

## CHAPTER II

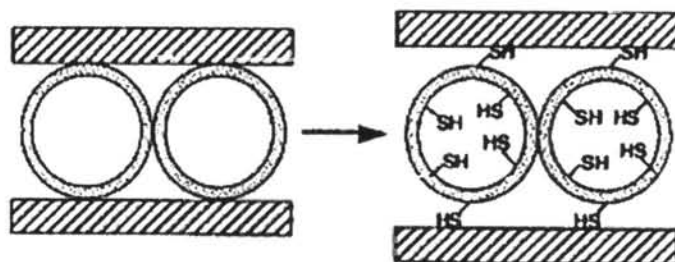
### LITERATURE REVIEW

#### 2.1 Porous Clay Heterostructures (PCH)

Since the surfactant used as templates for M41S synthesis can be intercalated into the interlayer galleries of clays, templated synthesis could be applied for the synthesis of highly porous clays. Many types of clay, such as fluorohectorite, synthetic saponite, montmorillonite and vermiculite, can be used to synthesize the porous clay heterostructures (PCH).

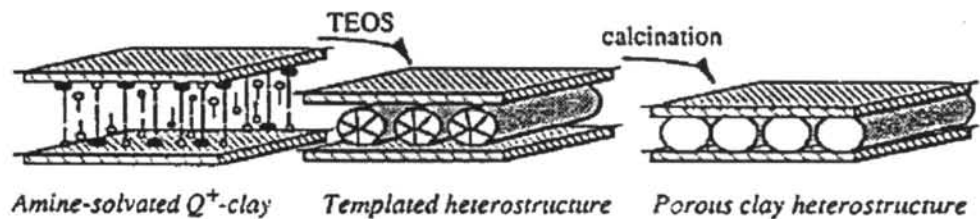
In 1995, Galarneau *et al.* reported on the discovery of a new material known as porous clay heterostructure (PCH). The PCH was prepared from fluorohectorite which are 2:1 mica-type layered silicate. These intercalation compounds are formed through the surfactant micelle ordering of silicate species in the restricted two-dimensional intragallery region of host smectite clay. The obtained materials afford the materials with uniform pore diameters in the supermicropore to small mesopore range (1.5 – 3.0 nm).

Mercier and Pinnavaia (1998) proposed the first potential environmental application of a porous clay heterostructure. A functionalized PCH for heavy metal ion ( $\text{Hg}^{2+}$ ) trapping was prepared by the grafting of 3-mercaptopropyl trimethoxysilane to the framework pore walls of a porous fluorohectorite clay heterostructure as shown in Fig. 2.1. The results showed that the immobilized thiol groups (up to 67%) are accessible for  $\text{Hg}^{2+}$  trapping.

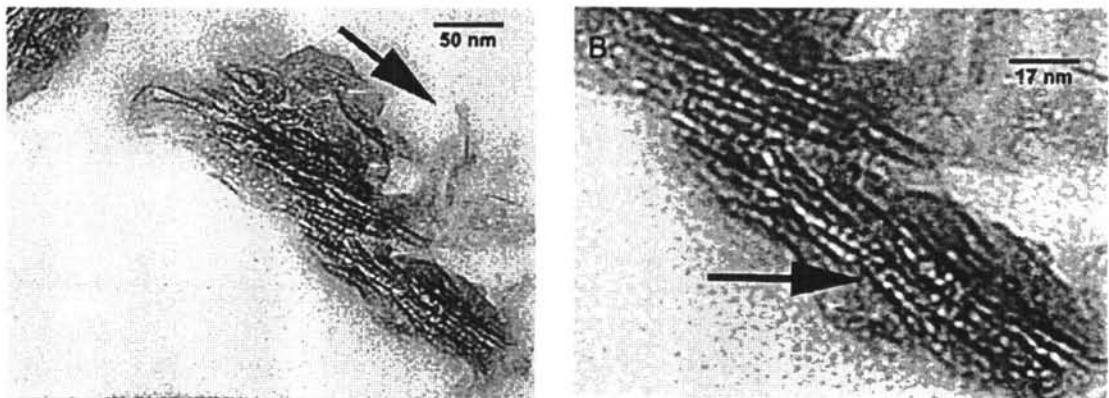


**Figure 2.1** Grafting of mercaptopropylsilane groups to the inner and outer walls of mesostructural silica intercalated in smectite clay (Mercier and Pinnavaia, 1998).

