

CHAPTER II

THEORY

2.1 Clay

Clay minerals are defined as fine-grained, crystalline, hydrous silicates or phyllosilicates with the structure of the layer-lattice type[30-31]. They are the most common products of water-rock interaction under earth-surface conditions. Clay minerals occur abundantly in nature and their high specific surface area, sorptive and ion exchange properties have been exploited for catalytic applications through decades. Their structures[32] consist of negatively charged layers with strong covalent bonding stacked in aggregates called tactoids and held together by electrostatic forces.

2.2 Structural Features of Clay[33]

All layered silicates can be constructed from two modular units: a sheet of corner-linked tetrahedra and a sheet of edge-linked octahedra. Phyllosilicate minerals have layer structures composed of aluminum octahedral and silica tetrahedral sheets. The tetrahedral sheets and octahedral sheets are held together by sharing apical oxygen.

2.1.1 Tetrahedral Sheets

In the tetrahedral sheet, the dominant cation is Si^{4+} (SiO_2), but Al^{3+} substitutes for it frequently and Fe^{3+} does occasionally. This sheet extends infinitely in two dimensions by each tetrahedron sharing the oxygens at all three corners with three other tetrahedra to form hexagonal network (see Figure 2.1). The apical oxygen points upward in the normal direction to the base.

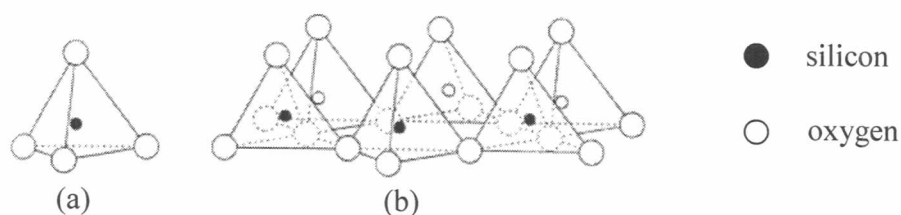


Figure 2.1 A single tetrahedral silica (a), sheet structure (b) of silica tetrahedra arranged in a hexagonal network.

2.2.2 Octahedral Sheets

The octahedral sheet can be thought of as two planes of closest-packed oxygen ions with cations occupying the resulting octahedral sites between the two planes. Connection of the neighboring oxygen ions form a tetrahedron and a sheet of edge-linked octahedra, again extending infinitely in two dimensions. The cations are usually Al^{3+} , Mg^{2+} , but Fe^{2+} or Fe^{3+} can substitute in the octahedral site occasionally.

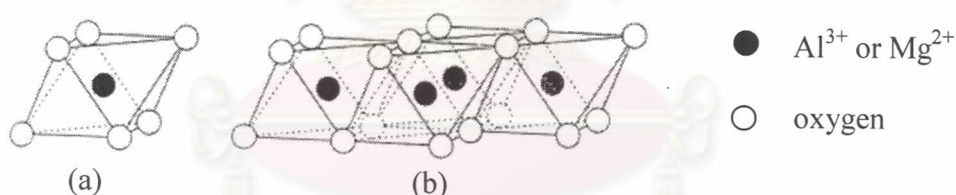


Figure 2.2 A single octahedral unit (a), sheet structure (b) of octahedral unit arranged in a hexagonal network.

2.3 Classification

2.3.1 1:1 Layer Type (T:O)

Each unit of clay layer is composed of one tetrahedral sheet (T) and one octahedral sheet (O). The apical oxygen atoms of tetrahedral sheet are pointed to the octahedral sheet and held together with sharing the oxygen atoms such as kaolinite.

2.3.2 2:1 Layer Type (T:O:T)

A 2:1 layer, two tetrahedral sheets to one octahedral sheet, is formed by inverting a tetrahedral sheet, bringing it down on top of the 1:1 layer. This assemblage makes a tetrahedral-octahedral-tetrahedral (T:O:T) sandwich *e.g.* bentonite, montmorillonite, hectorite.

