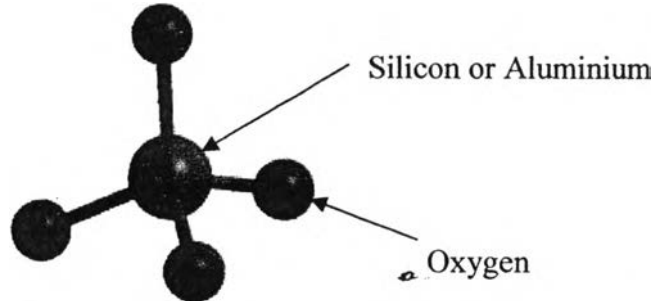


## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Zeolites

Zeolites are inert, microporous crystalline hydrated aluminosilicate with well-defined structure. Balancing cations are generally of metal group IA (alkali) and IIA (alkaline earth). The negative charge of framework units causes zeolite cation exchange. Zeolites are not only formed by natural process, such as faujasite, clinoptillolite and mordenite, but also formed by synthesis, like zeolite A, zeolite X, zeolite Z and zeolite beta. Zeolites are composed of primary unit cells that have silicon or aluminium as a central atom. The central atom bonds with four oxygens to form tetrahedral structure, called silicon dioxide ( $\text{SiO}_2$ ) and aluminium dioxide ( $\text{AlO}_2^-$ ) (Abbey Newsletter, 1996, Baerlocher *et al.*, 2007 and Bell, 2001).



**Figure 2.1** Primary building unit of zeolite.

Aluminium dioxide, performing the negative charge on zeolite structure, is balanced with positive charges from metal group IA or IIA. General unit cell formula of a zeolite is



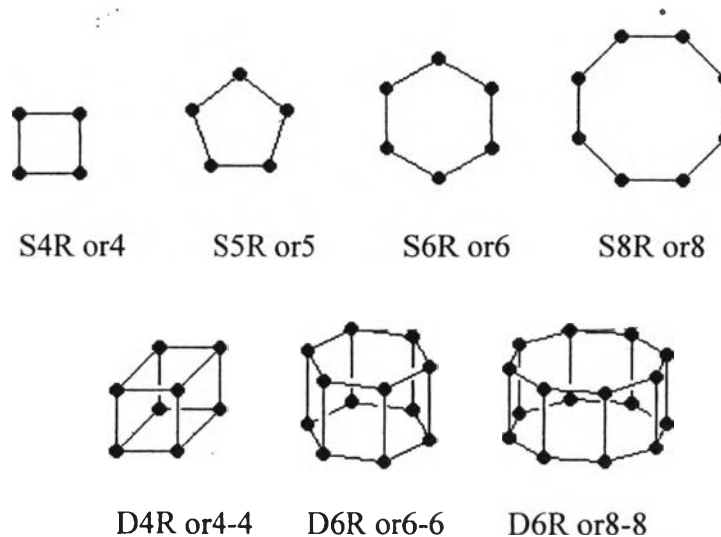
When  $n$  is charge of cation

$x$  is mole of aluminium dioxide ( $\text{AlO}_2^-$ )

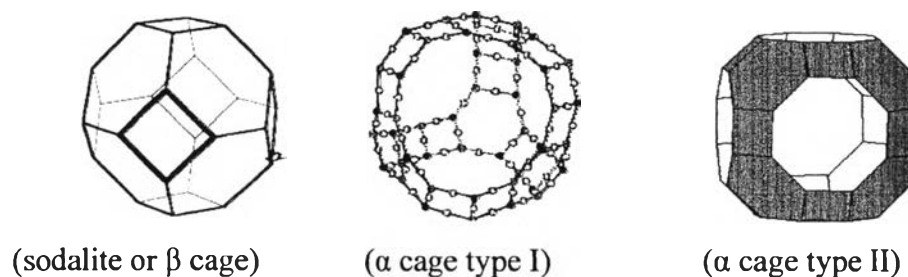
$y$  is mole of silicon dioxide ( $\text{SiO}_2$ )

$z$  is mole of water in one unit cell

Primary building unit connects together and forms secondary building unit (Figure 2.2). All zeolites consisting of the same primary building unit cell have a different secondary unit cells that make various types of the cage in zeolites (Figure 2.3) (Everyscience, 2004).



