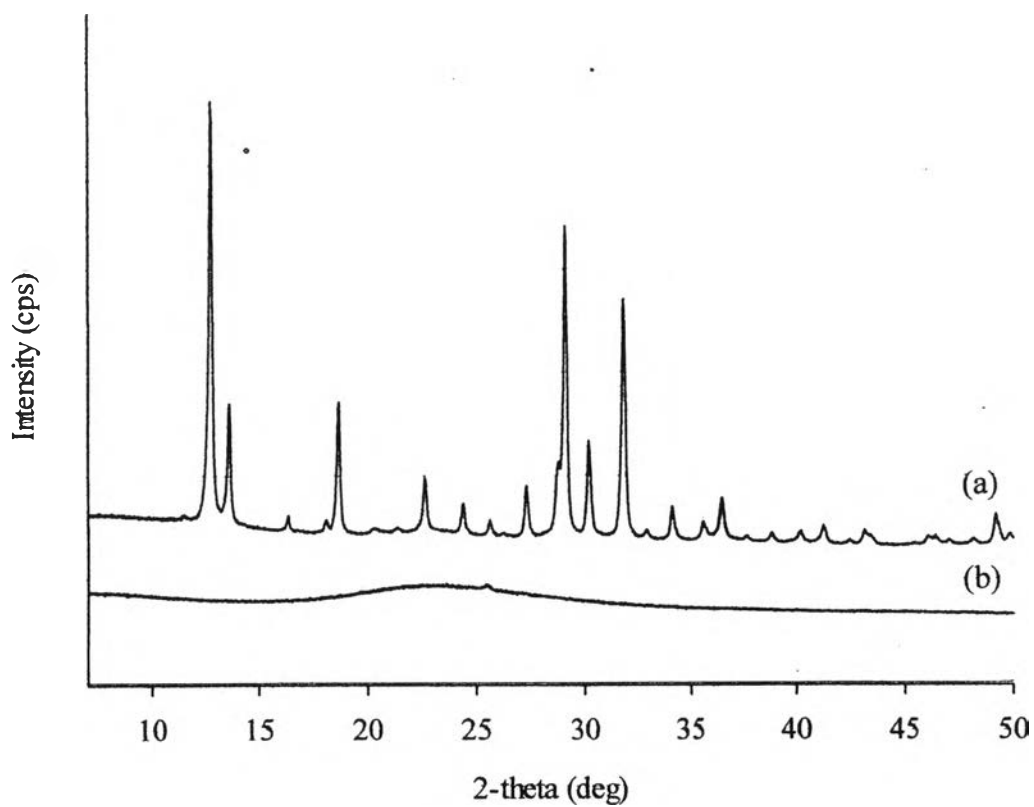


Figure 4.1 XRD spectra of (a) Li-A zeolite and (b) calcined Li-A zeolite 550°C.

