

CHAPTER II

THEORY

2.1 Clay

Clay minerals are crystalline hydrous aluminosilicates, classified as phyllosilicates, or layered silicate structures. They are the most common products of water-rock interaction under earth-surface conditions. Clay minerals occur abundantly in nature and the unique properties of clays contain high surface area, high sorption, reversible ion-exchange and high acidity. Their acidity as both Brønsted and Lewis types has been exploited for catalytic applications through decades. Many organic reactions use clays as an efficient heterogeneous catalyst. For example, modified smectite clays could be used as highly selective catalysts in organic transformations and green chemistry with excellent yield, high regio- and stereoselectivity. The advantage of clay catalysts over homogeneous catalyst shows at the work up of the reaction mixture which is very simple by filtration [27].

2.2 The structure of clay minerals

Clay minerals possess a layered structure, and their suspension in aqueous solution contains particles with the average diameter of about 2 μm [28]. All layered silicates can form two modular units: a sheet of corner linked tetrahedron and a sheet of edge-linked octahedron. The tetrahedral and octahedral sheets are held together by sharing apical oxygen atoms [29].

2.2.1 Basic units

Tetrahedral sheets

In tetrahedral sheet, the dominant cation is Si^{4+} (as in 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 three oxygen atoms with three other

tetrahedron to form a hexagonal network (Fig. 2.1). They are arranged in a hexagonal pattern with the basal oxygens linking and the apical oxygens pointing upward in the normal direction to the base.

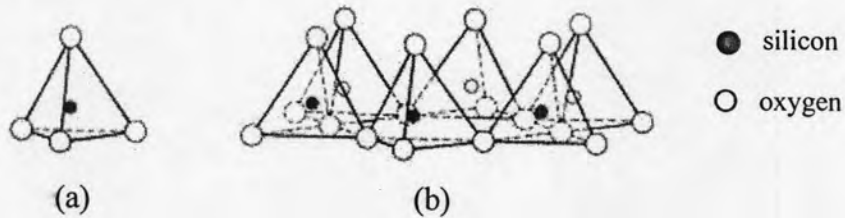


Figure 2.1 A single tetrahedral silica unit (a), and a sheet structure of silica tetrahedral units arranged as a hexagonal network (b).

Octahedral sheets

The octahedral sheet is composed of two planes of closest-packed oxygen ions with cation occupying the resulting octahedral sites between two planes (a). The dominant cation is Al^{3+} , but substituted frequently by Mg^{2+} and occasionally by Fe^{2+} and Fe^{3+} . Connection of the neighboring oxygen ions forms a sheet of edge-linked octahedron as hexagonal network, extending infinitely in two dimensions (b).

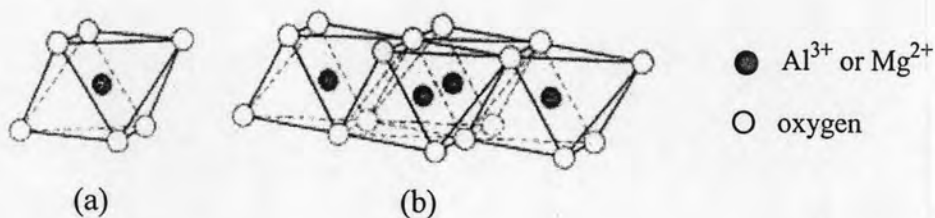


Figure 2.2 A single octahedral unit (a), and a octahedral sheet structure of octahedral unit arranged as a hexagonal network (b).

2.2.2 The combinations of basic sheets

The combinations of basic sheets of clays could be divided into 2 categories:

The 1:1 layered type (T:O)

Each unit of clay layer is composed of one tetrahedral sheet (T) and one octahedral sheet (O). The oxygen atoms at the edge of a tetrahedral sheet are pointed to the octahedral sheet and held together with sharing those atoms.

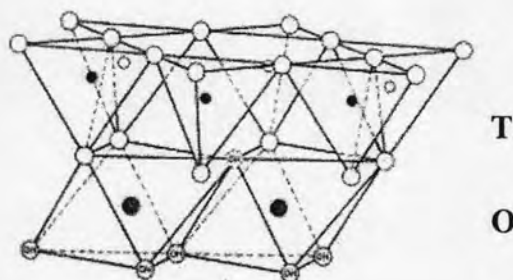


Figure 2.3 Structure of 1:1 layered type (T = tetrahedral sheet, O = octahedral sheet).