**Figure 2.2** Secondary building unit of zeolite. (Everyscience, 2004)



**Figure 2.3** Type of different cages in zeolites. (Everyscience, 2004)

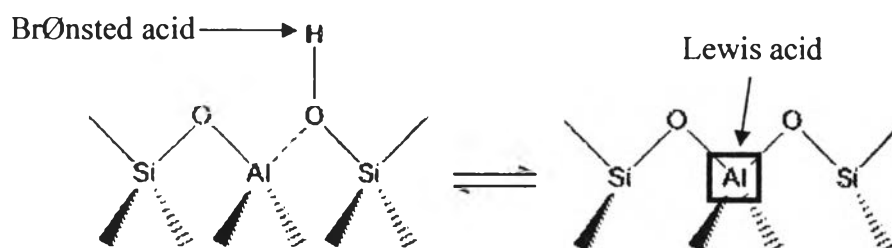
### 2.1.1 Properties of Zeolites

Zeolites are solid acid catalysts that are used as the heterogeneous catalyst in many reactions because of their high surface area, stability at high temperature, environmental safety, no corrosion problem, and reusability. (Abbey Newsletter, 1996, Baerlocher *et al.*, 2007 and Bell, 2001).

The mainly properties of zeolites are

### 1. Acidity

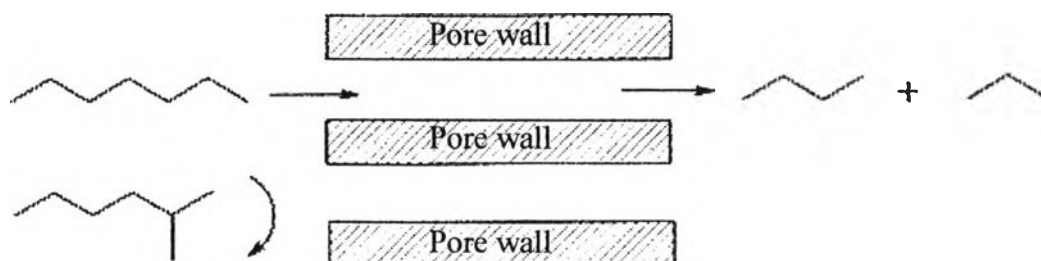
Zeolites are composed of 2 types of acid, Brønsted acid and Lewis acid. At high temperature, both types of acid can be obtained in an equilibrium state (Figure 2.4).



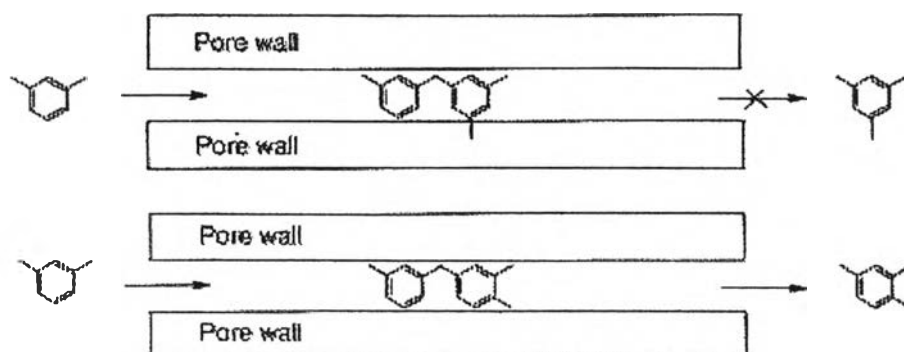
**Figure 2.4** Acidity of zeolite in an equilibrium state.

