CHAPTER IV
RESULTS AND DISCUSSION

4.1 Characteristics of Pillared-clay Catalysts upon Temperature Changes

It was reported that hydrotalcite clays have different thermal transition behaviors in the different calcination stages (Shen *et al.*, 1994; and Yong *et al.*, 2001). In this part, the changes in characteristics of pillared-clay such as phase transition, morphology, and surface area upon temperature were studied by several techniques, i.e., TGA, XRD, SEM, and BET.

4.1.1 Transition Weight Loss of Pillared-clays

The transition weight loss of pillared-clays upon temperature was investigated by TGA technique. The results showed transition weight loss behavior of pillared-clays from 30 to 800°C.

4.1.1.1 DA-clay Based Catalysts

The transition weight loss of DA-clay examined by TGA is shown in Figure 4.1. The weight loss appears in three zones. In the first zone, water located at surface and between interlayer of clay sheet was lost when the temperature was increased toward and beyond its boiling point. This first transition should be up to 300°C. The second transition is started between 300 and 500°C, and the third transition is beyond 500°C. In the second zones beyond the first transition, clay might have started to lose one by one their two layers of deoxycholate anions and hydroxy groups until the third transition at 500°C where the clay might have completely lost the layer structure and become mixed oxides.

4.1.1.2 *PW_{12}-clay Based Catalysts*

The transition weight loss of PW_{12}-clay determined from TGA is shown in Figure 4.2. The weight loss appears in three zones. Similar to DA-clay, the first transition is up to 300°C due to rearrangement of oxide surface on brucite layers in addition of loss of water. The second transition starts between 300 and 500°C which the layer structure might start to be lost. Beyond 500°C, it is a well-maintained zone.

4.1.2.3 *SiW_{12}-clay Based Catalysts*

Figure 4.3 shows the TGA and DTG of SiW_{12}-clay. The transition weight loss of SiW_{12}-clay was similar to PW_{12}-clay. The second transition is started between 300 and 500°C the layer structure might start to be lost. Beyond 500 °C, it is also a well-maintained region.

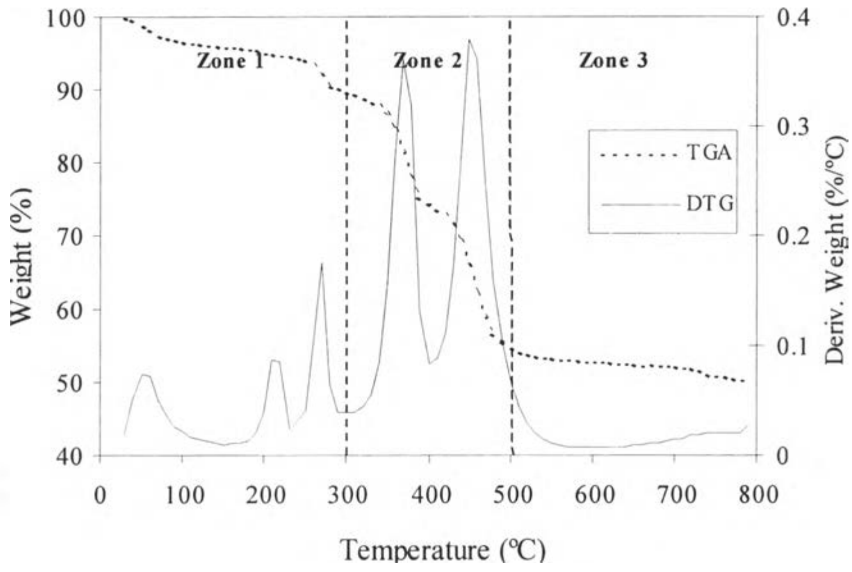


Figure 4.1 TGA and DTG of DA-clay.

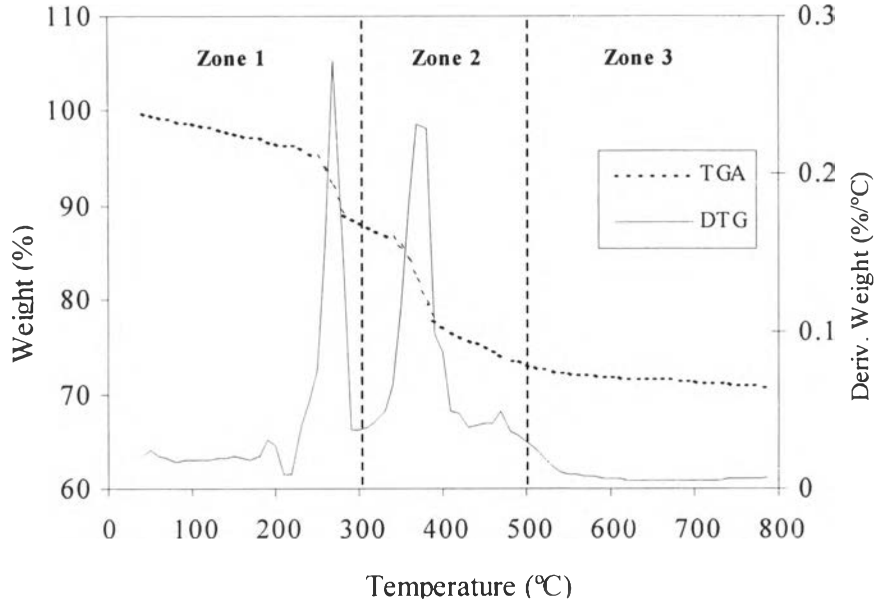


Figure 4.2 TGA and DTG of PW_{12}-clay.

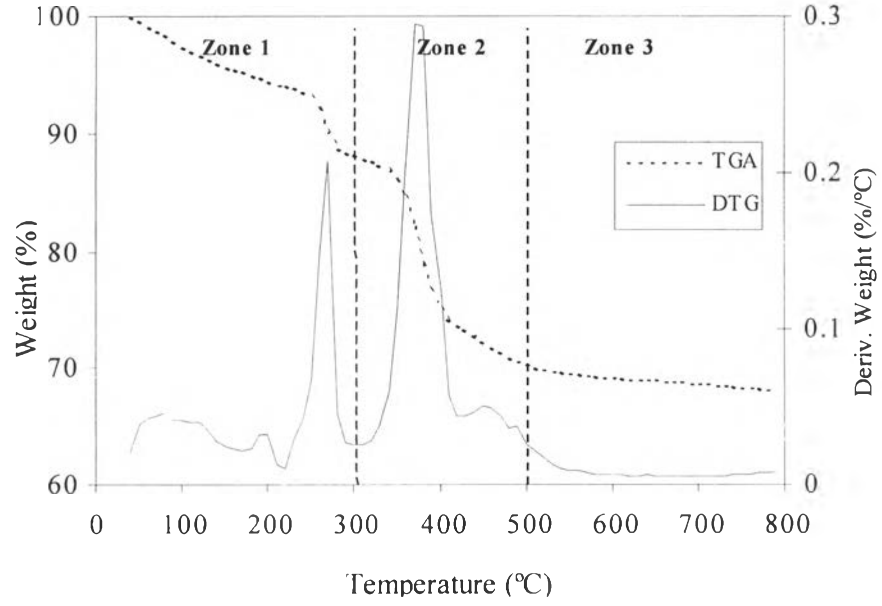


Figure 4.3 TGA and DTG of SiW_{12}-clay.

4.1.2 Phase Transitions of Pillared-clays

Phase of pillared-clays was changed after calcined at different temperatures. The calcined product components of each pillared-clay were analyzed by XRD technique.

4.1.2.1 DA-clay Based Catalysts

XRD patterns of DA clay based catalysts after dried and calcined at 250-500°C are shown in Figure 4.4(a). The (001) plane peak of dried DA-clay occurs at the 2θ angle of 2.65°, which has the d-spacing value of 32.90 Å. These values agree well with the data obtained from Ogawa ans Asai (2000), which showed the intercalated deoxycholate formed as a bilayer in the interlayer space where the carboxylate was believed to orient to the surface of the cationic brucite-like sheet. The XRD pattern of dried DA-clay also shows a $Mg(OH)_2$ phase at the 2θ angle of 18.36° and 38.04°, and the diffraction peaks at around 10-18° belong to deoxycholic acid phase. When the clay was calcined at 250°C, most of the peaks still occurs at the same 2θ angle, which means the structure of DA-clay did not change significantly at this temperature. The diffraction peak of DA-clay calcined at 300°C shows the flat plane peak at the 2θ angle of 3.78°, which has the d-spacing value of 23.36 Å. At this temperature, a magnesium oxide (MgO) phase is observed at the 2θ angle of 42.82° in addition to $Mg(OH)_2$ phase, indicating some deoxychalate ions and layer structure such as hydroxy groups might have started to be lost at this temperature. After the clay was calcined at 350 and 400°C, sharp peak of MgO phase is observed, indicating more deoxycholate ions and layer structure were lost. After calcined at 500°C, most of the peaks are disappeared, which deoxycholate ions and layer structure were believed to be almost or completely lost, and the clay structure became mixed oxides (MgO and Mg-Al-O). These observations agree well with the TGA results as shown in part 4.1.1.1.

After the clay was calcined at 900°C, higher crystalinity material was observed. The XRD pattern of this product is shown in Figure 4.4(b). It consists of sharp peaks of MgO and some trace of $MgAl_2O_4$ (spinel), indicating the change from the amorphous Mg-Al-O mixed oxide into $MgAl_2O_4$. This observation agrees with the evolution of general hydrotalcite clay that had been reported elsewhere (NIRE, 1995, and 1999).

