



CHAPTER IV

MODIFICATION OF ORGANOCCLAY AND POROUS CLAY HETEROSTRUCTURES

4.1 Abstract

In this work, bentonite clay was modified by quaternary alkylammonium cations (CTAB) to obtain organoclay. Subsequently, organoclay was reacted by co-surfactant and silica sources to obtain porous clay hetero structures (PCH). By calcination method, the surfactant templates were removed from PCH. Products were characterized by N_2 adsorption-desorption, XRD, SEM, and FTIR techniques. The results reveal that the organoclay had BET surface area of $8 \text{ m}^2/\text{g}$, average pore diameter in the range of 11.0 nm, and pore volume of 0.022 cc/g, respectively. While PCH had a result of $594 \text{ m}^2/\text{g}$, average pore diameter in the range of 5.0 nm, and pore volume of 0.737 cc/g, respectively. From the XRD results, organoclay had the basal spacing increased from the beginning (bentonite 1.21 nm) to 3.88 nm. The pattern of PCH was different from organoclay that confirmed the structure of clay was changed. From SEM images, bentonite and organoclay exhibited a layered or platelike structure, but the structure of PCH was different from initial material. The plate structure was disappeared but the rough structure was presented.

keywords : Porous clay heterostructures (PCH), Organoclay, Bentonite

4.2 Introduction

Recently, the discovery of a new class of porous materials known as porous clay heterostructures (PCH) has been proposed (Galarneau *et al.*, 1995). This porous material was prepared by surfactant-directed assembly of silica in the two dimensional interlayer spacing of clays (Pires *et al.*, 2004 and Polverejan *et al.*, 2000). The PCHs materials have important properties such as exhibiting high surface areas with uniform and specific pore sizes in the rarely observed supermicropore to small mesopore region (Polverejan *et al.*, 2002). In the synthesis of PCH, layered clays were

first intercalated with cationic surfactants. Neutral amine co-surfactant molecules were then intercalated along with silica species which leads to the polymerization of siloxane network surrounding the surfactant micelles in the clay galleries. Then, an open-framework of silica was formed in the galleries after surfactant removal (Zhu *et al.*, 2002). From this viewpoint, these porous materials could find application in many fields. The PCH surface area is higher than that of organoclay, making it suitable for easily modified by functional group and higher surface area for scavenging system. The previous work (Prakobna *et al.*, 2007) showed the dramatically enhanced surface area of PCH compared to bentonite and successfully attached the surface of PCH with methyl group. These modified PCH exhibited the increasing of ethylene adsorption. The expanded work (Srithammaraj *et al.*, 2008) involved the modification of PCH's surface by thiol group to enhance the conductive properties of these PCHs. In 2009, a PCH surface was modified by Fe ions and then blended with polylactide for low oxygen gas permeability in food packaging (Mattayan *et al.*, 2009).

This work was focused on another point of view: the PCH was prepared to increase the surface area, pore volume, and pore diameter in order to limit the particle size of sulphur that was mixed with PCH. Thus, the control release of sulphur could be obtained.

4.3 Experimental

4.3.1 Materials

Na-Bentonite, (Mac-Gel® GRADE SAC), was obtained from Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of bentonite is 100 mmol/100g of clay. Cetyltrimethylammonium [$C_{16}H_{33}N^+(CH_3)_3$] bromide (CTAB) was supplied by Fluka. Dodecylamine, $C_{12}H_{27}N$, (MW=185.35), (98% purified) was supplied by Aldrich. Tetraethyl orthosilicate (TEOS), (MW=208.33), were purchased from Fluka. Methanol (CH_3OH) was supplied by Lab Scan and Hydrochloric acid (HCl) was supplied by Carlo Erba.

4.3.2 Purification and pH Adjustment of Bentonite

Bentonite was pulverized and sieved through 325 mesh. The 100-g of the passing part was treated with 1000 ml of 0.5 M-HCl solution at room temperature for 24 h. After that, the solid part was separated by centrifugation and then washed with distilled water until the pH value near 7. The samples was dried in an oven overnight and again pulverized in a mortar.