Another type of clay was synthesized by Polverejan *et al.* (2000). It was a porous clay heterostructure from synthetic saponite clay with targeted layer charge densities in the range of  $x = 1.2 - 1.7 e^-$  units per  $Q^+_x[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4$  unit cell. The total acidity (0.64-0.77 mmol/g) increased with the saponite layer charge density ( $x$ ), indicating that the acidity is correlated with the number of protons balancing the clay layer charge after calcination. The BET surface areas are 800-920  $m^2/g$  and pore volumes are 0.38-0.44  $cm^3/g$ . The formation of porous clay heterostructure are presented in Fig. 2.2. Moreover, these materials showed the unique pore structure in the supermicropore to small mesopore range about 1.5-2.3 nm as can be seen in TEM images (Fig. 2.3) and the thermal stability is up to at least 750°C.



**Figure 2.2** Schematic representation of porous clay heterostructure (PCH) formation through surfactant-directed assembly of open framework silica in the galleries of a layered silicate co-intercalated by a quaternary ammonium ion and a neutral amine cosurfactant (Polverejan *et al.*, 2000).



**Figure 2.3** TEM images of saponite heterostructure (Polverejan *et al.*, 2000).

In 2002, they have further studied the functionalization of PCH derived from synthetic saponite through postsynthesis grafting reactions using  $\text{AlCl}_3$  and  $\text{NaAlO}_2$  as alumination agents (Polverejan *et al.*, 2002). The resulting Al-SAP/PCH intercalates still remain the pore in range of supermicropore to small mesopore and posses significantly enhanced acidity. Furthermore, they reported that the catalytic activity for cumene cracking is high (~50-60%), This opens up a new opportunites for applications in acid catalysis.

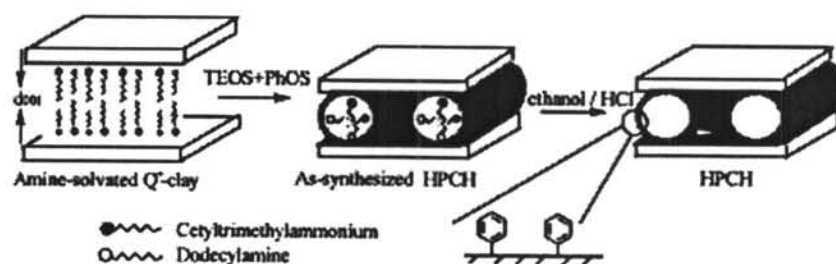
Ahenach *et al.* (2000) synthesized the porous clay heterostructures from the two different clays, natural montmorillonite and synthetic saponite, with large surface areas (~1000  $\text{m}^2/\text{g}$ ) and pore volumes (0.7  $\text{cm}^3/\text{g}$ ). Successful grafting of  $\text{AlO}_x$ -entities on the PCH surfaces has been carried out using the aluminium acetylacetonate complex. The acidity of the Al-grafted PCH materials has been investigated via the adsorption of probe molecule ( $\text{NH}_3$  and acetonitrile- $d_3$ ). As a result of the creation of Si-(OH)-Al bonds which give rise to a strong Bronsted acidity and thermally stable till 300°C.

The study of the cation exchange capacity (CEC) of calcined and extracted-porous clay heterostructures was reported by Benjelloun *et al.* (2001). By exchange of ammonium cations in the pore structure of the two PCH, derived from natural montmorillonite and synthetic saponite. They proposed three possible methods for the formation of  $\text{NH}_4^+$ -exchanged PCH forms : (1) adsorption of ammonium under a gas flow on PCH in acidified methanol; (2) direct exchange in  $\text{NH}_4\text{Cl}$  solution; (3) solvent extraction with  $\text{NH}_4\text{Ac}/\text{EtOH}/\text{H}_2\text{O}$ . When comparing the different methods for exchange PCH, the adsorption under  $\text{NH}_3$  gas flow proves to be the best method. Furthermore, the extracted PCH have a higher surface area and pore volume than the calcined ones. Solvent extraction results in the removal ~85-90% of the organics from the PCH precursors.