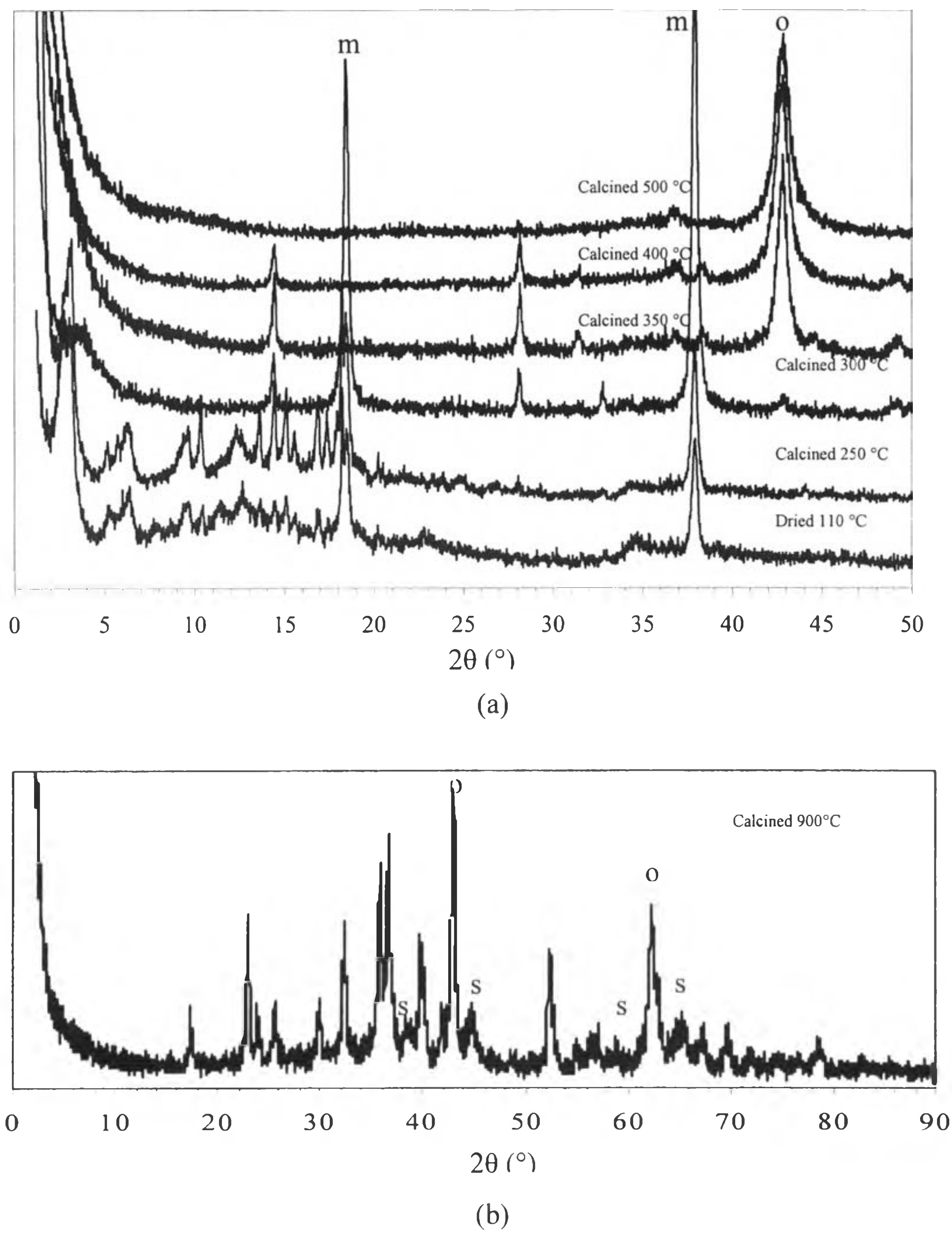
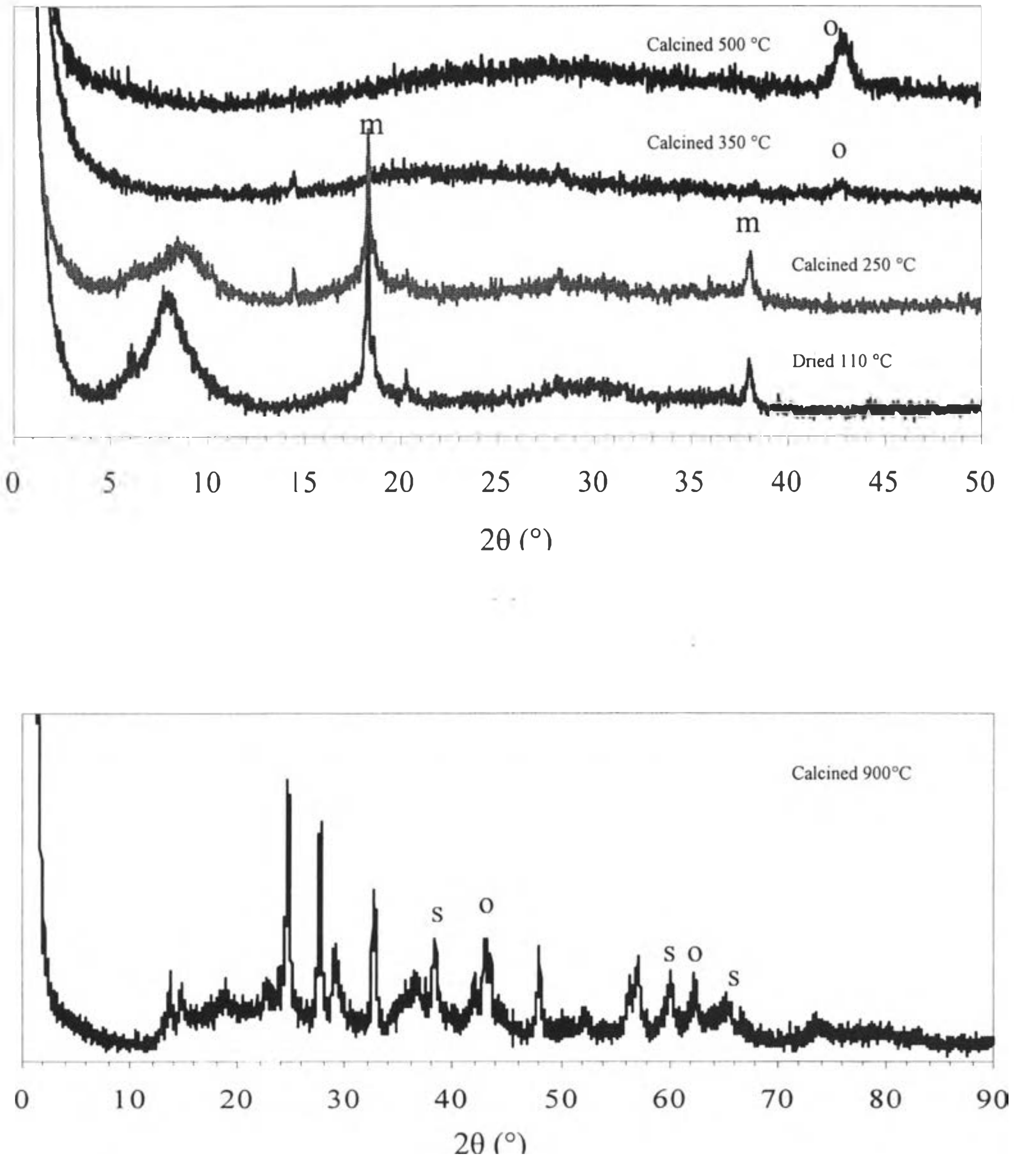


Figure 4.4 XRD patterns of (a) DA-clay dried at 110°C, and calcined at 200, 300, 350, 400, and 500°C, and (b) DA-clay calcined at 900°C: (m) $Mg(OH)_2$ phase, (o) MgO phase, and (s) spinel phase.

4.1.2.2 PW_{12}-clay Based Catalysts

Figure 4.5(a) shows the XRD patterns of dried PW_{12}-clay, and PW_{12}-clay after calcined at 250-500°C. The (001) plane peak of dried PW_{12}-clay appears at the 2θ angle of 6.02°, which has the d-spacing value of 14.67 Å. Similar to DA-clay, after this clay was calcined at 250°C, most of the peaks still occurred at the same 2θ angle, which means the structure of PW_{12}-clay did not change significantly at this temperature. When PW_{12}-clay was calcined at 350°C, the plane peak was disappeared, the first peak was observed at the 2θ angle of 11.86, which has the d-spacing value of 7.46 Å. Similar to the DA-clay, a magnesium oxide (MgO) phase was also observed at this temperature but less than the DA-clay. The peaks of PW_{12}-clay were almost disappeared after calcined at 500°C, indicating the clay sheet was already collapsed, and the clay characteristic was completely lost at this temperature.

After the clay was calcined at 900°C, crystalinity peaks of MgO and $MgAl_2O_4$ (spinel) phases were observed similarly to DA-clay. The XRD pattern of these mixed phases is shown in Figure 4.5(b).