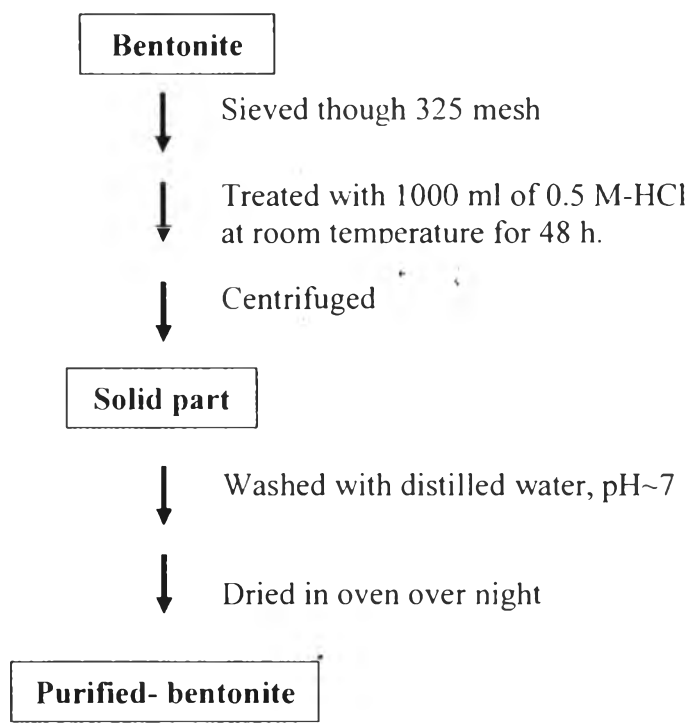


Figure 4.1 Diagram of purification of bentonite.

4.3.3 Synthesis of Organomodified Bentonite

Each purified-bentonite was converted into a quaternary ammonium exchange form by ion exchange with cetyltrimethylammonium bromide. In first container, 100 g of Na-bentonite was swollen in 2 L of water for 24 h, and in second container 0.1 M of CTAB was prepared for 2000 ml. The solution was heated at 50°C until it became transparent. Then solutions of two containers were mixed for 24 h at 50°C 400 rpm. The organomodified bentonite was filtered and washed with mixture of methanol and water (1:1 v/v) several times. It was dried in a vacuum oven at 80°C until completely dried.