### 2. Shape and Size Selectivity

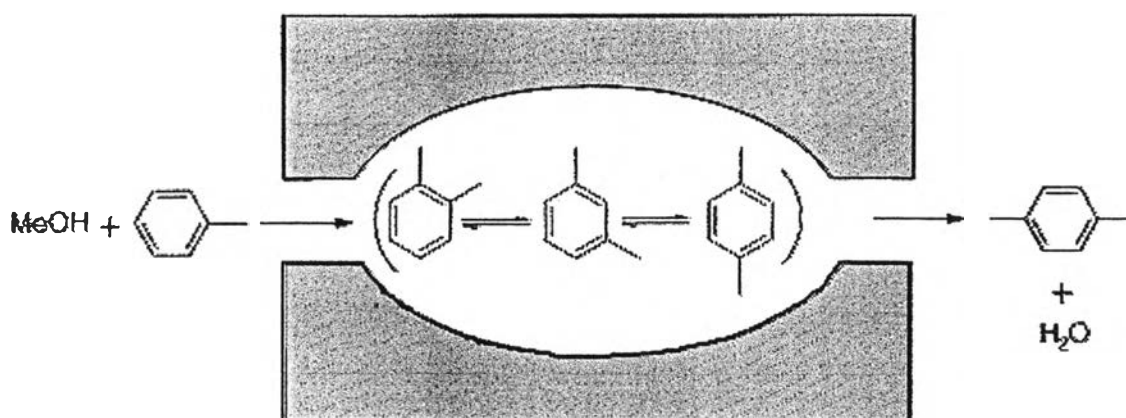
Since the apertures of zeolites have certain size in nanoscale, zeolites are considered as the catalyst that have high shape and size selectivity, called molecular sieve property. The selectivity of zeolites is divided into three categories, viz. reactant selectivity, transition state selectivity, and product selectivity. For example, zeolites allow the reactants that are smaller than the pore of zeolites to entrance and occur the reaction inside the pore (Figure 2.5). Moreover, only the appropriate size and shape of the transition state can be transferred to the product (Figure 2.6) and the products that have the suitable size and shape can exit from the pore (Figure 2.7).



**Figure 2.5** Reactant selectivity. (Davis *et al.*, 2012)



**Figure 2.6** Transition state selectivity. (Davis *et al.*, 2012)



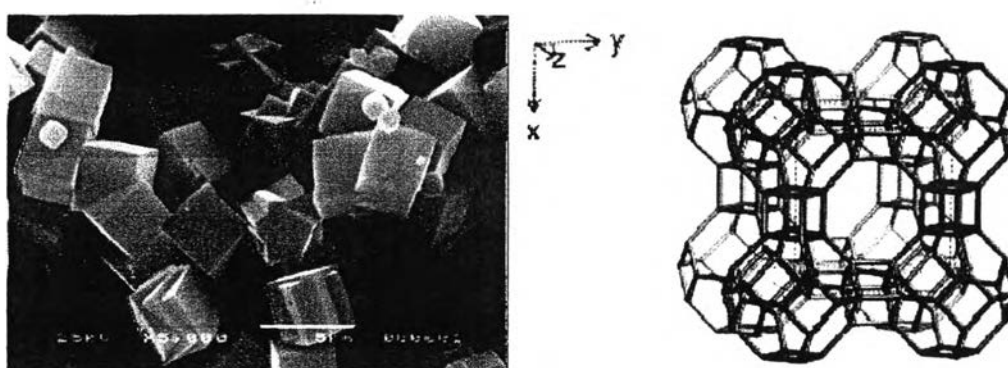
**Figure 2.7** Product selectivity. (Davis *et al.*, 2012)

Since microwave heating provides many advantages, e.g., shorter reaction time, ability to access a broad composition range, high purity product, and small particles size and narrow particles size distribution (Sathupunya *et al.*, 2004), in this work, we will thus use the combination of hydrothermal crystallization with the microwave heating technique to synthesize various types of zeolite. In addition, different precursors from the previous works will be used. Those are to use fumed silica and aluminium hydroxide instead of silatrane and alumatrane, respectively, to synthesize Na-A zeolite. Furthermore, different types of cation will also be investigated, viz. lithium ( $\text{Li}^+$ ), and potassium ( $\text{K}^+$ ) ions, to study the influences of the cation charge and the charge size on the catalytic performance although the type