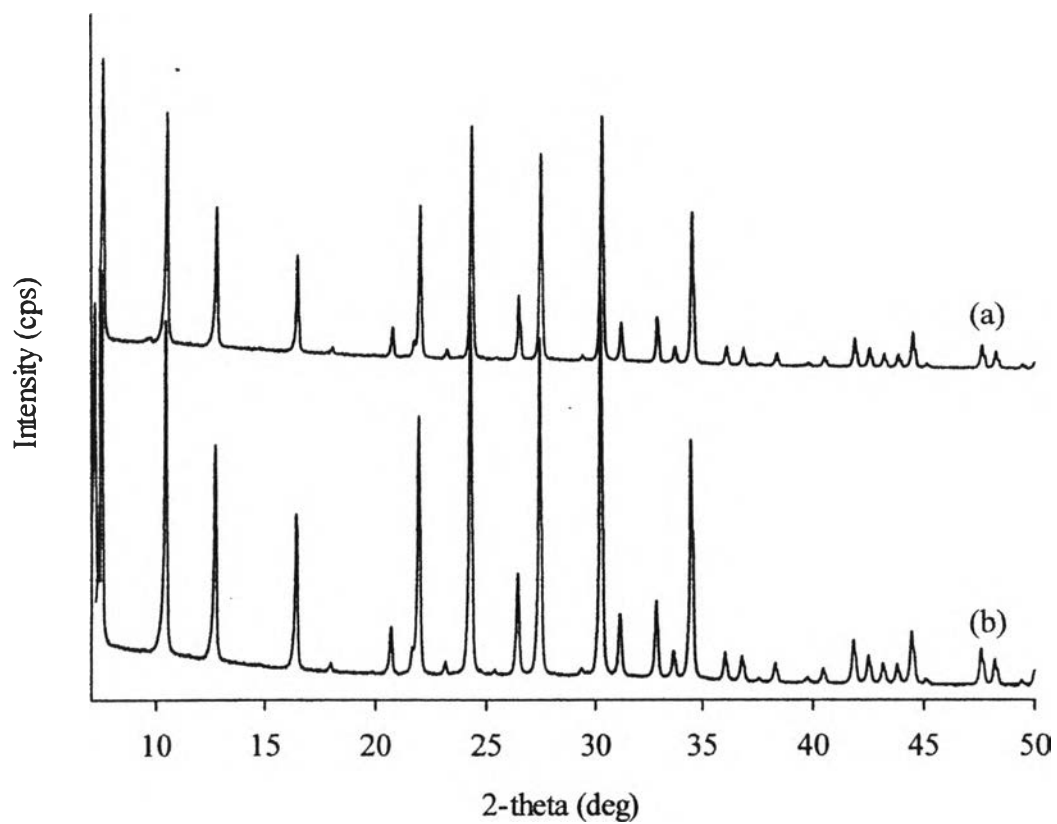


Figure 4.2 XRD spectra of (a) Na-A zeolite and (b) calcined Na-A zeolite 550°C.

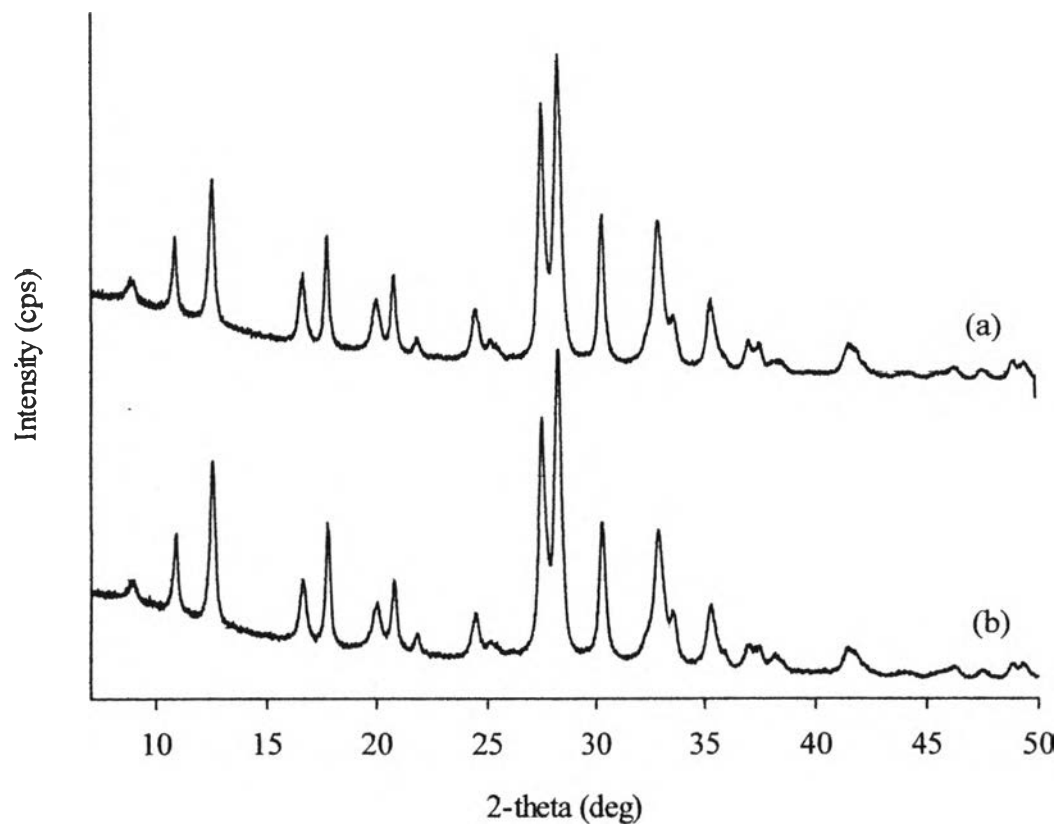


Figure 4.3 XRD spectra of (a) K-A zeolite and (b) calcined K-A zeolite 550°C.