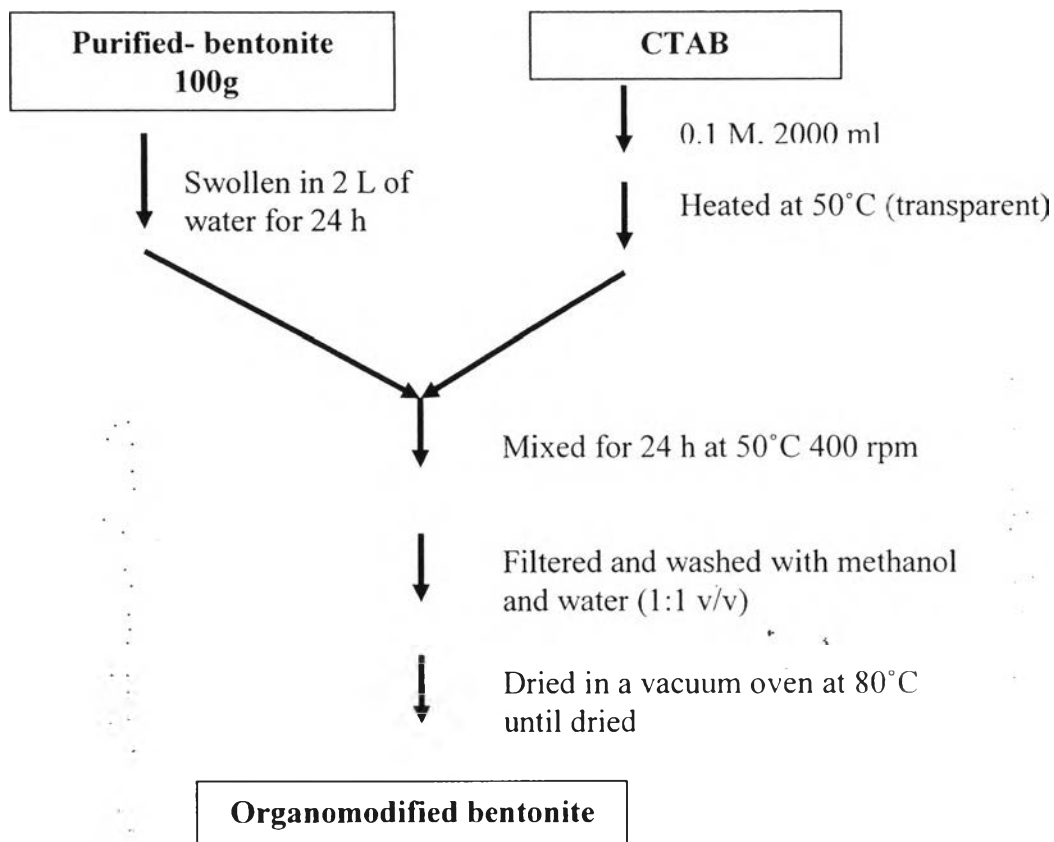


Figure 4.2 Diagram of preparation of organomodified bentonite.

4.3.4 Synthesis of Porous Clay Heterostructures (PCH)

The obtained organoclay was stirred in dodecylamine for 30 min at 50°C following which TEOS was added (at molar ratio of organoclay:dodecylamine:TEOS was 1:20:50). The resulting suspension was stirred for further 4 h at room temperature. After the reaction time the solid was separated from solution again by filtration and dried at 80°C until dried. The surfactant was removed from the as-synthesized PCH by calcination, The as-synthesized PCH was calcined at 600°C for 6 h using a temperature ramp rate of 10°C /min.

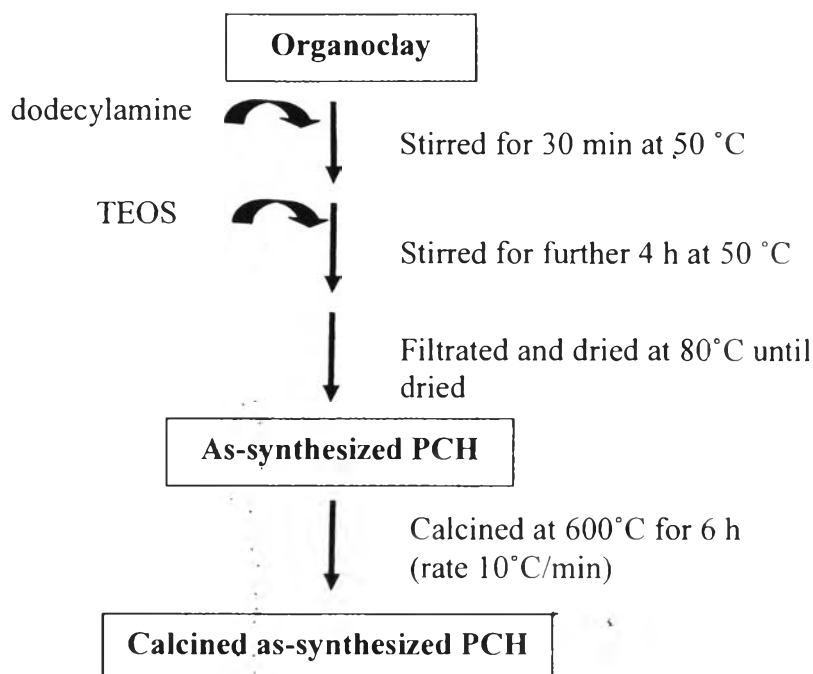


Figure 4.3 Diagram of synthesis of PCH.

4.3.5 Characterization

X-ray diffraction patterns were measured on a Bruker AXS model D8 Discover diffractometer with Ni-filtered Cu K_{α} radiation operated at 40 kV and 40 mA. The powder samples were observed on the 2θ range of 1-10 degree with a scan speed of 0.5 sec/step and an increment 0.02 degree/step.

N_2 adsorption-desorption isotherms were obtained at -196°C on a Quantachome Autosorb-1. Powder samples were degassed at 150°C during 12 h under vacuum prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.

Scanning electron microscopy was performed on Hitachi S-4800 Model. The specimens were coated with platinum under vacuum to make them electrically conductive.

FT-IR spectra of bentonite, organoclay, and PCH were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of $4000\text{--}400\text{ cm}^{-1}$

with 32 scans at a resolution of 2 cm^{-1} . KBr pellet technique was applied in the preparation of powder samples. The incorporation of organic group into silicate network was investigated by using FTIR technique.