Recently, Zhou *et al.* (2004) explored the possibility of the synthesis of a novel nanoporous silicoaluminum montmorillonite heterostructures (Si/Al-MMT) by adding alumina isopropoxide, using ion exchange and self-assembly techniques. The acidity of Si/Al-MMT was improved owing to the formation of mixed oxide pillars with a slight loss of thermal stability when comparison to montmorillonite heterostructures (Si-MMT) which prepared by the analogous procedures. The

synthetic Si/Al-MMT are potentially effective solid acid catalysis for the Friedel-Crafts alkylation of catechol with *tert*-butyl alcohol to synthesize butyl 4-*tert*-butylcatechol (4-TBC). Under experimental condition, the conversion of catechol is 76.8% and the selectivity of 4-TBC is 85.2%.

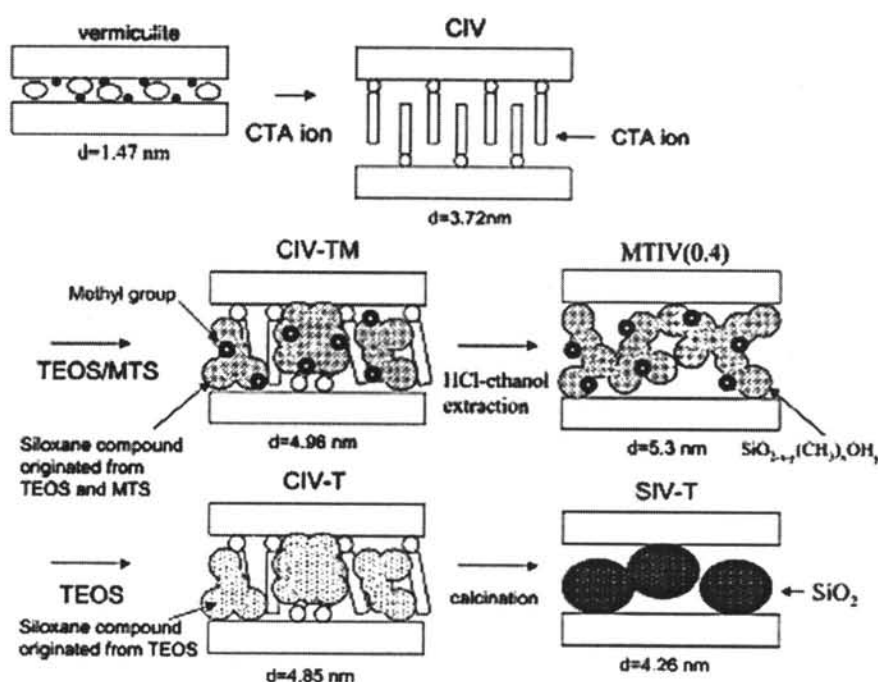
Wei *et al.* (2004) synthesized a novel ordered organic-inorganic hybrid porous clay heterostructure (HPCH). This material prepared through the surfactant-directed assembly of organosilica in the galleries of montmorillonite. The reaction involved hydrolysis and condensation of phenyltriethoxysilane and tetraethoxy silane (also called “one-pot synthesis”) in the presence of intergallery surfactant templates. The formation mechanism of hybrid porous clay heterostructure are illustrated in Fig. 2.4. The surfactant templates were removed from the pores by solvent extraction. HPCH had BET surface areas of 390–771 m<sup>2</sup>/g, pore volumes of 0.3–0.59 cm<sup>3</sup>/g, and the framework pore sizes in the supermicropore to small mesopore range. These hybrid porous clay heterostructures with hydrophobicity and acidity possibly find their application in catalysis, adsorption and separation chemistry.