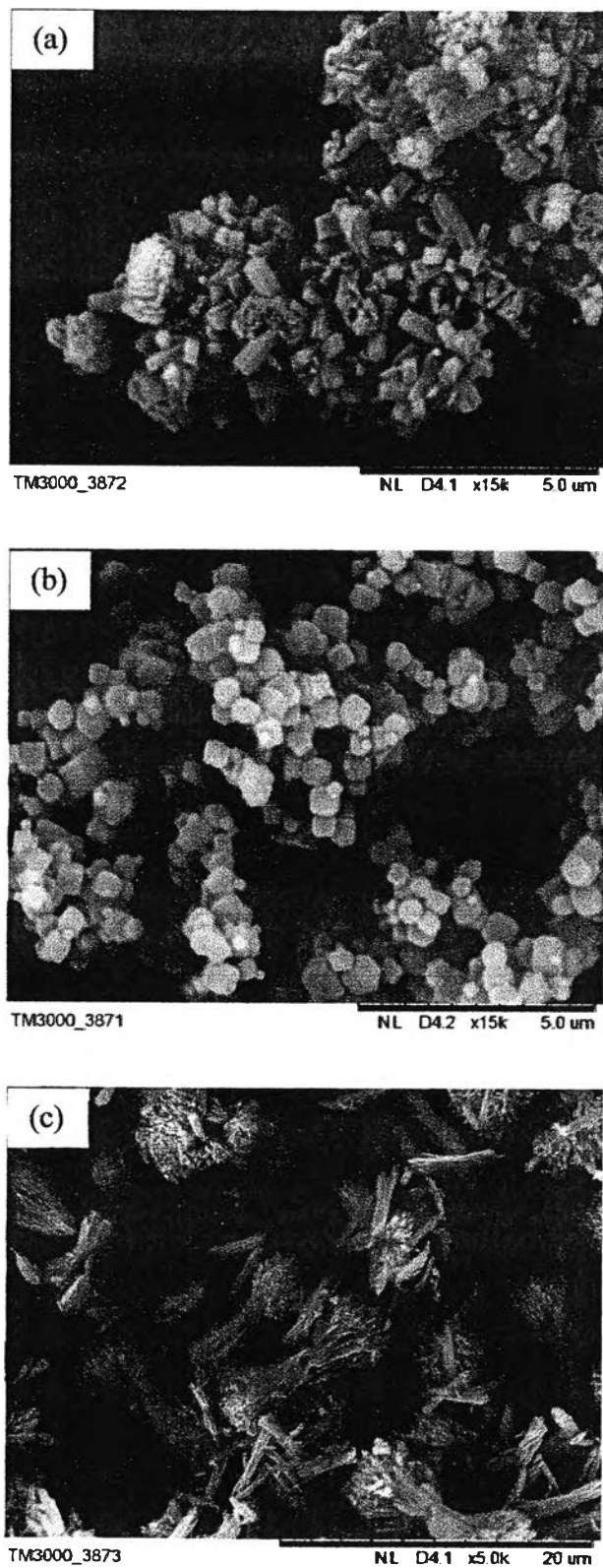


Figure 4.4 SEM micrographs of synthesized (a) Li-A, (b) Na-A, and (c) K-A zeolites.