4.4 Results and Discussion

4.4.1 FTIR Results

Bentonite, Organoclay, and PCH were initially characterized by using FTIR method to confirm the presence of surfactant in organoclay and the change of structure of PCH. The broad peak around 3500 cm^{-1} was assigned to the stretching vibration of the silanol associated with the silica structure. The peak at 1100 , 1000 , and 800 cm^{-1} were assigned to the stretching vibration of the SiO_4 units, the asymmetric and symmetric stretching vibrations of the Si-O-Si linkage, respectively. The sharp peaks at 2935 and 2860 cm^{-1} in organoclay were assigned to asymmetric and symmetric vibrations of methyl and methylene groups of surfactant. The FTIR spectra of PCH was much different from starting bentonite indicated by the shift of peak at 1000 cm^{-1} to 1100 cm^{-1} and the absent of peaks 2935 and 2860 cm^{-1} were confirmed that the surfactant was removed after the calcination.

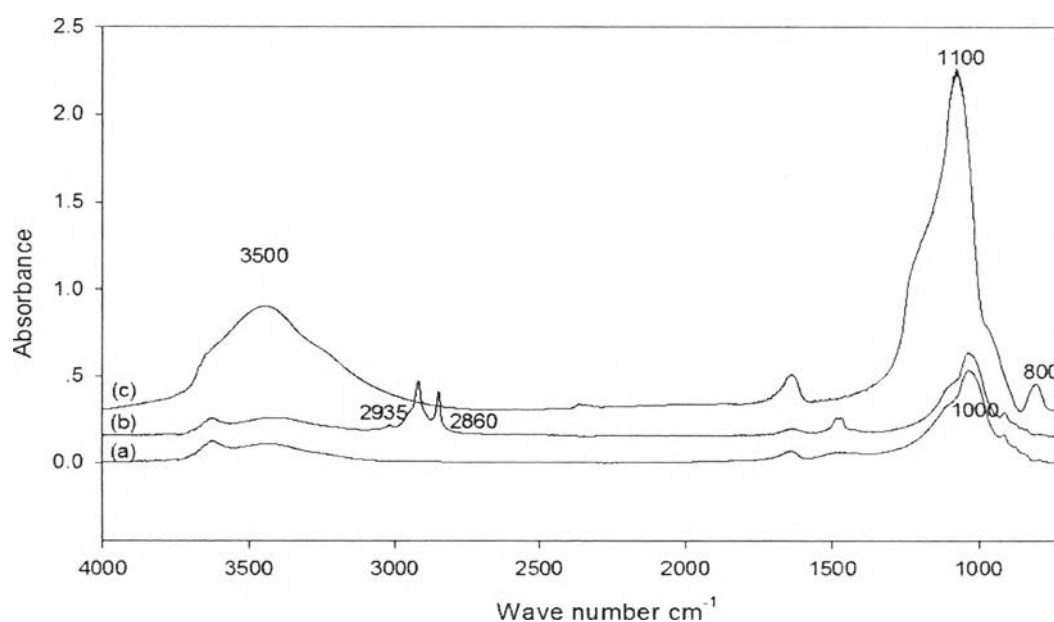


Figure 4.4 FTIR spectra of bentonite (a), organoclay (b) and PCH (C).