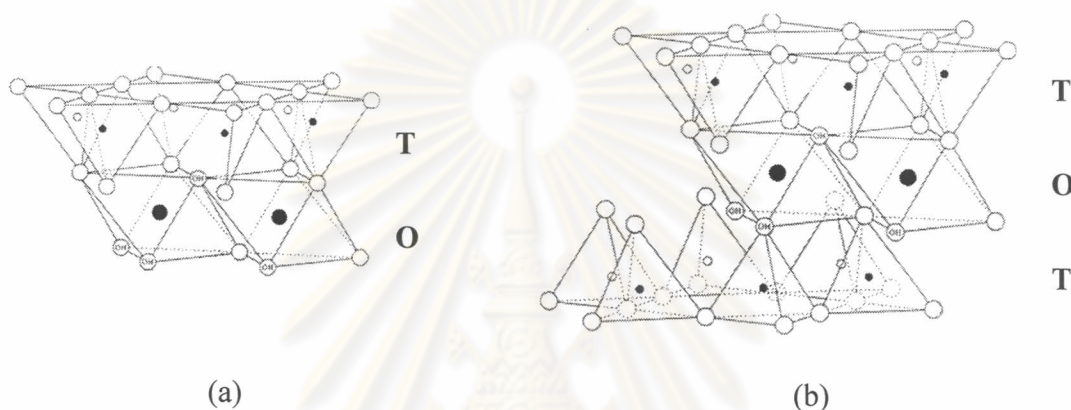


Figure 2.3 1:1 layer type, T:O (a) and 2:1 layer type, T:O:T clay (b) (T = Tetrahedral sheet, O = Octahedral sheet).

2.4 Smectite Clay[34]

Smectite clays are derived from the mineral talc and pyrophyrite which consist of a stacking of charged-neutral layers of the composition $\text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$ and $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$ respectively. Each layer is made of three sheets: an octahedral sheet containing either aluminum or magnesium cations, sandwiched between two tetrahedral sheets consisting of corner-sharing (SiO_4) tetrahedra. Cation substitution[3] either in the tetrahedral or the octahedral sheet results in negative layer charge, which is balanced by additional cations located between the 2:1 layer.

The repeating distance between the clay-layer is called the basal spacing, d_{001} . This value is easily identified by X-ray diffraction technique and it is calculated by Bragg

equation. For example XRD pattern of montmorillonite shows the d_{001} spacing at about 15 Å in air-dried condition.

$$2d \sin\theta = n\lambda \dots\dots\dots \text{Bragg equation}$$

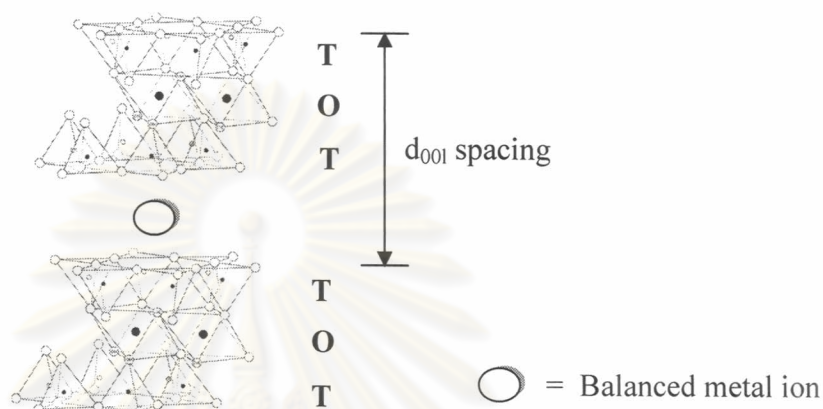


Figure 2.4 Structure of smectite clay.

The most important aspect of the smectite group[5] is the ability for water molecules to be adsorbed between the layers, causing the volume of the minerals increase when they come in contact with water. Thus, the smectites are expanding clays with the basal spacing 10 to 20 Å. The most common smectite, with a general chemical formula of montmorillonite, is $(\frac{1}{2}\text{Ca,Na})(\text{Al,Mg,Fe})_4(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$.

2.4.1 Bentonite Clay[32]

Montmorillonite is the main constituent of bentonite, derived by weathering of volcanic ash. In montmorillonite Mg/Al substitution occurs in the octahedral sheet, with idealized formula $(\text{Si}_8)(\text{Al}_{4-x}\text{Mg}_x)\text{O}_{20}(\text{OH})_4\text{A}_x \cdot n\text{H}_2\text{O}$ (where A is a monovalent or divalent cation). Montmorillonite can expand by several times of its original volume when it adsorbs water.

2.4.2 Hectorite Clay[32]

Hectorite is a natural clay mineral classified as smectite group similar to a bentonite, but there are different cations in octahedral sheet. The octahedral sheets of hectorites are contained of Mg^{2+} . Hectorite have Li/Mg substitution in the octahedral sheet. The general formular of hectorite is $(Si_8)(Mg_{6-x}Li_x)O_{20}(OH)_4A_x \cdot nH_2O$ (where A is a monovalent or divalent cation).