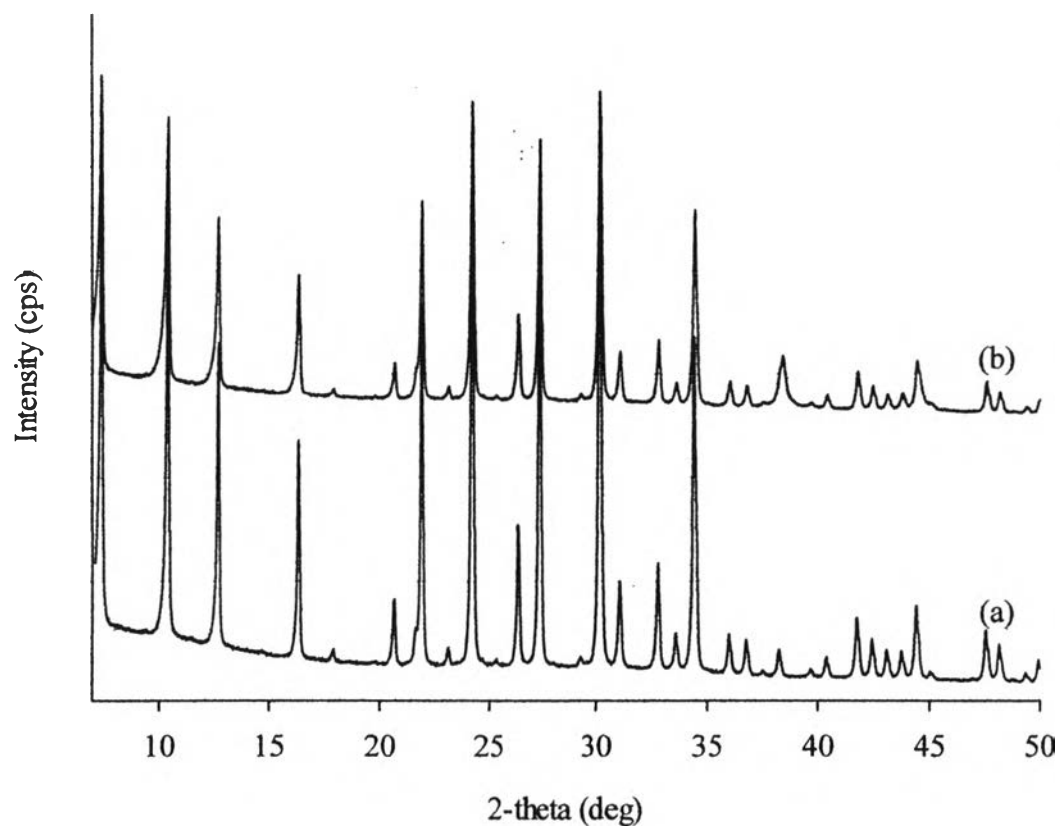


Figure 4.5 XRD spectra of (a) calcined unloaded at 550 °C and (b) calcined Au loaded Na-A zeolite at 500°C.

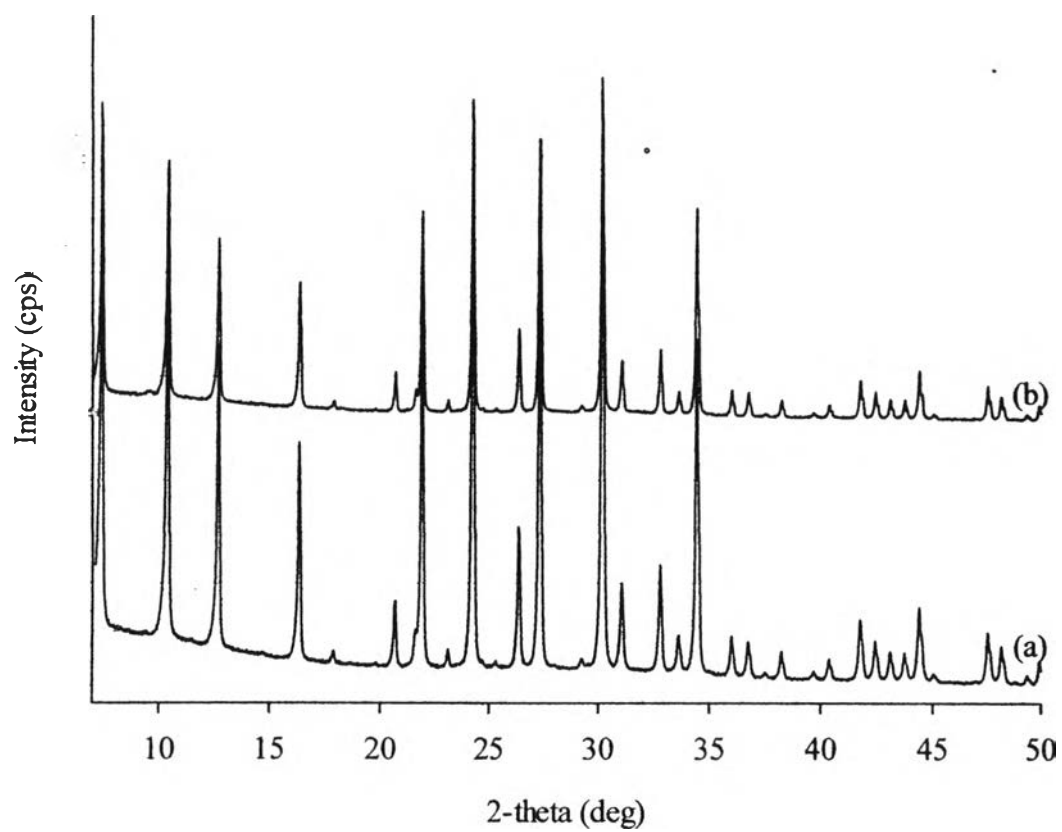


Figure 4.6 XRD spectra of (a) calcined unloaded at 550 °C and (b) calcined Pt loaded Na-A zeolite at 500°C.