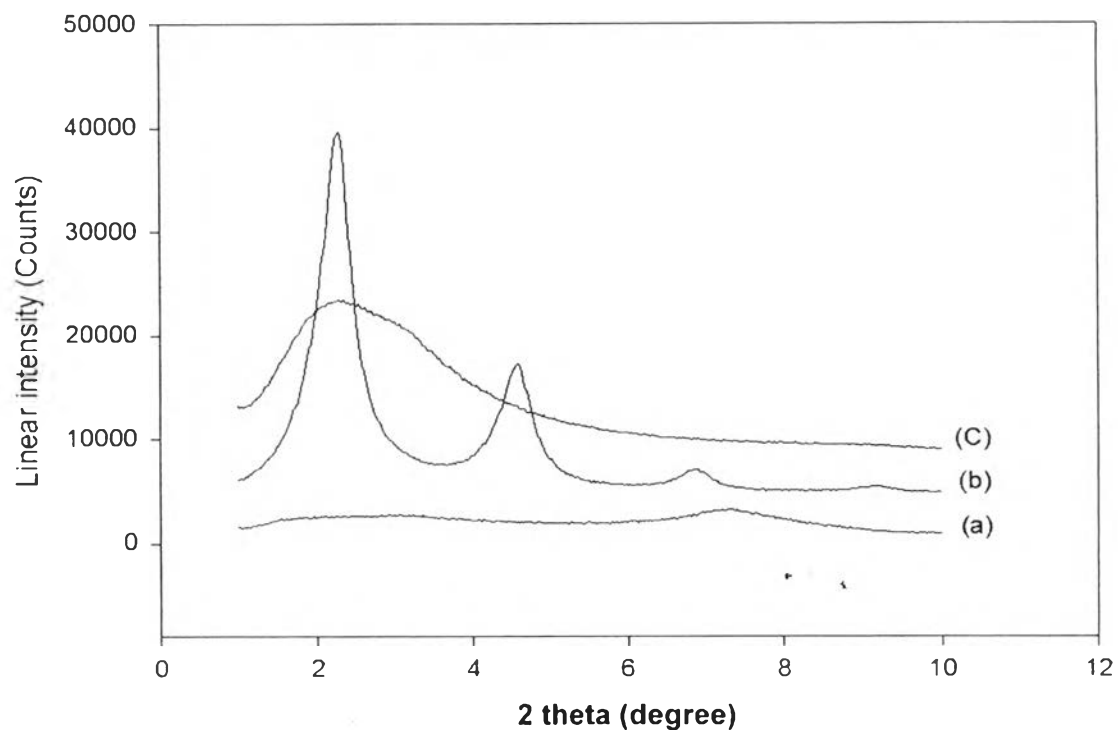


Figure 4.5 XRD patterns of : (a) bentonite, (b) organoclay, (c) PCH.

Table 4.1 Basal spacing of Bentonite, Organoclay, and PCH

Sample	2 θ (degree)	d-value (nm)
Bentonite	7.32	1.21
Organoclay	2.28	3.88
PCH	2.21	3.82

4.4.2 XRD Results

The XRD patterns of bentonite, organoclay, and PCH are shown in Figure 4.5 and Table 4.1 presented that the basal spacing of BTN is 1.21 nm. After bentonite was treated with cetyltrimethyl-ammonium bromide (CTAB) to obtain organoclay, the peak of starting clay at $2\theta = 7.32^\circ$ ($d = 1.21$ nm) disappeared (Figure 4.5(b)). Two strong peaks were observed at lower angle as a result of the successful intercalation of cationic surfactant in the interlayer of bentonite. The clay galleries

were first opened up by the intercalation of the surfactant cetyltrimethylammonium cation. Subsequently, neutral amine co-surfactant was then intercalated between clay layers to form micelle templates. Then silica sources (TEOS) was introduced to polymerize surrounding the surfactant micelles in the galleries of clay. By calcination method, the surfactant templates were removed from as-synthesized PCHs, resulting in the formation of porous structures.

The XRD patterns of PCH are shown in Figure 4.5(c). PCH peak was observed board peak at $2\theta = 2.21^\circ$ ($d = 3.82$ nm) and the pattern was different from organoclay. A possible reason might be due to the disordered structure of silica framework which was formed in the galleries of clay shielding a highly regular interstratifications of the clay layers but it still had some pattern order structure that presenting in PCH.

4.4.3 N₂ Adsorption-Desorption Results

The N₂ adsorption-desorption results are presented in Figure 4.6 and Table 4.2. The isotherm of Bentonite shows a characteristic of non-porous solid indicating low adsorption amount of nitrogen and present a plateau exactly parallel to the pressure axis. Moreover, the BET surface area of bentonite was 55 m²/g. After modification of organoclay, it showed a decrease in surface area and pore volume; however an increase in pore diameter was observed. A possible reason might be due to the presence of surfactant in the interlayer clay, it blocked N₂ gas to adsorb into the pore. After modification of PCH, the surface area PCH was significantly increased to 594 m²/g that confirmed the structure of clay was changed from plate structure to porous structure.