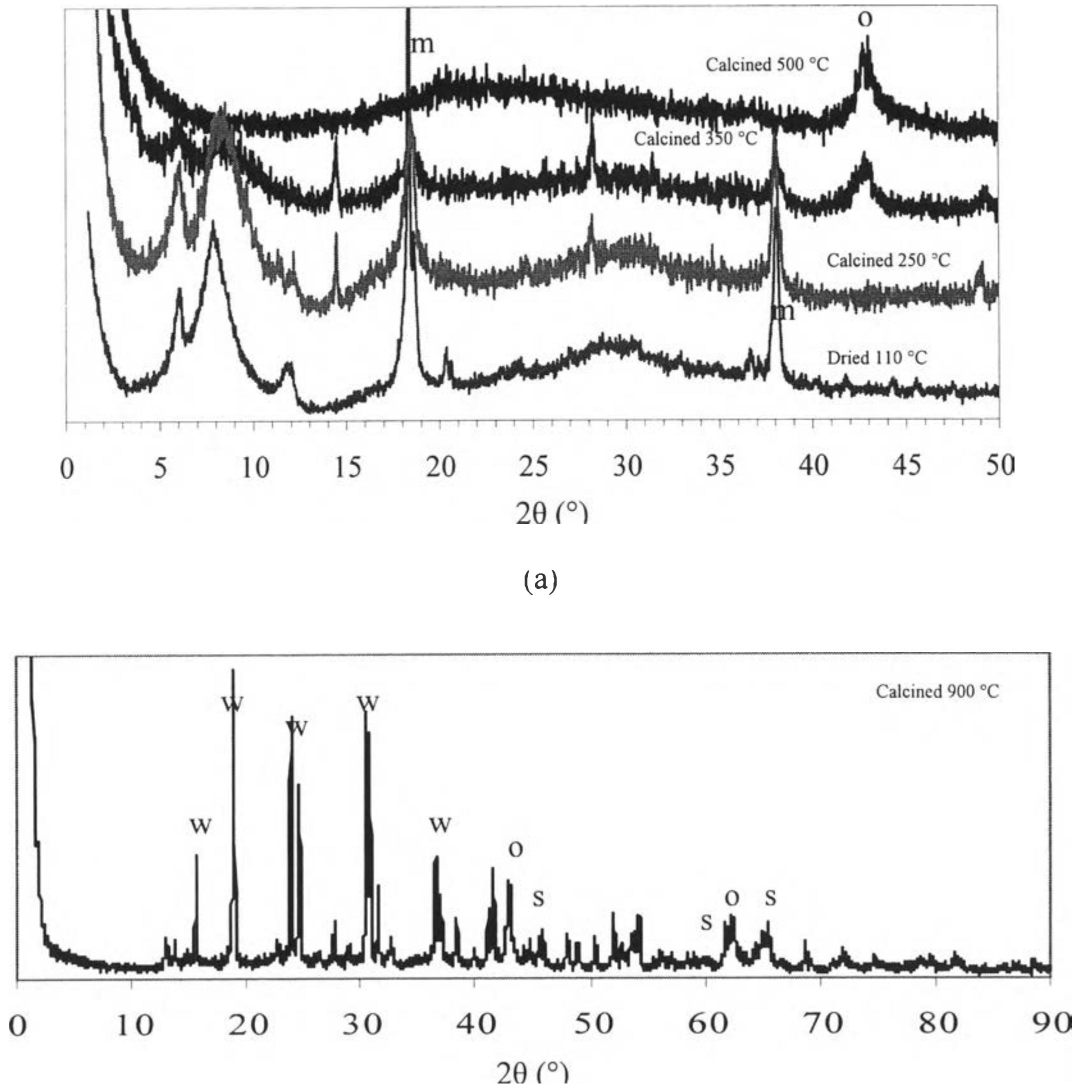
(b)

Figure 4.5 XRD patterns of (a) PW_{12}-clay dried at 110°C, and calcined at 250, 350, and 500°C, and (b) PW_{12}-clay calcined at 900°C: (m) $Mg(OH)_2$ phase, (o) MgO phase, and (s) spinel phase.

4.1.2.3 SiW_{12}-clay Based Catalysts

Dried SiW_{12}-clay has the (001) plane peak at the 2θ angle of 6.02°, which has the d-spacing value of 14.67 Å (Figure 4.6a). After it was calcined at 250 and 350°C, major characteristic peaks are still remained, indicating this pillared-clay might be the highest thermal stability clay. However, the first peak of SiW_{12}-clay calcined at 350 °C occurs at the 2θ angle of 8.92 with d-spacing value decreasing from 14.67 to 9.91 Å. A magnesium oxide (MgO) phase was formed as same as in the DA-clay and PW_{12}-clay cases. Similar to PW_{12}-clay, the clay was lost its structure and characteristic after calcined at 500°C.

After the clay was calcined at 900°C, crystalinity peaks of MgO and $MgAl_2O_4$ (spinel) phases were also observed similar to DA-clay and PW_{12}-clay. In addition, there are some peaks of $MgWO_4$ phase occurred at this temperature, indicating the phase of keggin interlayer ions in this pillared-clay were changed. The XRD pattern of SiW_{12}-clay calcined 900°C is shown in Figure 4.6(b).



(a)

(b)

Figure 4.6 XRD patterns of (a) SiW_{12}-clay dried at 110°C, and calcined at 250, 350, and 500°C, and (b) SiW_{12}-clay calcined at 900°C: (m) $Mg(OH)_2$ phase, (o) MgO phase, (s) spinel phase, and (w) $MgWO_4$ phase.

4.1.3 Structure Models of Pillared-clays

The structure models of pillared-clay catalysts at different calcination temperatures were proposed related to TGA and XRD. Five structure models were suggested in order to represent dried pillared-clays, pillared-clay calcined at 250°C, pillared-clay calcined at 350°C, pillared-clay calcined at 500°C, and pillared-clay calcined at 900°C of DA-clay and keggin-clays ($PW_{12}O_{40}$ and $SiW_{12}O_{40}$).

Figure 4.7 shows the structure models of DA-clay based catalyst. At first, dried DA-clay has deoxycholate anions formed as a bilayer in the interlayer, and the space between each anion was filled with water molecules (Figure 4.7a). After that, water located at surface and interlayer of clay sheet was lost when the clay was calcined at 250°C, then the clay structure become denser, and decrease in the d-spacing (Figure 4.7b). When the clay was calcined beyond 300°C, it might have started to lose their two layers of deoxycholate anions and hydroxy groups forming new compounds of deoxycholate, MgO and Mg-Al-O groups in the product, then the structure of this clay should appear in higher amorphous form (Figure 4.7c). After the clay was calcined at 500°C, completely amorphous structure from mixed oxides was suggested (Figure 4.7d). Finally, crystallinity spinel compound was formed mixing with the mixed oxides product at 900°C (Figure 4.7e).

The structure models of the keggin-clays ($PW_{12}O_{40}$ and $SiW_{12}O_{40}$) were also proposed, and they are shown in Figure 4.8. Dried keggin-clay shows keggin anions in the interlayer space with interlayer water (Figure 4.8a). After the clay was calcined at 250°C, the clay structure become denser (Figure 4.8b). When the clay was calcined at 350°C, some layer structures was lost creating amorphous mixed oxide around the keggin anions (Figure 4.8c). The additional XRD result shows that keggin phase was changed at 500°C (Figure B1), therefore, created new keggin phase mixing with the mixed oxides product (Figure 4.8d). At 900°C, the spinel compounds and new compounds from keggin deformation such as $MgWO_4$ were occurred in the product (Figgure 4.8e).

Therefore, all dried pillared-clays show four different phases at 250, 350, 500, and 900°C. These would be the calcination temperatures use for prepare catalysts in the catalytic testing part.

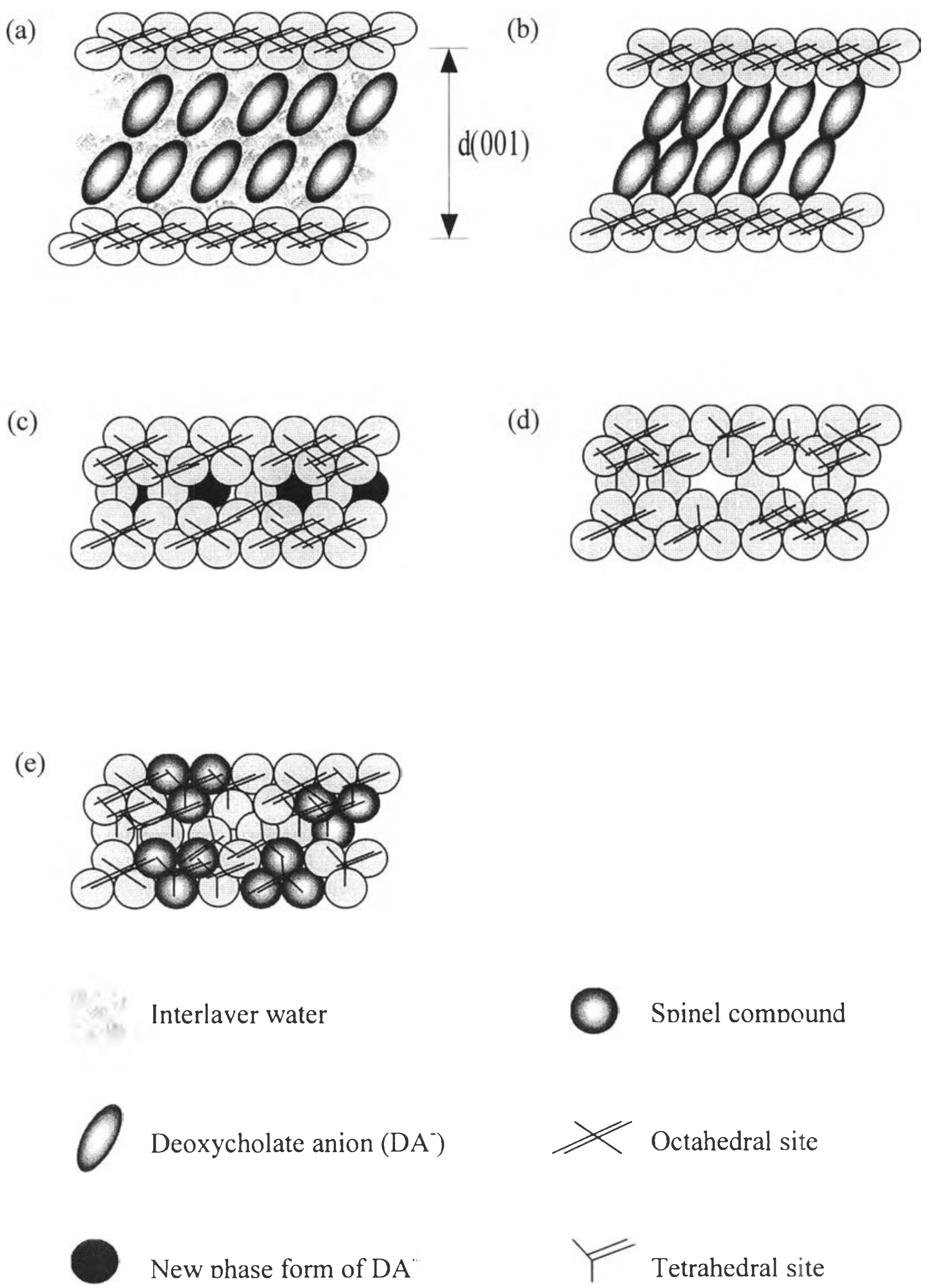


Figure 4.7 Structure models of DA-clay at different temperatures: (a) dried, (b) calcined at 250°C, (c) calcined at 350°C, (d) calcined at 500°C, and (e) calcined at 900°C (adapted from Yong *et al.*, 2001 for pillared-hydrotalcite-type clay cases).