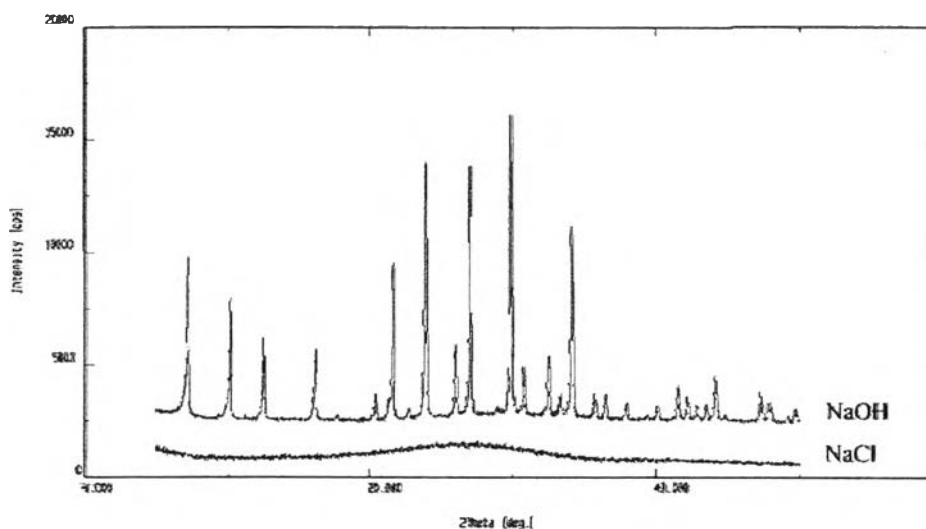
of cation strongly affects the gel formation and the transformation to crystalline aluminosilicate (Sathupunyaa *et al.*, 2004).

### 2.1.2 Na-A Type Zeolite

Na-A zeolite is commonly used in gas separation membranes to enhance the selectivity of the support (Sathupunyaa *et al.*, 2003). Na-A zeolite was synthesized by either conventional or microwave heating technique. From previous works studied by Sathupunyaa *et al.* (2003), Na-A zeolite was completely synthesized via sol-gel process and microwave technique using silatrane and alumatrane as precursors. They fixed the condition at the ratio of 1:1 SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> and 110 °C microwave heating temperature while increasing sodium dioxide concentration (Na<sub>2</sub>O) as sodium hydroxide (NaOH), leading to a shorter microwave heating time and a smaller particle sizes and particle sizes distribution. However, the agglomerated crystals were also increased as increasing sodium dioxide concentration. Moreover, they also considered the effect of water content and found that as the water content increased, large crystal sizes and number of irregularity crystals were formed. The crystals were in cubic shape (Figure 2.8) and XRD spectra of Na-A zeolite is shown in Figure 2.9.



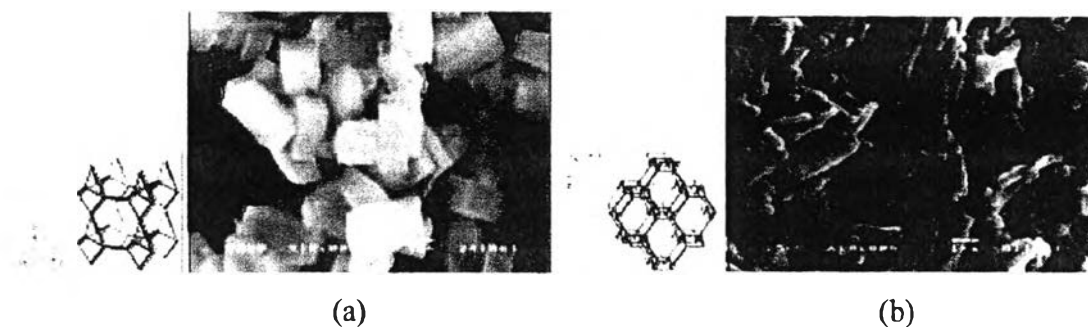
**Figure 2.8** Unit cell structure and crystal morphology of Na-A zeolite synthesized using SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>:3Na<sub>2</sub>O:410H<sub>2</sub>O at 110°C for 180 min. (Sathupunyaa *et al.*, 2003)