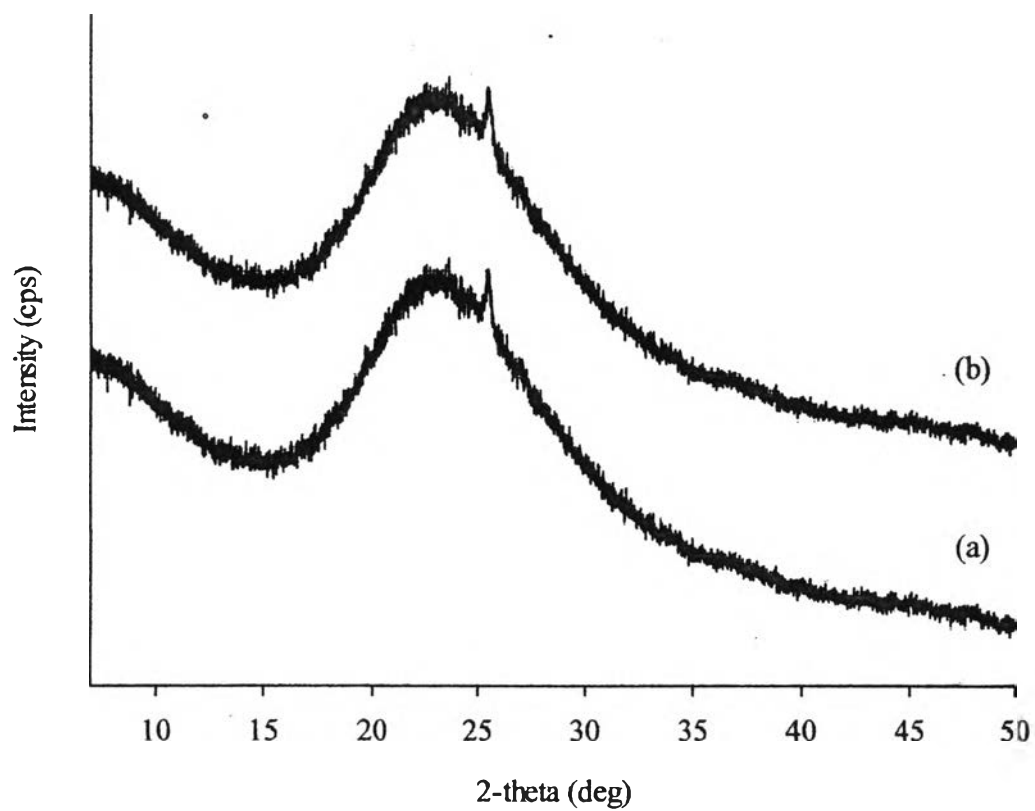


Figure 4.7 XRD spectra of (a) calcined unloaded at 550 °C and (b) calcined Pt loaded Li-A zeolite at 500°C.