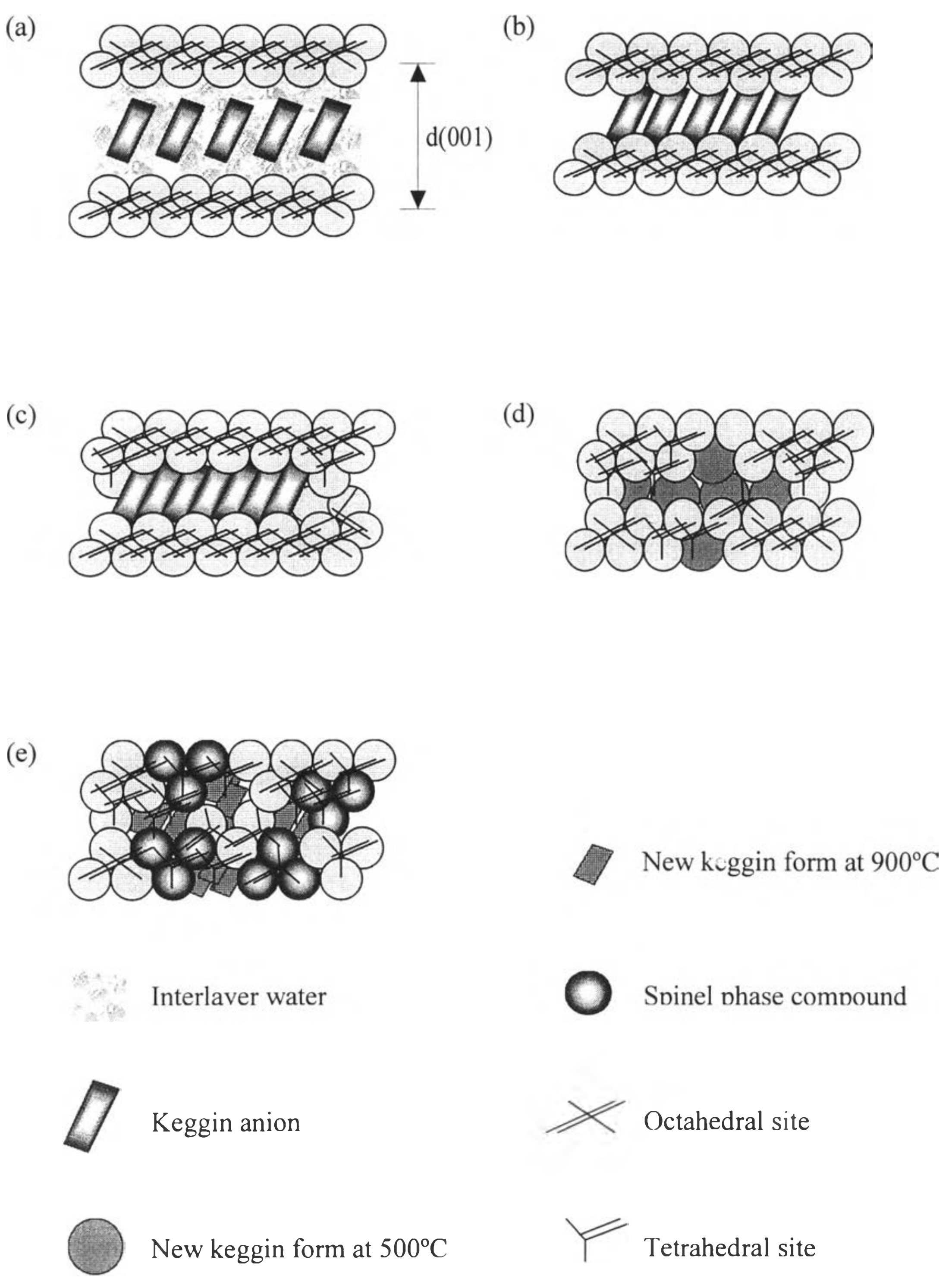
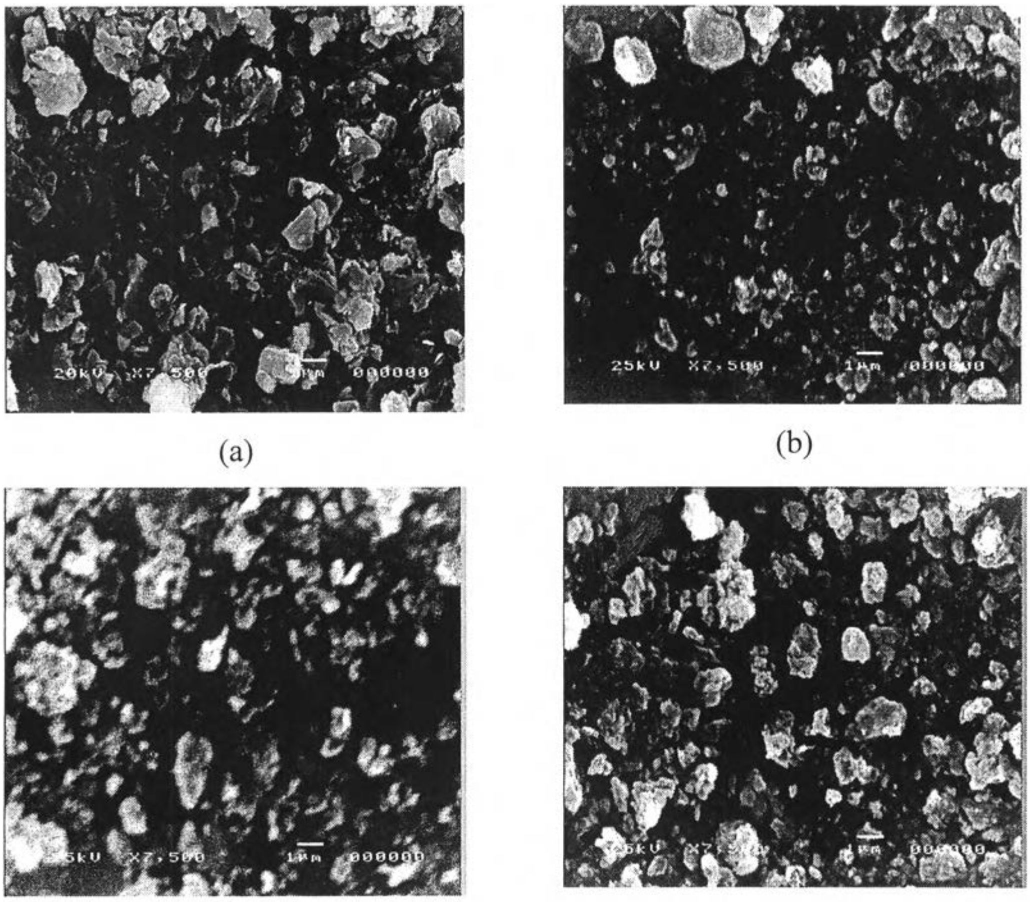


Figure 4.8 Structure models of keggin-clay (PW_{12}-clay or SiW_{12}-clay) at different temperatures: (a) dried, (b) calcined at 250°C, (c) calcined at 350°C, (d) calcined at 500°C, and (e) calcined at 900°C (adapted from Yong *et al.*, 2001 for pillared-hydrotalcite-type clay cases).