Table 4.2 Porosity characteristics of bentonite, organoclay, and PCH

Sample	Multipoint BET surface area (m ² /g)	Average pore diameter (nm)	Total pore volume (cc/g)
Bentonite	55	8.7	0.120
Organoclay	8	11.0	0.022
PCH	594	5.0	0.737

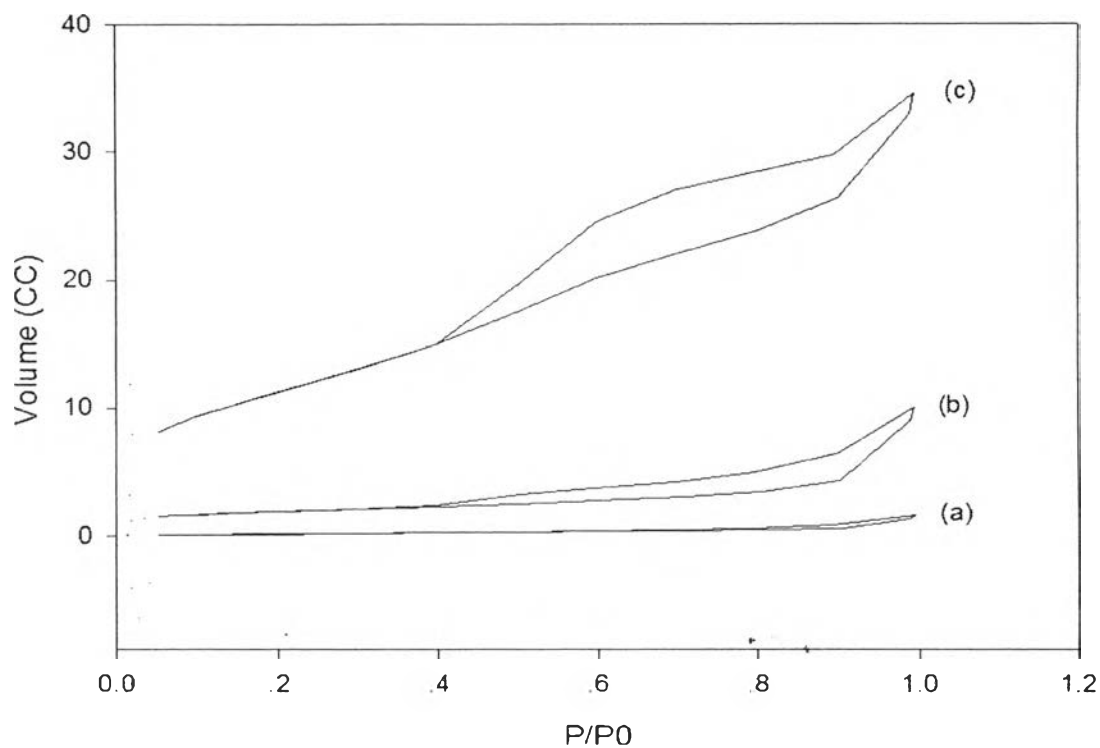


Figure 4.6 N₂ adsorption-desorption isotherms of (a) organoclay, (b) bentonite, (c) PCH.

4.4.4 SEM Results

Bentonite exhibited a layered or platelike structure in SEM image (Figure 4.7(a)–(b)), the plates were tightly overlapped that confirmed by d-value of XRD. After modification of organoclay, the plate structure was still observed, it could not find the difference of structure by using only SEM image because organoclay had wider spacing than bentonite.

After modification of PCH, the structure of clay was different from initial material. The plate structure was disappeared but the rough structure was presented, due to the replaced of silica source between interlayer of clay. Since the interlayer was expanded and the new formulation of silica not strong enough, it collapsed during modification of PCH formulation process and crushing process.