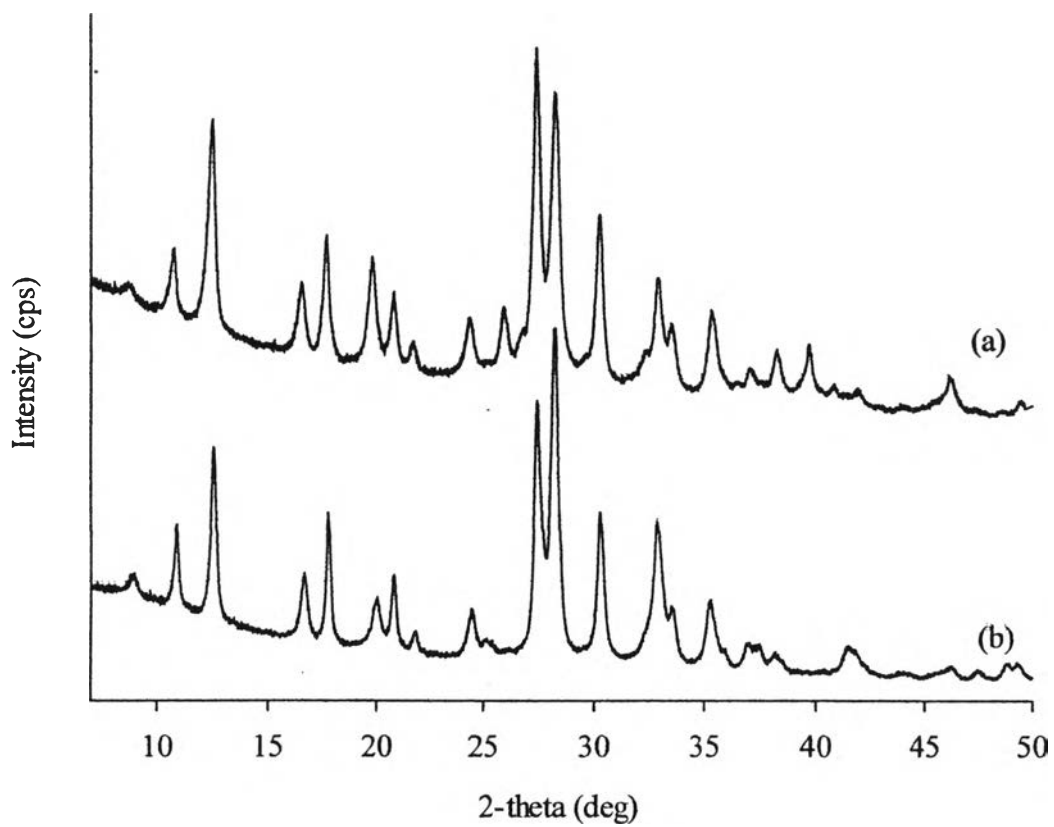


Figure 4.8 XRD spectra of (a) calcined unloaded at 550 °C and (b) calcined Pt loaded K-A zeolite at 500 °C.

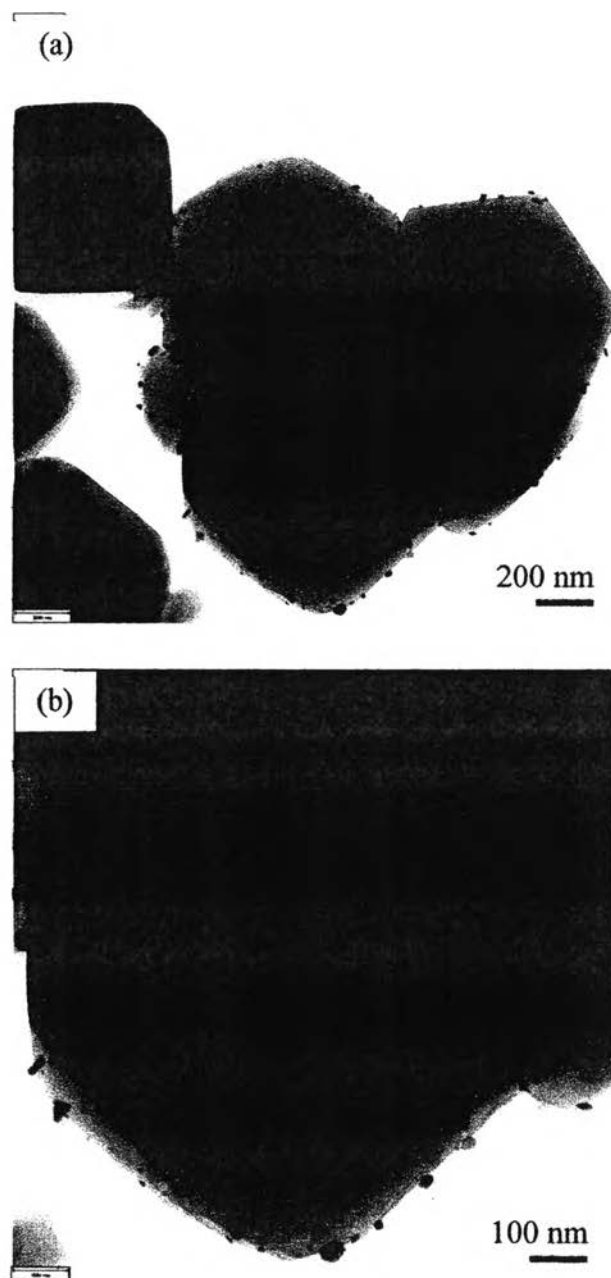


Figure 4.9 TEM micrographs of calcined platinum loaded Na-A zeolite at 500°C with magnification of (a) 10000x and (b) 20000x.