4.1.4 Surface Morphology of Pillared-clays

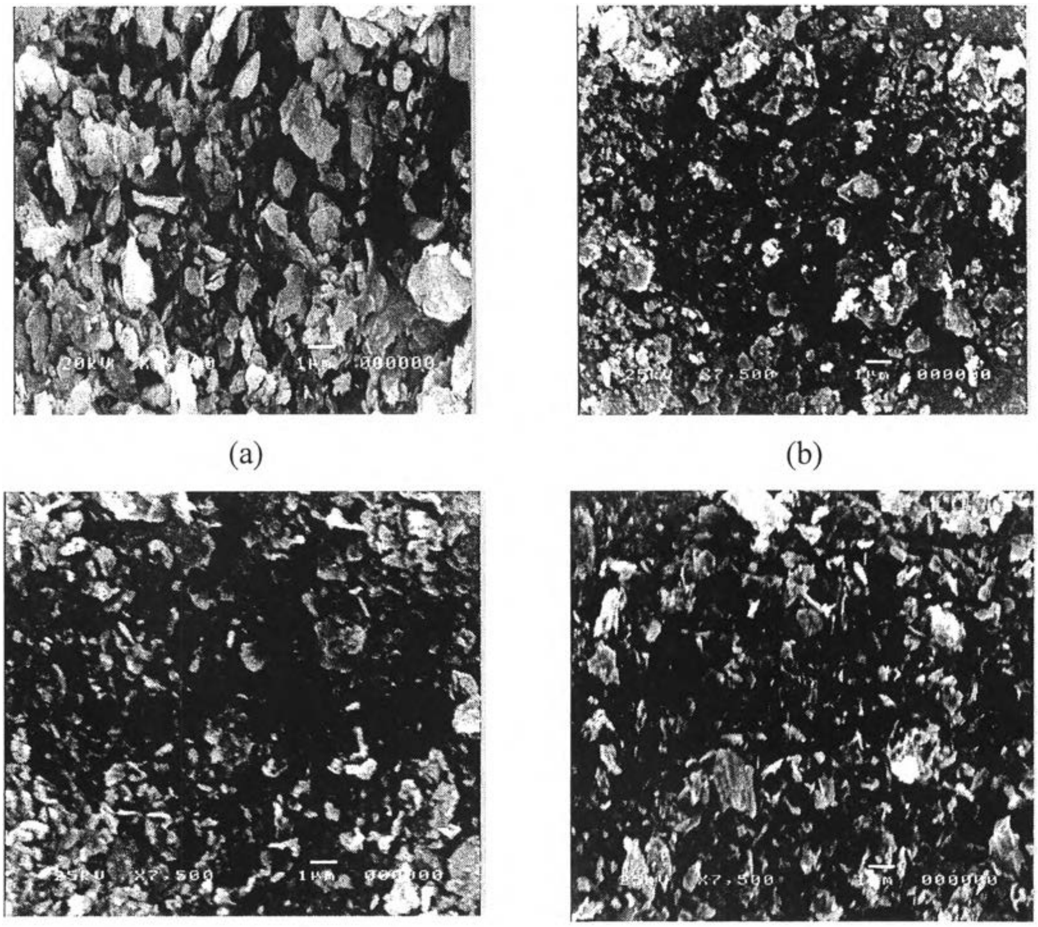
The change in surface morphology of pillared-clay catalysts upon temperatures was studied by using SEM technique.

The surface morphology of dried and calcined pillared-clay catalysts was shown in Figures 4.9 to 4.11. All dried pillared clays were found in cornflake shape of crystalline morphology. After all pillared clays were calcined at 350 and 500°C, similar amorphous surface morphology was observed. Then, higher crytallinity was recovered after the material was further calcined at 900°C. This result agreed with the weight loss and phase changes as described in TGA and XRD parts.



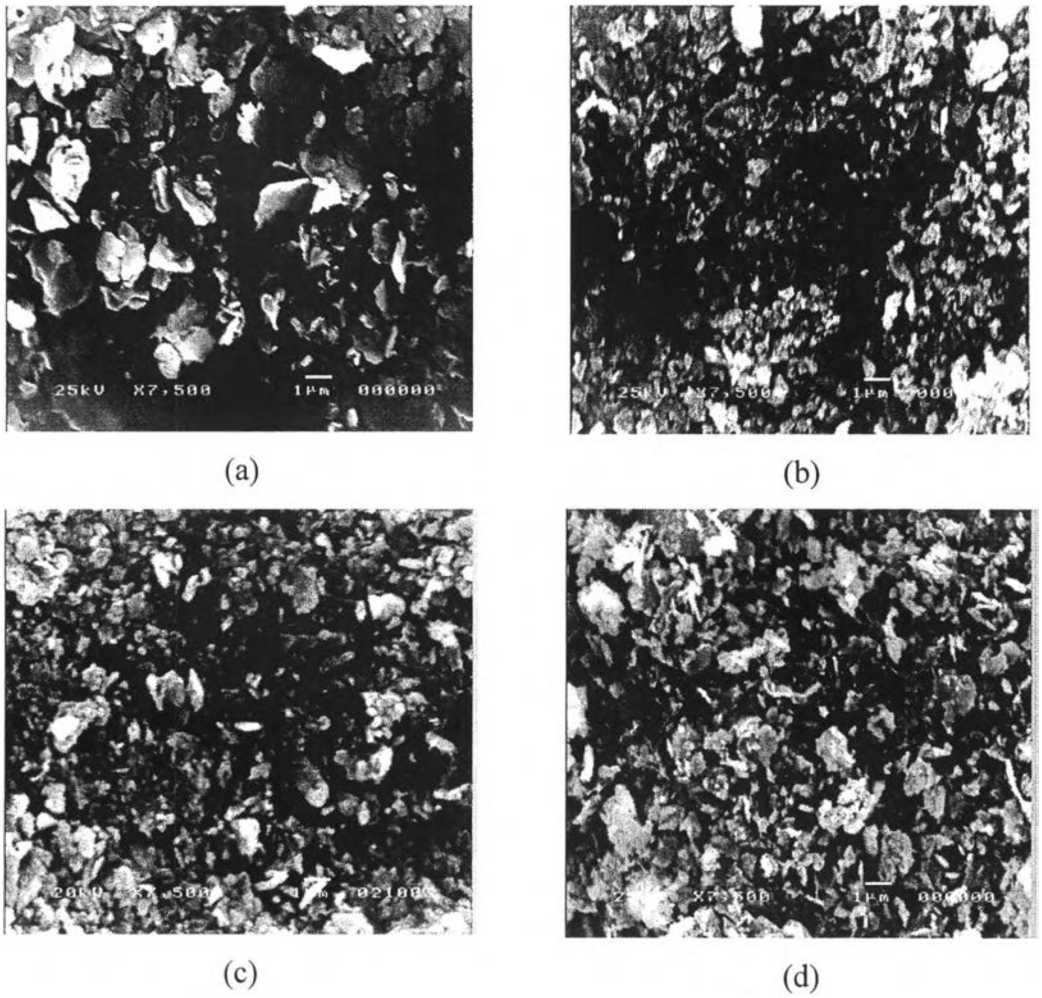
(a) (b) (c) (d)

Figure 4.9 Scanning electron micrographs at 7500X magnification of (a) DA-clay dried, (b) DA-clay calcined at 350°C, (c) DA-clay calcined at 500 °C, and (d) DA-clay calcined at 900 °C.



(a) (b) (c) (d)

Figure 4.10 Scanning electron micrographs at 7500X magnification of (a) PW_{12}-clay dried, (b) PW_{12}-clay calcined at 350°C, (c) PW_{12}-clay calcined at 500°C, and (d) PW_{12}-clay calcined at 900°C.



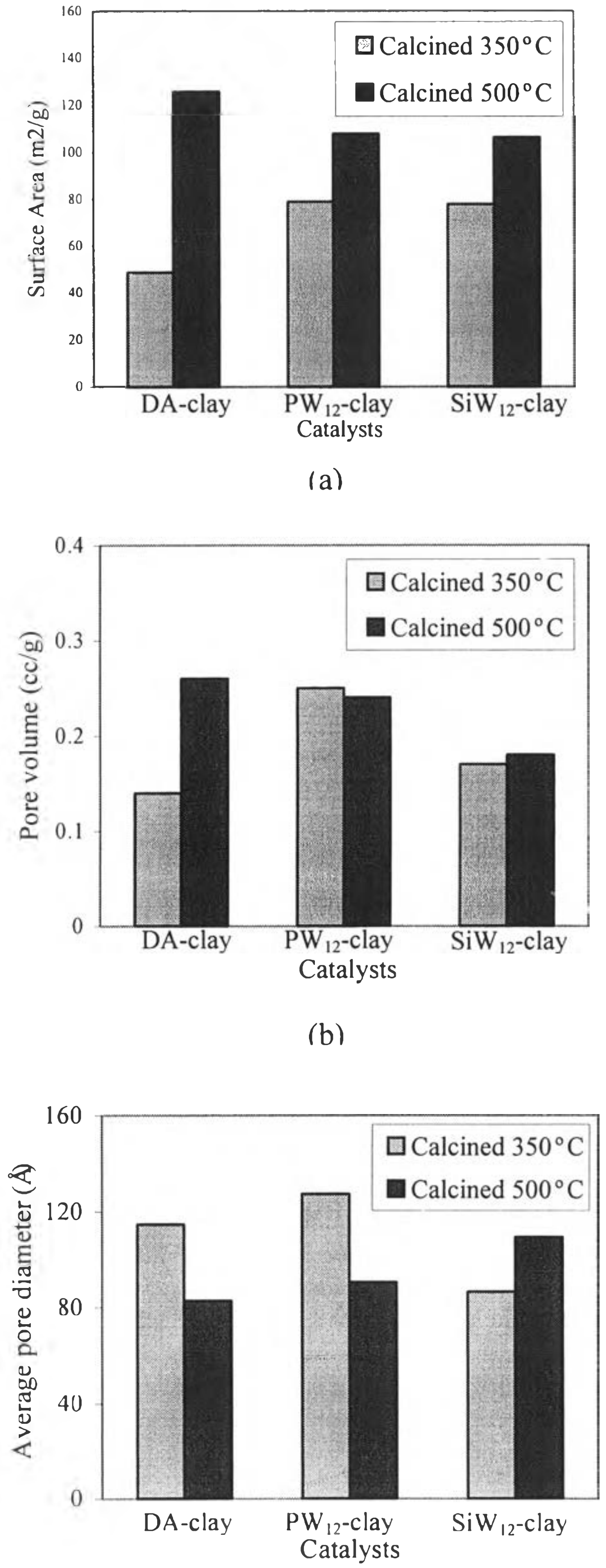
(a) (b)

(c) (d)

Figure 4.11 Scanning electron micrographs at 7500X magnification of (a) SiW_{12}-clay dried, (b) SiW_{12}-clay calcined at 350°C, (c) SiW_{12}-clay calcined at 500°C, and (d) SiW_{12}-clay calcined at 900°C.