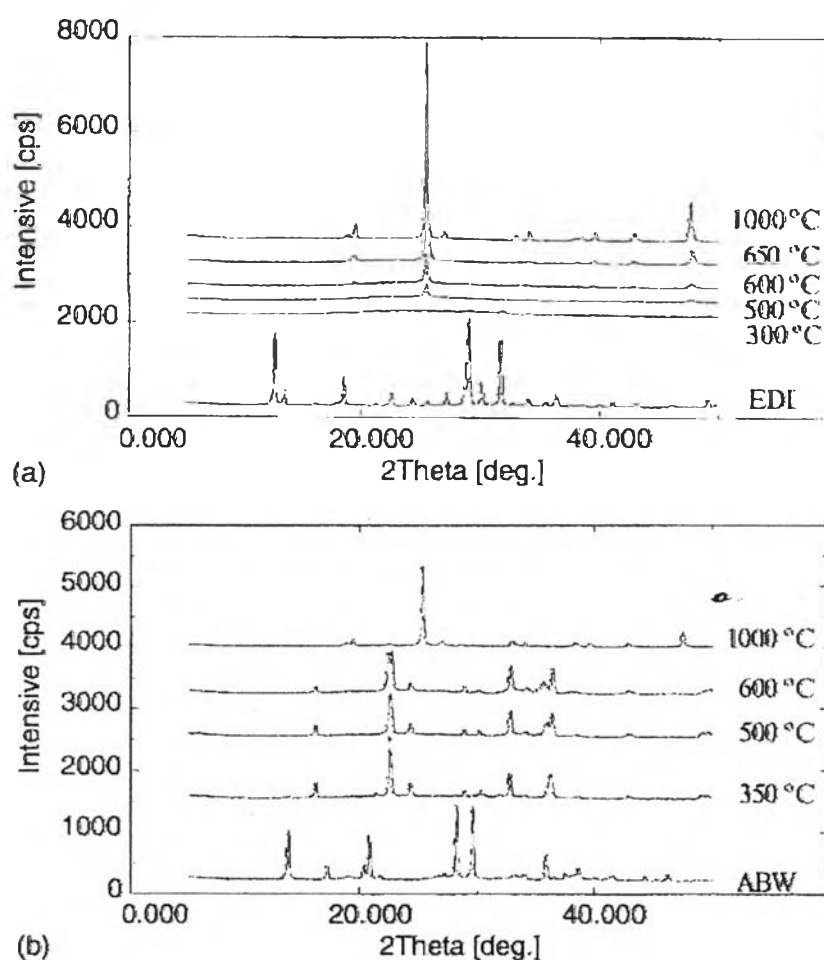
**Figure 2.9** spectra of Na-A zeolite synthesized from  $\text{SiO}_2:\text{Al}_2\text{O}_3:3\text{Na}_2\text{O}:410\text{H}_2\text{O}$  at  $110^\circ\text{C}$  for 180 min in NaOH. (Sathupunyaa *et al.*, 2003)

### 2.1.3 Li-A Type Zeolite

In 2004, Sathupunyaa *et al.* studied on the synthesis of Li-A zeolite from silatrane and alumatrane using microwave preparation. They still used sol-gel process and microwave technique like the synthesis of Na-A zeolite, but lithium hydroxide as a hydrolytic agent was used instead of sodium hydroxide. Because of the smaller radius of lithium ion, a less steric hindrance in aluminosilicate formation was expected. Moreover, the energy requirement of aluminosilicate formation is lower. Therefore, a mixture of EDI and ABW were obtained at  $110^\circ\text{C}$  and fixing ratio at  $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Na}_2\text{O}:410\text{H}_2\text{O}$  (Figure 2.10-2.11). EDI type zeolite, perfect crystalline zeolite, was achieved at  $90^\circ\text{C}$  after heating for 60 min while ABW type zeolite was produced at  $110^\circ\text{C}$  after heating for 300 min. Thus, EDI product had lower packing density than ABW product. Nevertheless, both of them were not thermal stability. They could change to lithium aluminate silicate, denser material, at a temperature higher than  $500^\circ\text{C}$  due to a higher ring strain of the unit cell structure.