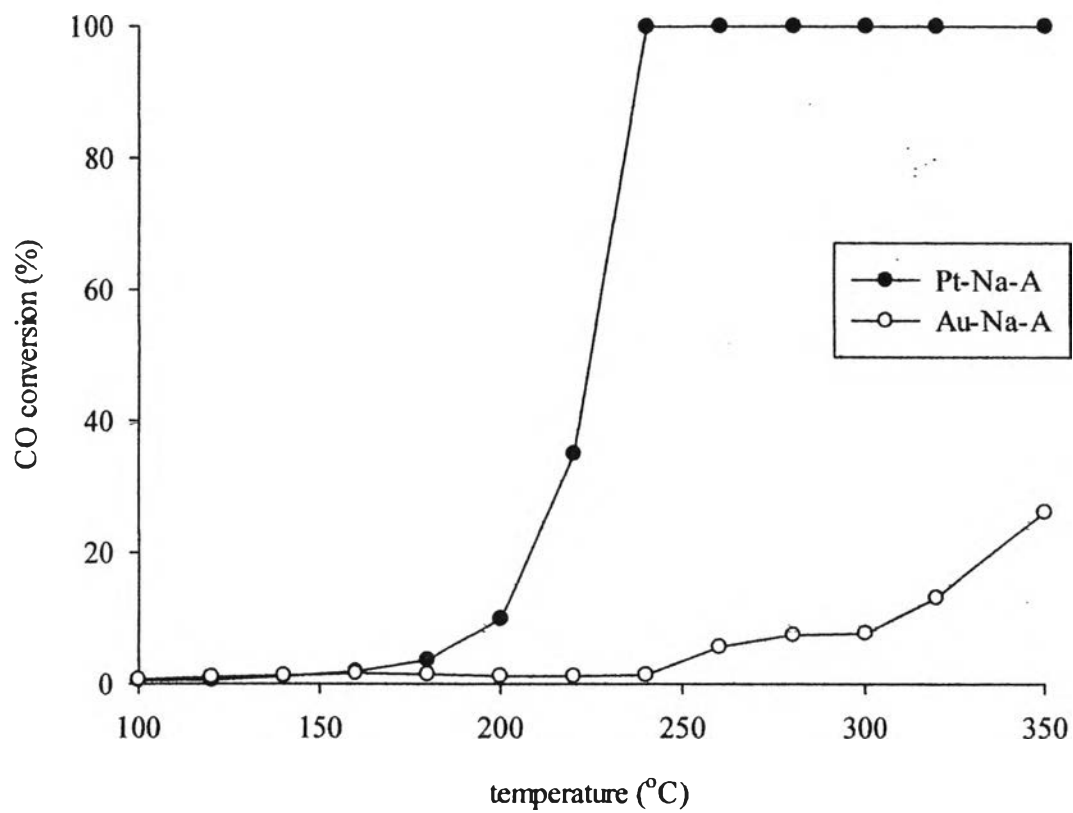


Figure 4.10 CO conversion of (●) platinum and (○) gold loaded Na-A zeolite.