4.1.5 BET Surface Area, Total Volume, and Average Pore Diameter

BET technique was employed for determining BET surface area, pore volume, and average pore diameter of pillared-clay catalysts calcined at 350 and 500°C. The results are shown in Figure 4.12, and tabulated in Appendix B. The surface area of these catalysts is in the range of 48.71 – 125.60 m^2/g (Figure 4.12a). Pillared-clay calcined at 350°C showed surface area of around 48.71 – 78.99 m^2/g. After they were calcined at 500°C, the surface area of about 107.9 – 125.60 m^2/g was obtained, which is much larger than that calcined at 350°C. The BET surface area of all pillared-clay catalysts was exhibited in the same trend, indicating deformation of layer structure into more amorphous phases (as shown in part 4.1.2) might result in the increase in surface area. The pore volume of pillared-clay catalysts is between 0.14 and 0.26 cc/g (Figure 4.12b), and the average pore diameter is in the range of 82.68-127.40 Å (Figure 4.12c).



(a)

(b)

(c)

Figure 4.12 BET characterization of all catalysts: (a) BET surface area, (b) pore volume, and (c) average pore diameter.

4.2 SCR Catalytic Activity of Pillared-clay Catalysts

The SCR activities for the pillared-clay catalysts were examined at different temperatures in the range 150-450°C. The reactant mixture containing 1000 ppm NO, 1000 ppm NH_3, 2% O_2 balanced with helium was fed to the reactor with the flow rate of 500 ml/min. The conversion was determined when NO concentration in the product was steady.

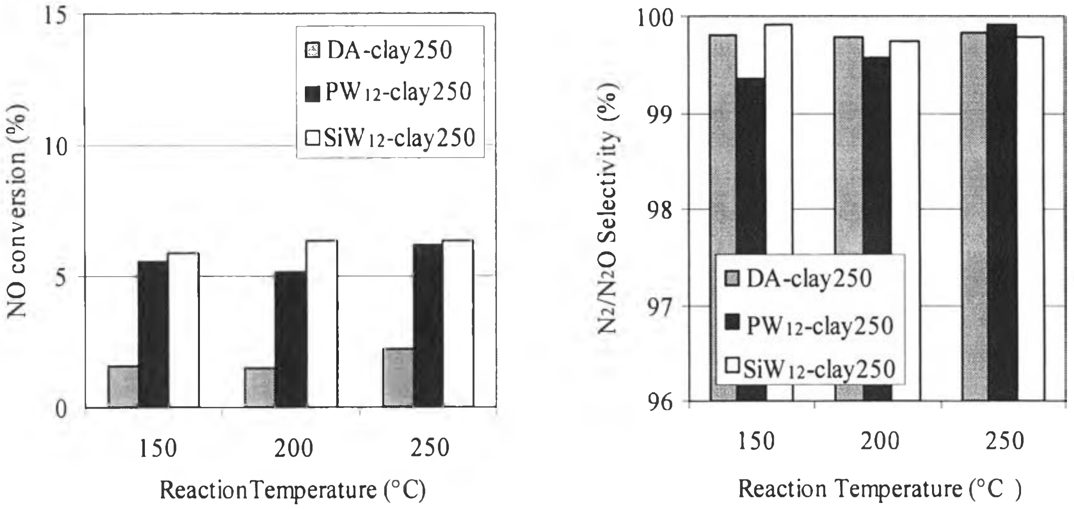
4.2.1 Effect of Phase Changes

The effects of phase changes to the activity and selectivity of pillared-clays catalysts were determined in this section. According to TGA and XRD results, all pillared-clay catalysts can be divided into 4 groups: (i) pillared-clay catalysts calcined at 250°C, (ii) pillared-clay catalysts calcined at 350°C, (iii) pillared-clay catalysts calcined at 500°C, and (iv) pillared-clay catalysts calcined at 900°C.

4.2.1.1 Pillared-clay Catalysts Calcined at 250°C

Pillared-clay catalysts calcined at 250°C still possesed all of the pillared-clay characteristics as mentioned in TGA and XRD parts. This catalyst is represented as a pillared-clay with large d-spacing and crystallinity as same as dried pillared-clay. The activity of pillared-clay catalyst calcined 250°C was determined in the temperature range of 150-250°C. The NO conversion of these catalysts is shown in Figure 4.13(a). The NO conversion of DA-clay is about 2% at all testing temperatures while the others showed higher NO conversion of around 6%.

The N_2/N_2O selectivity of pillared-clay catalysts calcined 250°C is shown in Figure 4.13(b). The N_2/N_2O selectivity of all catalysts was around 99.5%. Thus, these pillared-clay catalysts exhibit no or little oxidation of NH_3 forming N_2O in the tested temperature range (Yang *et al.*, 1992).



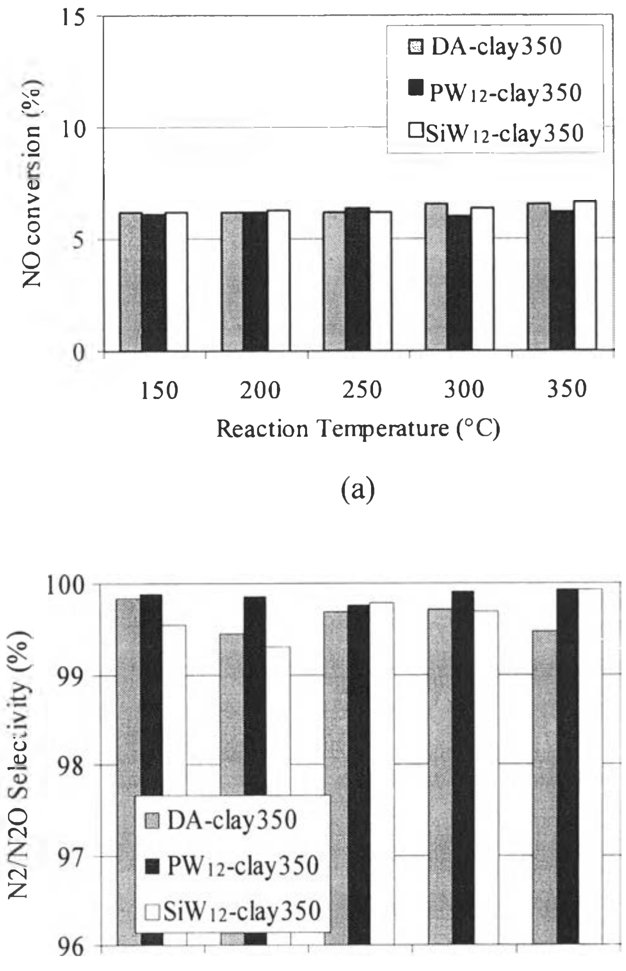
(a) (b)

Figure 4.13 SCR activity results of pillared-clay catalysts calcined at 250°C: (a) NO conversion and (b) N_2/N_2O selectivity, at different reaction temperatures.

4.2.1.2 Pillared-clay Catalysts Calcined at 350°C

The pillared-clay catalysts at 350°C are represented as the intermediate between dried clay and mixed oxide state. At this calcination temperature, some parts of clay structure became mixed oxide (Mg-Al-O) and MgO, but clay characteristics were remained. The activity of catalysts calcined at 350°C was studied in the temperature range of 150-350°C. Figure 4.14(a) shows the NO conversion of these pillared-clay catalysts. The NO conversion of all catalysts was about 6% at all testing temperatures. The activity of DA-clay catalyst calcined at 350°C significantly increased comparing to the one calcined at 250°C while the activity of the others was almost the same as the one calcined at 250°C.

The N_2/N_2O selectivity of pillared-clay catalysts calcined 350°C was about 99.5% as same as these calcined at 250°C (Figure 4.14b).



(a)

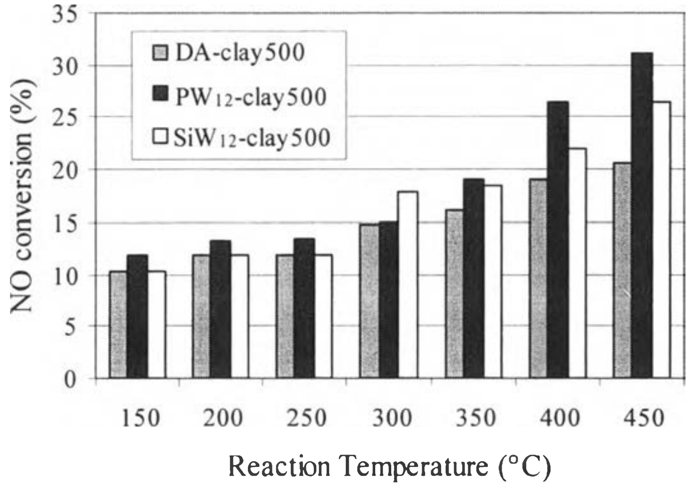
(b)

Figure 4.14 SCR activity of pillared-clay catalysts calcined at 350°C: (a) NO conversion and (b) N_2/N_2O selectivity, at different reaction temperatures.