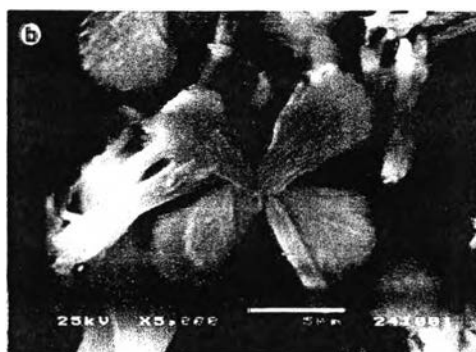
**Figure 2.10** Unit cell structure and crystal morphology of (a) EDI and (b) ABW products. (Sathupunyaa *et al.*, 2004)



**Figure 2.11** XRD spectra of (a) EDI and (b) ABW products synthesized from  $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$  at  $110^\circ\text{C}$  for 180 min. (Sathupunyaa *et al.*, 2003)

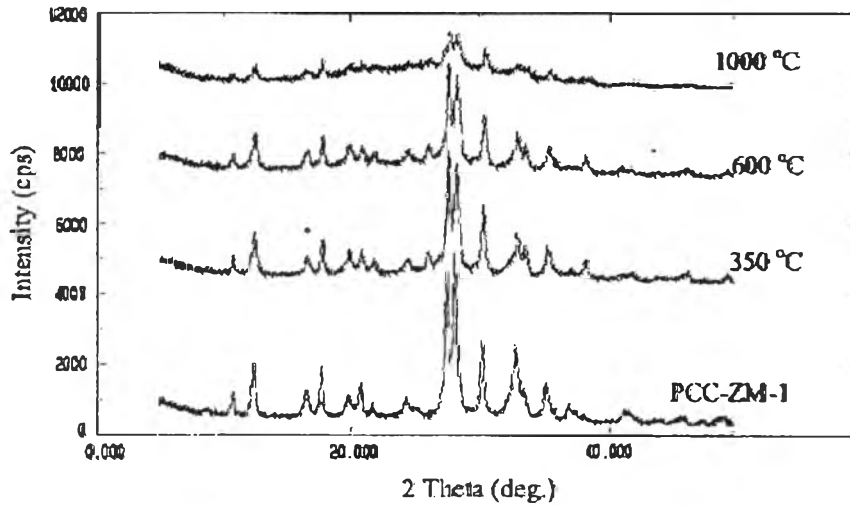
#### 2.1.4 K-A Type Zeolite

After successful synthesis of Na-A type zeolite and Li-A type zeolite, Sathupunya *et al.* (2004) continued researching other types of zeolites using microwave-assisted technique, e.g. zeolite K-H (Figure 2.12). They used silatrane and alumatrane as sources of silica and alumina, respectively, and potassium hydroxide as the hydrolytic agent via sol-gel process. By fixing composition at  $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  at  $150^\circ\text{C}$  microwave temperature for 240 min, K-A zeolite, named as PPC-ZM-1, was obtained. Gittleman *et al.* (2004) reported that potassium ion ( $\text{K}^+$ ) restrained the crystallization rate and inhibited the aggregation of the amorphous by forming a double layer around the silica particles. The zeolite shape looks like the flower petal. In addition, the synthesized product are very hygroscopic and can absorb high amount of moisture. However, when increasing the heating temperature and hydrolytic agent ratio, small particle size and bundle-like morphologies were obtained, instead of flower-petal-like.