2.5 Properties of Clay[35]

2.5.1 Ion Exchange

Isomorphous substitution of cations in the lattice by lowervalent ions, such as the substitution of aluminum for silicon, magnesium and/or ferrous ion for aluminum or sometimes lithium for magnesium, leaves a residual negative charge in the lattice that is balanced by cations between the layers. These balance cations can be readily replaced by other cations in aqueous solution. In swelling clay mineral, such as, smectites, the interlayer cations can undergo exchange with cations from external solutions. The concentration of exchangeable cations is called CEC, usually measured in milliequivalents per 100 g of dried clay. Since smectites have the highest concentration of interlayer cations, they have the highest cation exchange capacities (typically 70 to 120 meq /100 g). Structural defects at layer edges give rise to additional CEC and a small amount of anion exchange capacity.

2.5.2 Swelling

Many clay minerals adsorb water between their layers, which move the layers apart and the clay swells. For efficient swelling, the energy released by cations and/or layer solvation must be sufficient to overcome the attractive forces (such as hydrogen bonding) between the adjacent layers. In 1:1 clay minerals (kaolinite), water forms strong

hydrogen bonds with hydroxyl groups on hydrophilic octahedral layers, allowing swelling to occur.

With 2:1 clay minerals, the ability to swell depends on the solvation of interlayer cation and layer charge. Clays with 2:1 structures and low layer charge (*e.g.* talc and pyrophyllite) have very low concentration of interlayer cations and therefore do not swell readily. At the other extreme, those with very high layer charges (*e.g.* mica) have strong electrostatic forces holding alternate anionic layers and the interlayer cations together, thus preventing swelling. Those with univalent interlayer cations swell most readily. For those with divalent, trivalent and polyvalent cations, swelling decreases accordingly. The extent of swelling can be observed by measuring interlayer separations using power X-ray diffraction.

2.5.3 Acidity

The interlayer cations contribute to the acidity of clay minerals. Some of these cations may be protons or polarizing cations (*e.g.* Al^{3+}) which give rise to strong Brönsted and Lewis acidity, respectively. The higher electronegativity of M^+ generated the stronger the acidic sites. Brönsted acidity also stems from the terminal hydroxyl groups and from the bridging oxygen atoms. In addition, clay minerals have layer surface and edge defects, which would result in weaker Brönsted and/or Lewis acidity, generally at low concentrations.

2.6 Intercalation[36]

Intercalation is the insertion of guest species in the interlayer region of a layered solid with preservation of the layered structure. The material obtained is called an intercalation compound. Intercalation is proven by the XRD pattern, which must unambiguously show a change in the spacing between adjacent layers, *i.e.* a change in the basal spacing.

2.7 Pillaring[36]

Pillaring is the process by which a layered compound is transformed into a thermally stable micro- and/or mesoporous material with retention of the layer structure. The material obtained is a pillared compound or a pillared layered solid. A pillared derivative is distinguished from an ordinary intercalate by virtue of intracrystalline porosity made possible by the lateral separation of the intercalated guest.

2.8 Pillaring Agent[36]

A pillaring agent is any compound, which can be intercalated between adjacent layers of a layered compound, which maintains the spacing between adjacent layers upon removal of the solvent, and which induces an experimentally observable pore structure between the layers.

2.9 Pillared Clay[37]

Pillared clays are a new family of materials obtained by intercalation of guest molecules such as inorganic polyoxocations or organic molecules to form pillars between the layers of smectite silicates. With a suitable choice of polyoxocations the separation between layers can be kept stable. The resulting material has a high specific surface area and a characteristic porous structure which is of great interest because of its potential application in various fields *e.g.* catalysis and adsorption.