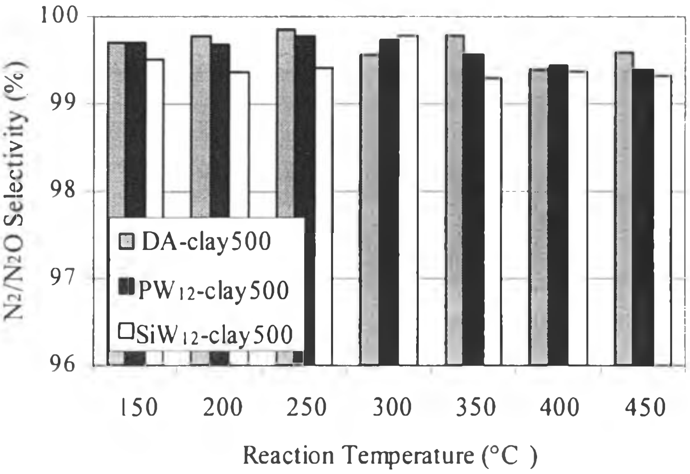
4.2.1.3 Pillared-clay Catalysts Calcined at 500°C

The pillared-clay at 500°C contained the mixed oxide phases without clay characteristics. Their activity was determined in the temperature range of 150-450°C. Figure 4.15(a) shows NO conversion of pillared-clay catalysts calcined at 500°C. About 11-14% NO conversion was obtained at 150-250°C for all pillared-clay catalysts. The activity of all catalysts increased significantly beyond 300°C, and reached the highest activity at 450°C. At 450°C, PW_{12}-clay gave the highest NO conversion of 31.2%. DA-clay itself used as precursor of all catalysts gave 20% NO conversion, and SiW_{12}-clay showed 26% NO conversion.

The N_2/N_2O selectivity of these pillared-clay catalysts is shown in Figure 4.15(b). The N_2/N_2O selectivity of all catalysts was around 99.3 – 99.8%.



(a)

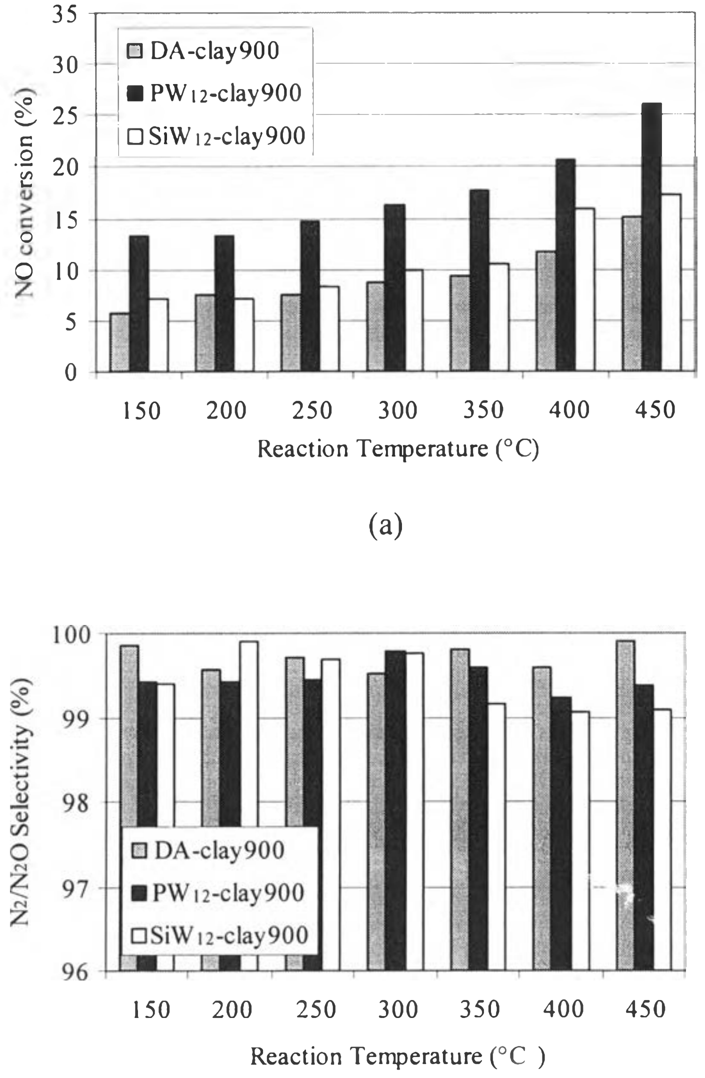


(b)

Figure 4.15 SCR activity of pillared-clay catalysts calcined at 500°C: (a) NO conversion and (b) N_2/N_2O selectivity, at different reaction temperatures.

4.2.1.4 Pillared-clay Catalysts Calcined at 900°C

The pillared-clay catalysts at 900°C represent the spinel phase and new crystalline phases that formed after deformation. The activity of pillared-clay catalysts calcined at 350°C was investigated in the temperature range of 150-450°C. The NO conversion is shown in Figure 4.16(a). The NO conversion of DA-clay and SiW_{12}-clay is around 7-10% at low temperatures (150-300°C). The PW_{12}-clay gave the highest activity of 26% at 450°C. The N_2/N_2O selectivity of all catalysts was around 99.1-99.9%. PW_{12}-clay and SiW_{12}-clay showed lower selectivity at 400 and 450°C (Figure 4.14b).



(a)

(b)

Figure 4.16 SCR activity of pillared-clay catalysts calcined at 900°C: (a) NO conversion and (b) N_2/N_2O selectivity, at different reaction temperatures.

4.2.1.5 Relationship between Activity and Catalyst Phases

The SCR activity of all pillared-clays are listed in Appendix B. The pillared-clay catalysts calcined at 500°C gave significantly higher activity than the others at all testing temperatures. The activity of pillared-clay catalysts decreased in the order of: pillared-clay catalysts calcined at 500°C > pillared-clay catalysts calcined at 900°C > pillared-clay catalysts calcined at 350°C > pillared-clay catalysts calcined at 250°C. The reasons for these observations might be explained in term of clay properties changing upon temperature.

When pillared-clays were heated at 250°C, they dehydrated, but the products still retained a layer structures and interlayer ions. Mostly, SCR activity of this phase might be contributed from interlayer ions between layers of each clay. The organic deoxycholate anions in DA-clay layers gave lowest activity even though it has the highest d-spacing.

It has been accepted that the Brønsted acidity is the most important property of catalyst in SCR of NO by NH_3 (Cheng *et al.*, 1996; Long and Yang, 1999; 2000a; 2000c). When pillared-clays were heated to 350°C, the interlayer, deoxycholate ions of DA-clay were removed causing some changes on layer structure. Moreover, dehydroxylation process causes the formation of MgO, and Mg-Al-O, and the Mg-Al-O group is the source of Brønsted acidity. The formation of Mg-Al-O groups in all clay catalysts; therefore, promoted the SCR reaction and increased the activity of all catalysts, especially DA-clay one.

After all catalysts were calcined at 500°C, the number of Brønsted acid sites might be increased by increasing the formation of Mg-Al-O groups from dehydroxylation process. Moreover, surface area and pore volume were increased by the deformation of layer structure (as shown in part 4.1.4). Thus, the activity of this phase was much higher than previous phases. In addition, new phase of keggin occurred at this temperature might promote the activity on PW_{12}-clay and SiW_{12}-clay at high reaction temperatures (300-450°C).

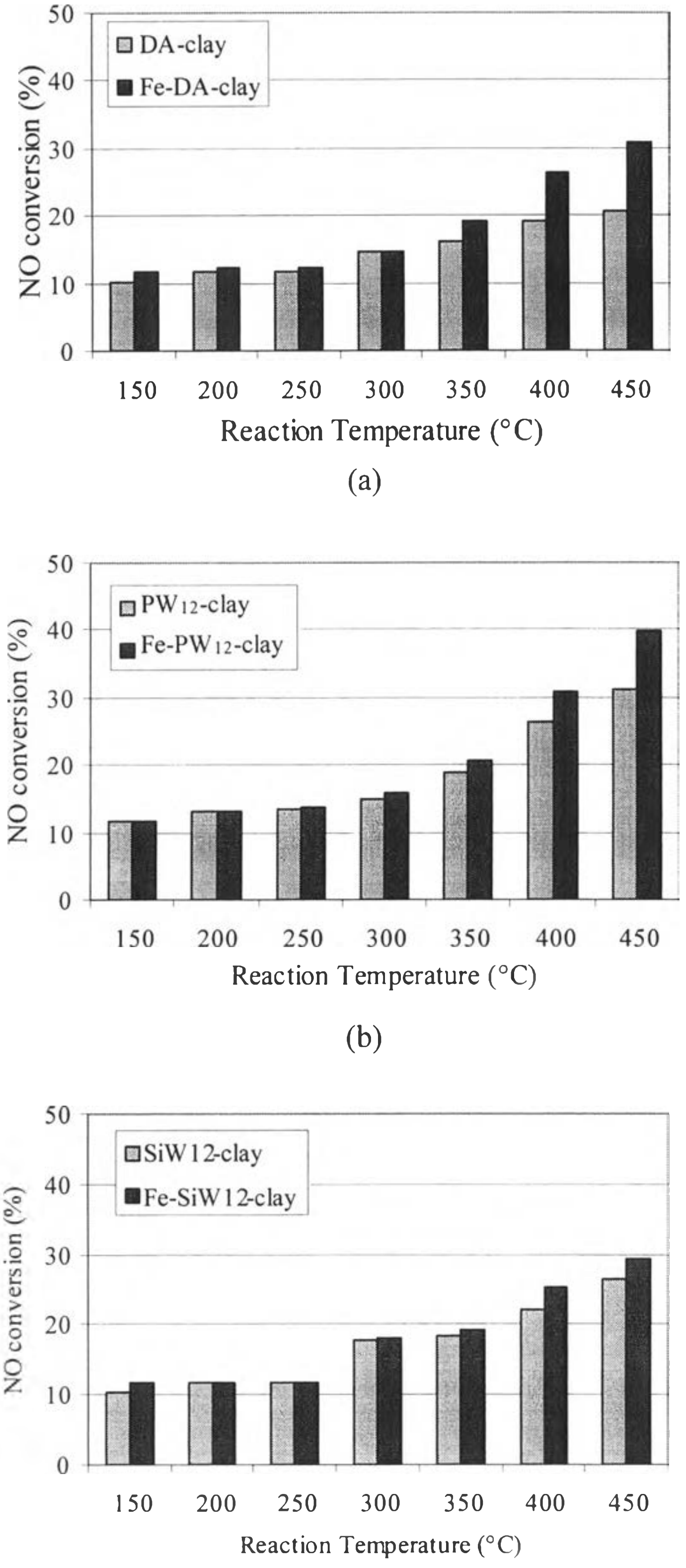
At 900°C, the result shows lower activity than catalysts calcined at 500°C. New phases such as spinel might affect the activity, and cacination at high temperature might also decrease the Brønsted acidity on all clay catalysts, and then decreased the activity. The evolution of the pillared-clay structure described above is illustrated in Figures 4.7 and 4.8.