**Figure 2.12** Crystal morphology of K-A zeolite synthesized using  $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  at  $150^\circ\text{C}$  for 300 min. (Sathupunya *et al.*, 2004)

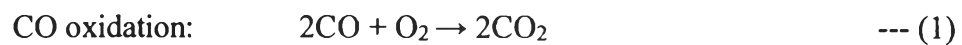




**Figure 2.13** XRD spectra of K-A zeolite (PCC-ZM-1) synthesized from  $\text{SiO}_2:0.1\text{Al}_2\text{O}_3:3\text{K}_2\text{O}:410\text{H}_2\text{O}$  at  $150^\circ\text{C}$  for 300 min. (Sathupunya *et al.* (2004))

## 2.2 Carbon Monoxide Oxidation (CO Oxidation)

One of the drawbacks for proton exchange membrane (PEM) fuel cells is the sensitivity toward CO generated from steam reforming of hydrocarbon. CO oxidation is, thus, considered to solve this problem due to its high activity for CO oxidation. The CO conversion to carbon dioxide is demonstrated in Eq. 1.



Carbon monoxide selectivity ( $S$ ), conversion ( $X_{\text{CO}}$ ), and oxygen conversion ( $X_{\text{O}_2}$ ) are calculated using the following equations;

- Carbon monoxide conversion ( $X_{\text{CO}}$ )

$$X_{\text{CO}} = \left( \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \right) \times 100 \quad \text{---(2)}$$

- Oxygen conversion ( $X_{\text{O}_2}$ )

$$X_{\text{O}_2} = \left( \frac{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}}{[\text{O}_2]_{\text{in}}} \right) \times 100 \quad \text{---(3)}$$

where  $[CO]_{in}$  and  $[O_2]_{in}$  are the concentrations of the introduced reactants  
 $[CO]_{out}$  and  $[O_2]_{out}$  are the concentrations of the corresponding composition  
 in the effluents

Noble metals are known to provide a high activity in the conversion of CO. In 2008, Luengnaruemitchai's group presented on a comparative study of synthesized and commercial A-type zeolite-supported Pt catalysts for selective CO oxidation in H<sub>2</sub>-rich stream. They reported that the commercial zeolite supported catalyst had higher surface area and metal dispersion than the synthesized zeolite supported catalyst. After loading platinum, the synthesized zeolite supported catalyst still maintained cubic single crystal while the shape of the commercial zeolite supported catalyst was rather round, egg-like, and more irregular. Both of catalysts showed a good performance on CO conversion and selectivity. They also found that CO<sub>2</sub> did not have significantly effect on the performance of both catalysts, but the presence of water decreased the efficiency of the catalyst. Yu *et al.* in 2007 reported that the size of gold particles was related to the activity of PROX. Therefore, Luengnaruemitchai *et al.* (2009) researched on Au/ZnO and Au/ZnO-Fe<sub>2</sub>O<sub>3</sub>, prepared by deposition-precipitation, and studied their activities on PROX. and found that Au/ZnO and Au/ZnO-Fe<sub>2</sub>O<sub>3</sub> catalysts were able to succeed the CO conversion at low temperature with higher catalyst activities. Moreover, the resistances of water and CO were enhanced when using ZnO-Fe<sub>2</sub>O<sub>3</sub>. In addition, the size of particles played an important role in increasing the PROX activity. Smaller particle size was more active in the PROX reaction. In the same year, they carried out the same catalysts with different preparation methods using photodeposition under UV-visible light. They obtained gold nanoparticles and showed higher catalytic activity than the previous preparation. Moreover, Kudo *et al.* (2010) also studied on a new preparation method of Au/ferric oxide catalyst for low temperature CO oxidation. They prepared the catalyst using coprecipitation method by adding gold solution after the growth of iron hydroxide grain to a certain size. They found that CO adsorption ability and CO oxidation were significantly enhanced when comparing with conventional method. Two year later, Lui *et al.* (2012) proposed that oxygen vacancy promoted CO oxidation over Pt/CeO<sub>2</sub> catalysts: A reaction was taken place at Pt-CeO<sub>2</sub> interface.

Catalyst was prepared by impregnation method. As a result, the reaction rate declined with Pt content in the catalyst. However, the conversion of CO was shifted to a lower temperature when using a higher amount of Pt.