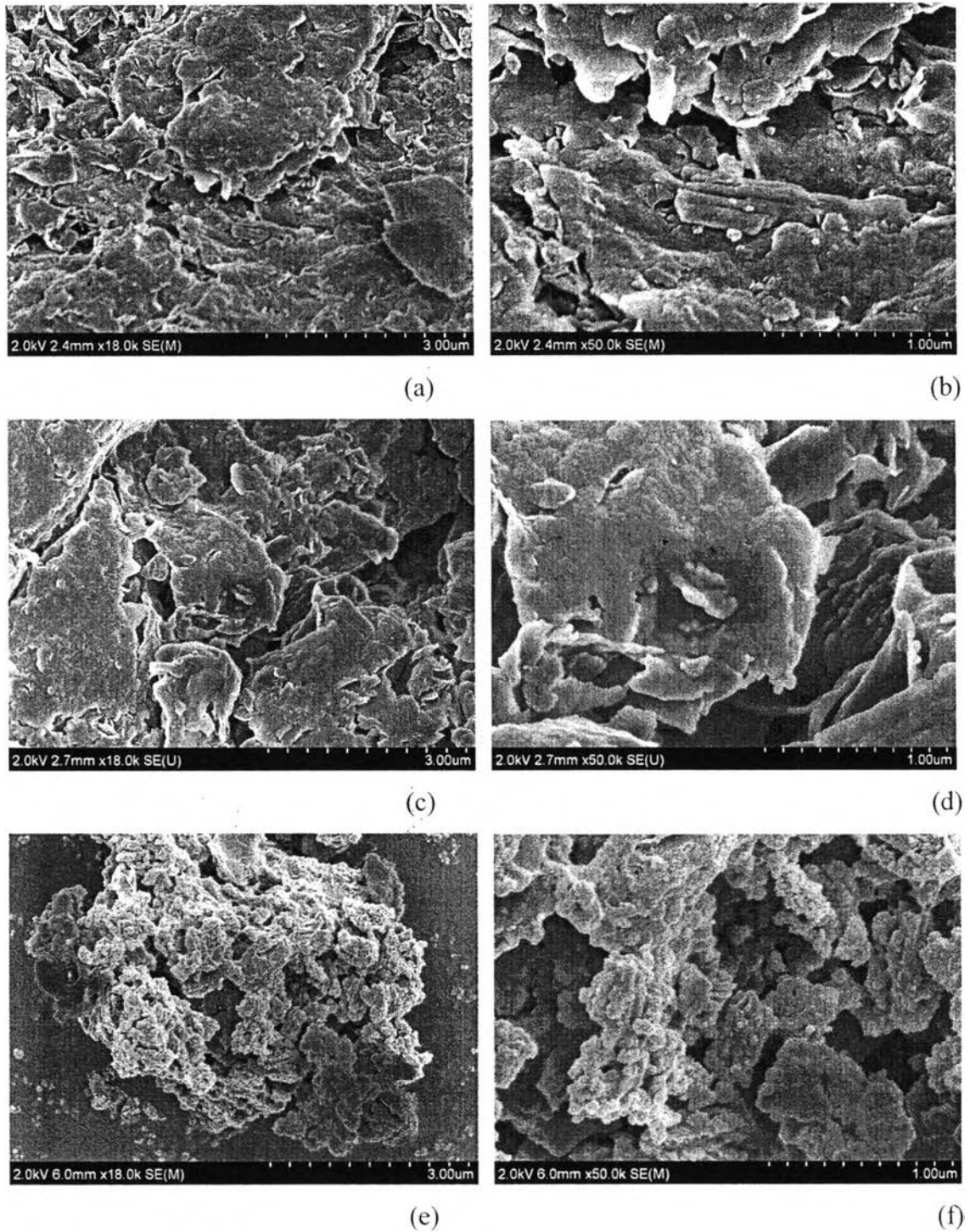


Figure 4.7 SEM images of (a) and (b) bentonite, (c) and (d) organo clay, (e) and (f) PCH with magnification 18.000X and 50.000X, respectively.

4.5 Conclusions

Na-bentonite clay was derived to organoclay and porous clay heterostructures (PCH), respectively. When bentonite was treated with CTAB to be organoclay, the distance between clay layers increased as investigated by XRD. Furthermore, there was obvious broad peak observed in the XRD patterns of PCH due to the disordered structure of silica framework which was formed in the galleries of clay shielding a highly regular interstratifications of the clay layers, but it remain had some pattern order structure that presenting in PCH. From the analysis of N_2 adsorption-desorption data, the results showed that PCHs had the highest surface area of $594 \text{ m}^2/\text{g}$. The isotherms of PCH belong to type IV, corresponding to mesoporous adsorbents. From SEM images, bentonite and organoclay exhibited a layered or platelike structure, but the structure of PCH was much different from initial material. The plate structure was disappeared but the rough structure was presented. Above data provides the potential of PCH which owns high surface area and high porous for sulphur bentonite preparation.

4.6 Acknowledgements

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4.7 References

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