4.2.2 Promoting Effect of Fe

Iron was loaded on pillared-clay catalysts calcined 500°C in order to determine the promoting effect of Fe. The comparison of activity of unloaded and 5%Fe-loaded catalysts is shown in Figure 4.17. It was found that 5%Fe loading significantly increased NO conversion at temperature beyond 350°C. The highest 40% NO conversion was achieved at 450°C on Fe-PW_{12}-clay catalysts.

The N_2/N_2O selectivity of all pillared-clay catalysts is shown in Figure 4.18. Most catalysts exhibit more than 99% N_2/N_2O selectivity at all testing temperatures, indicating no or little amount of N_2O was formed on Fe-loaded clay catalysts.

Cheng *et al.* (1996) suggested that both Fe=O and Fe-OH, which are the Brønsted acid sites Fe_2O_3/Cr_2O_3 on TiO_2 catalyst were necessary for SCR reaction. The mechanism is illustrated in Figure 4.19. Therefore, it is reasonable to suggest that Fe-loading increases the Brønsted acidity of pillared-clay catalysts, and then enhances the activity.



(a)

(b)

(c)

Figure 4.17 Comparison between unloaded and Fe-loaded pillared-clay catalysts: (a) DA-clay, (b) PW_{12}-clay, and (c) SiW_{12}-clay.

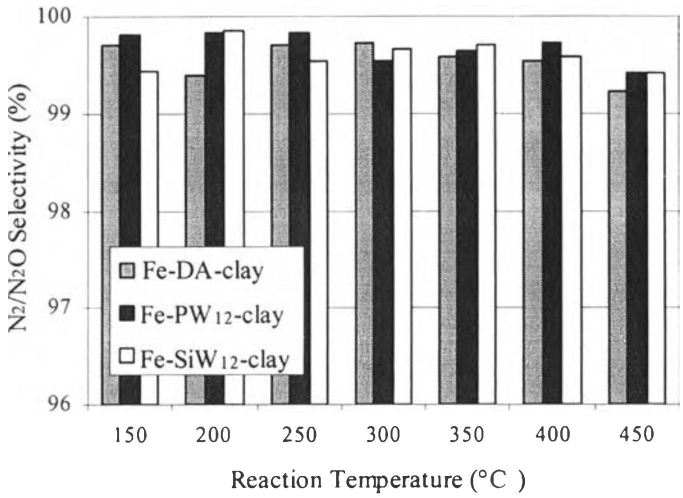


Figure 4.18 N_2/N_2O selectivity of all Fe-loaded pillared-clay catalysts at different reaction temperatures.

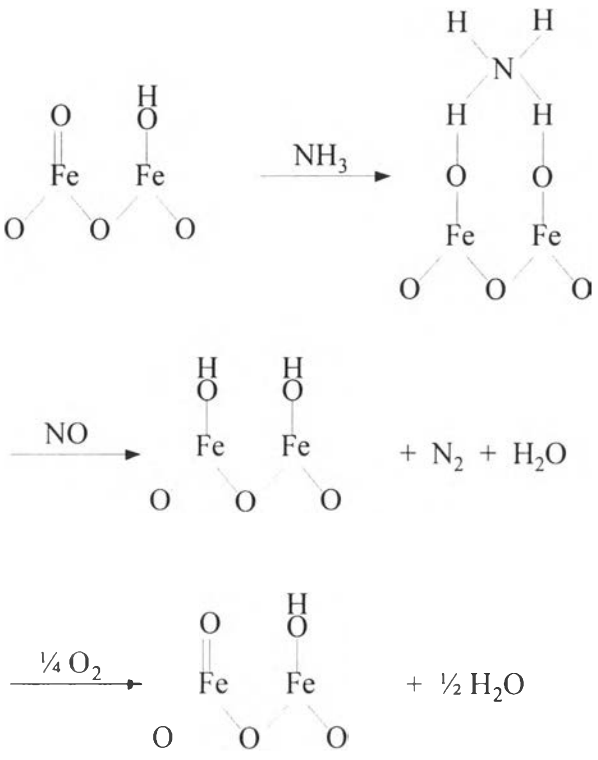
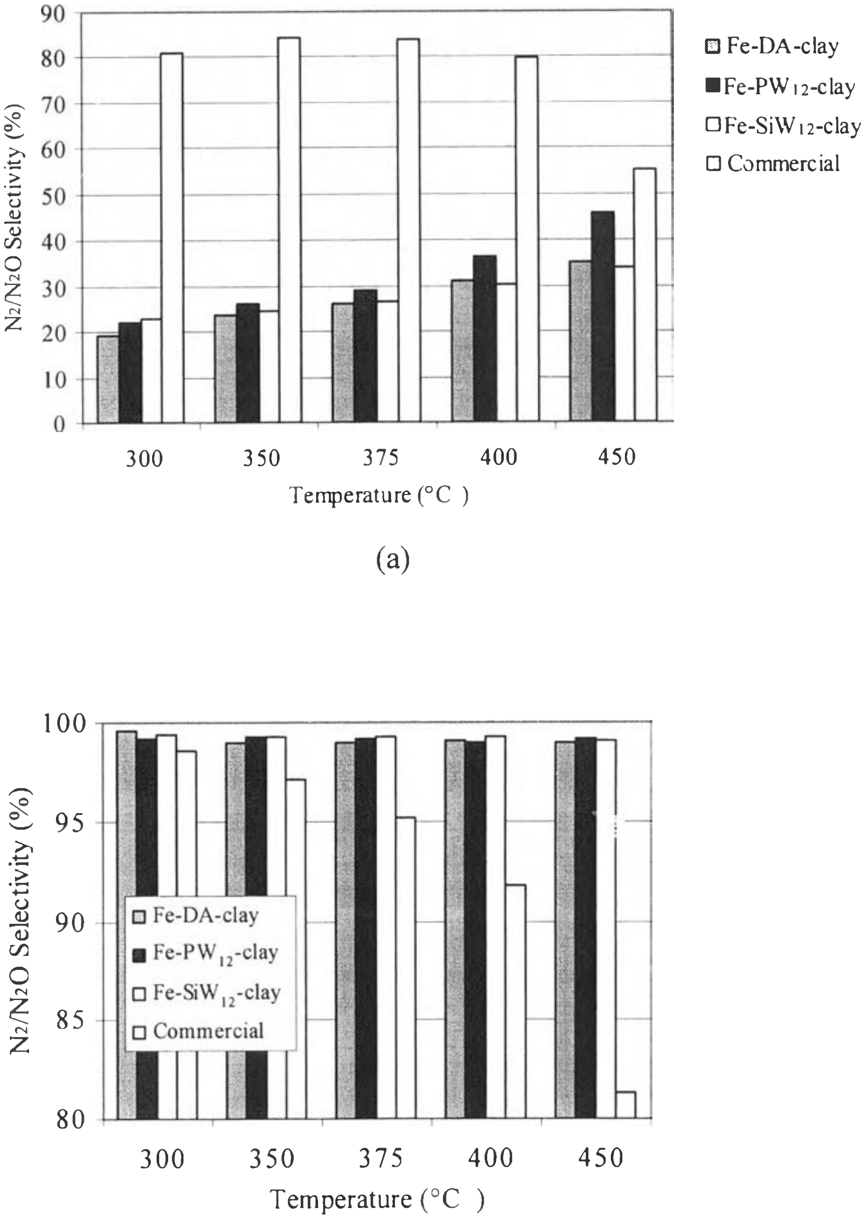


Figure 4.19 Proposed mechanism of the SCR reaction on Fe-Cr/TiO_2 (Cheng *et al.*, 1996).

4.2.3 Comparison between Clay-based Catalysts and the Commercial Catalyst

The NO conversion and N_2/N_2O selectivity data of the commercial catalyst (4.4% V_2O_5 + 8.2% WO_3/TiO_2) were taken from Long and Yang (1999a) for comparison. Figure 4.20 shows NO conversion and N_2/N_2O selectivity of Fe-pillared clay catalysts and the commercial catalyst at 300-450°C. By comparison, the commercial catalyst gave higher NO conversion at all testing temperatures. However, NO conversion of the commercial catalyst decreased after passing though a maximum at 375°C. In addition, the N_2/N_2O selectivity for the commercial catalyst more decreased with increasing temperature of over 350°C. This observation indicated that NH_3 oxidation by O_2 occurred on the commercial catalyst resulting in the decrease in NO conversion at high temperatures (Yang *et al.*, 1992). However, on the other hand, over 99% N_2/N_2O selectivity was achieved over all Fe-pillared-clay catalysts at all testing temperatures.

Although the commercial catalyst gave high NO conversion, another toxic gas N_2O was generated over this catalyst at the commercial SCR operating temperature of 350 – 450°C. Therefore, the clay-based catalysts have high potential to be developed for using as catalysts in SCR process. Although their conversion may be lower than the commercial catalyst, the selectivity at operating temperatures is much higher. More amount may be needed to get higher conversion with still high selectivity.



(a)

(b)

Figure 4.20 Catalytic activity comparison between the commercial catalyst and Fe-pillared-clay catalysts: (a) NO conversion and (b) N_2/N_2O selectivity.