**Figure 2.4** Schematic illustration of mechanism for formation of hybrid porous clay heterostructure (HPCH) through surfactant-directed assembly of organosilica in the galleries of clay (Wei *et al.*, 2004).

Nakatsuji *et al.* (2004) reported on the synthesis of porous vermiculite with organic-inorganic hybrid pillars using HCl/ethanol method after intercalation of tetraethoxysilane (TEOS), methyltriethoxysilane (MTS) or TEOS/MTS into the cetyltrimethylammonium ion (CTA)-exchanged vermiculite. The products retained their layered structure, due to the formation of stable pillars by the polymerization of

hydrolyzed TEOS and MTS during the HCl/ethanol treatment up to  $0.5 \text{ mol/dm}^3$ . The BET surface areas increase to above  $500 \text{ m}^2\text{g}^{-1}$  with an increase in the HCl concentration to  $0.4 \text{ mol/dm}^3$ , corresponding to that of the calcined product. However, the pore sizes of HCl/ethanol-treated materials were narrower than those of the calcined product, owing to the formation of the polysiloxane networks in the gallery as can be seen in Fig. 2.5. A water adsorption study showed that the product treated with a TEOS/MTS mixture had a hydrophobic surface as a result of the successful incorporation of methyl groups at the surface of the pillars. This novel method is advantageous for the synthesis of organophilic pillared clays with different kinds of organic materials in the interlayers.



**Figure 2.5** Schematic representation of the formation of the pillars in vermiculite (Nakatsuji *et al.*, 2004).

The adsorption properties of porous clay materials which prepared by the gallery templated synthesis were studied by Pires *et al.* (2004). The possibility of using such materials as adsorbents of volatile organic compounds, due to their textural and hydrophobic characteristics, was studied by the adsorption of ethanol and methyl ethyl ketone and water for comparison. Their potential uses as adsorbents

for the purification of methane, e.g., for upgrading natural or landfill gas, were also studied by the determination of the room temperature adsorption isotherms of carbon dioxide, ethane, methane and nitrogen, where high initial selectivity values were obtained for the methane/carbon dioxide separation.

## 2.2 Polypropylene Nanocomposites

Polypropylene (PP)-clay hybrids (PPCH) have been prepared by simple melt-mixing of three components, i.e., PP, maleic anhydride modified polypropylene oligomers (PP-g-MA), and clays intercalated with stearylammonium (Kawasumi *et al.*, 1997). It is found that there are two important factors to achieve the exfoliated and homogeneous dispersion of the layers in the hybrids: (1) the intercalation capability of the oligomers in the layers and (2) the miscibility of the oligomers with PP. Almost complete hybrids were obtained in the case where the PP-g-MA has both intercalation capability and miscibility.

The preparation of nanoclay-reinforced polypropylene nanocomposites by mean of melt processing was investigated (Ton-that *et al.*, 2004). In order to better understand the effect of formulation and processing conditions on dispersion and the interface of PP nanocomposites, which greatly affect their morphology and performance. They found the preparation of PP nanocomposites is strongly influenced by various parameters: chemistry and concentration of the coupling agent, chemistry and concentration of the organo-nanoclay, and mixing conditions, etc.

Recently, Ding *et al.* (2005) reported on the structure and properties of PP/organo-clay nanocomposites compatibilized with PP solid-phase graft by the melt intercalation method. The intercalated structure of the nanocomposites was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD and TEM results showed that a typical intercalated structure was formed in the composites. The results of mechanical properties showed that the impact strength and the modulus of the nanocomposites were improved significantly compared with those of the neat PP.

Fabio *et al.* (2006) studied the thermal degradation of polypropylene-montmorillonite nanocomposites prepared by melt mixing. They found that the

absence of pristine clusters of the clay and the presence of intercalated and exfoliated structures were shown for all investigated samples. The nanocomposites prepared by using maleic anhydride grafted PP showed a widespread exfoliation. The thermal behavior and degradation have been studied by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The incorporation of the montmorillonite improves the thermal stability in air atmosphere of all the investigated PP, due to a physical barrier effect of the silicate layers.