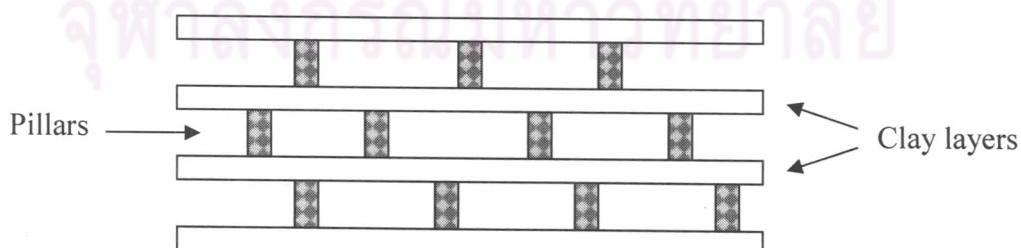
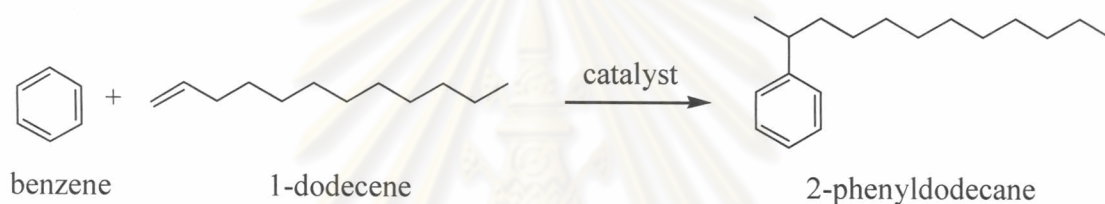


Figure 2.5 The model of pillared clay structure (cross section).

2.10 Alkylation[38-40]

Reactions of carbocations with aromatic compounds were first studied in 1877 by the French alkaloid chemist Charles Friedel and his American partner, James Crafts. Carbocations are perhaps the most important electrophiles capable of substituting onto aromatic rings, because this substitution forms a new carbon-carbon bond. This useful reaction is called Friedel-Crafts alkylation. In alkylation, an alkyl group is attached with an aromatic ring in the presence of an acid catalyst and loss of a proton from the intermediate then yields the alkylated aromatic ring. For example the alkylation of benzene with 1-dodecene yields phenyldodecane.



Scheme 2.6 Alkylation of benzene with 1-dodecene.

2.10.1 Carbocation sources for Friedel-Crafts alkylation

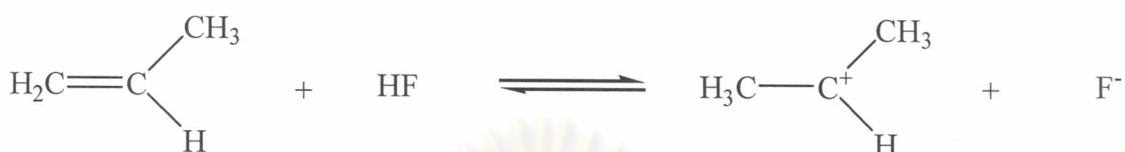
It has several ways to generate carbocations for Friedel-Crafts alkylation. Three methods are most commonly used.

1. In the presence of Lewis acid catalysts such as aluminum chloride (AlCl_3), alkyl halides were found to alkylate benzene to give alkylbenzenes.



Scheme 2.7 Generating carbocation from alkyl halides.

2. Alkenes are protonated by HF to give carbocations. The fluoride ion is a weak nucleophile and does not immediately attack the carbocation. If benzene is present, electrophilic substitution occurs.



Scheme 2.8 Generating carbocation from alkene.

3. Alcohols are another source of carbocation for Friedel-Crafts alkylations. Alcohols commonly form carbocations when treated with boron trifluoride (BF_3). If benzene is present, electrophilic substitution occurs.



Scheme 2.9 Generating carbocation from alcohol.

2.10.2 Limitations of the Friedel-Crafts alkylation

1. Friedel-Crafts reactions work on with benzene, halobenzenes, and activated benzene derivatives. On the other hand, this reaction does not occur on the strongly deactivated systems such as nitrobenzene, benzenesulfonic acid and phenyl ketone.

2. Like other carbocation reactions, the Friedel-Crafts alkylation is susceptible to carbocation rearrangements.

3. Since alkyl groups are activating substituents, the product of the Friedel-Crafts alkylation is more reactive than the starting material so that multiple alkylations can occur.

2.11 The advantages of heterogeneous organic reaction[41]

Heterogeneous organic reactions effected by reagents immobilized on the porous solids are useful to chemists involved with laboratory- and manufacturing-scale synthesis. There are numerous potential advantages but the most important are the followings

1. Good dispersion of active sites can lead to significant improvement in reactivity
2. The constrains of the pore and the characteristic of surface adsorption can lead to useful improvements in reaction selectivity
3. solids are generally easier and safer to handle than liquid or gaseous reagents
4. the supported reagent is easy to remove from the final reaction
5. some supported reagents may be easily reused



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