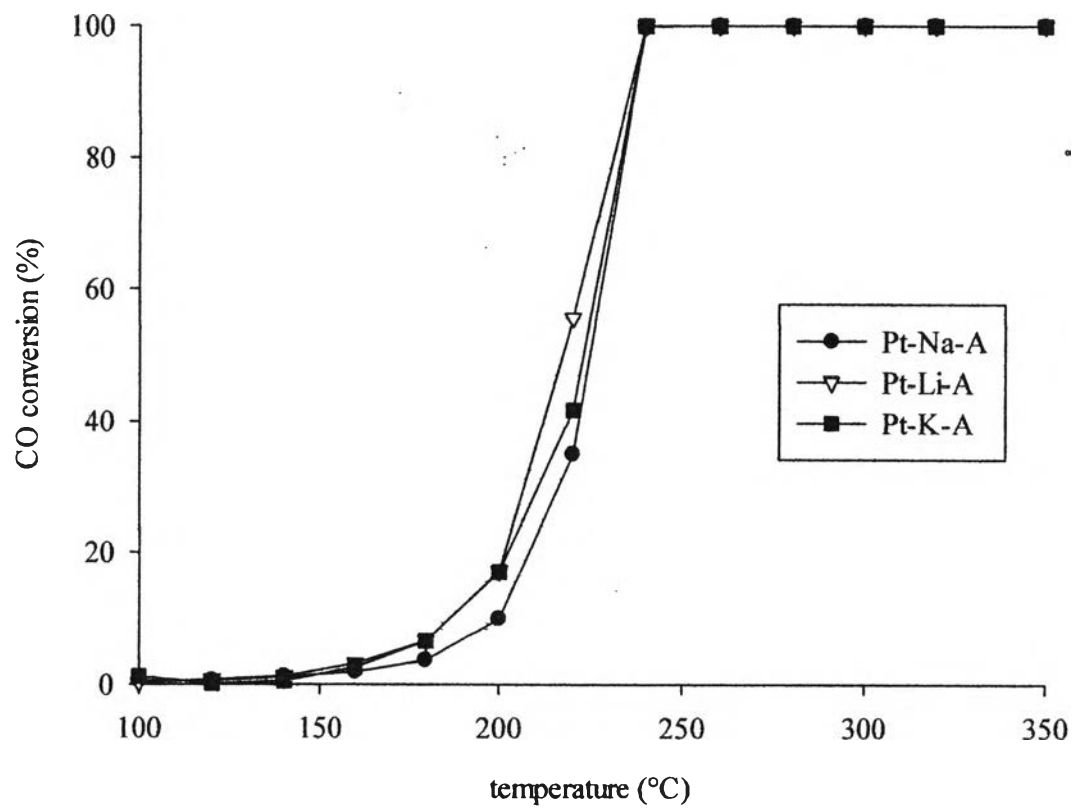


Figure 4.11 CO conversion of platinum loaded (∇) Li-A, (\bullet) Na-A, and (\blacksquare) K-A zeolite.

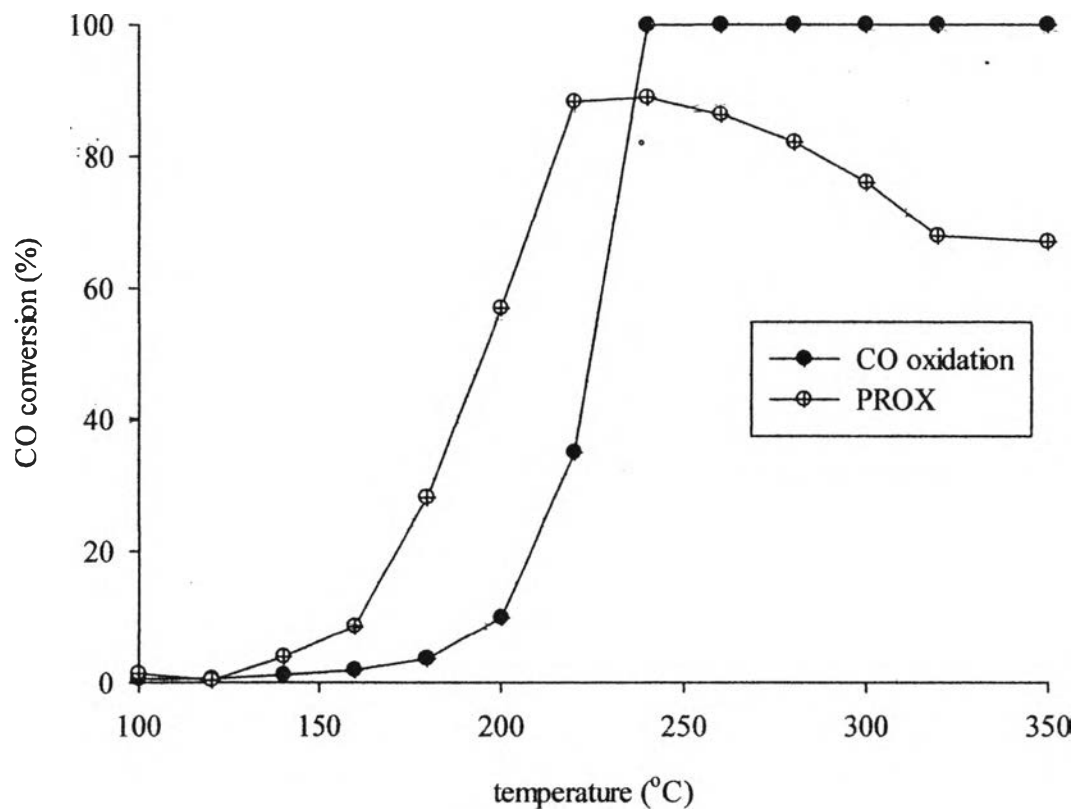


Figure 4.12 CO conversion of (●) CO oxidation and (⊕) PROX reaction using platinum loaded Na-a zeolite as catalyst