The most common of this type of clay is kaolinite, which has the chemical formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It consists of an octahedrally coordinated layer of aluminum oxide and a tetrahedrally coordinated layer of silicon oxide in 1:1 ratio. Kaolinite has the neutral-charged layer; therefore, they are held together by Van der Waals forces. The thickness of each clay layer is about 7 Å, which gives rise to a corresponding characteristic X-ray diffraction peak of about 7 Å.

The 2:1 layered type (T:O:T)

The basic structure of 2:1 clay minerals is made from two silicon tetrahedral layers and one octahedral layer. This combination makes a tetrahedral-octahedral-tetrahedral (T:O:T) sandwich. Pyrophyllite $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$ and talc $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$ are the simplest members of this group.

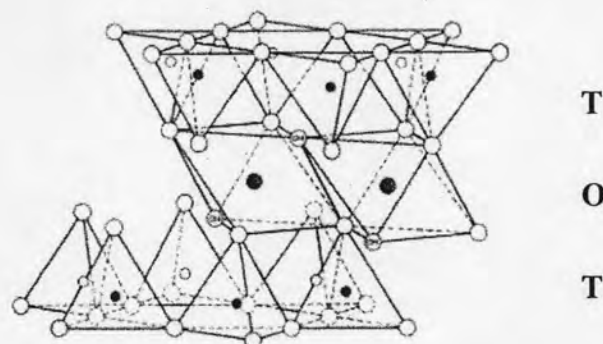


Figure 2.4 Structure of 2:1 layered type (T = Tetrahedral sheet, O = Octahedral sheet).

2.3 Smectite clay minerals [30]

Smectite clays are a family of expandable 2:1 phyllosilicate clay minerals, and are derived from the mineral talc and pyrophyrite which consist of a stacking of charged-neutral layers of the composition $Mg_6Si_8O_{20}(OH)_4$ and $Al_4Si_8O_{20}(OH)_4$, respectively. Cation substitution in either the octahedral sheet (typically from the substitution of low charge species such as Mg^{2+} , Fe^{2+} or Mn^{2+} for Al^{3+}) or tetrahedral sheet (The substitution of Al^{3+} or occasionally Fe^{3+} substitutes for Si^{4+}) results in negative layered charge, which must be balanced by additional cations locating between the interlayer of clay. The interlayer is hydrated, which cations are solvated by water or solvent molecules and is able to move freely in and out of the structure.

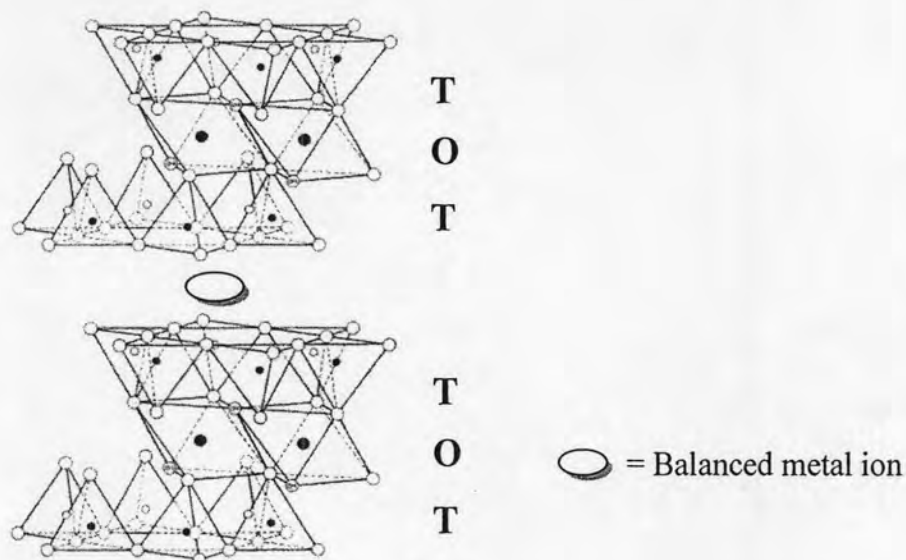


Figure 2.5 Structure of smectite clay.

The most important aspect of the smectite group is the ability for H₂O molecules to be adsorbed in the interlayer region, causing the volume of the clay minerals to increase when they come in contact with water. Thus, the smectites are expanding clays with the basal spacing of 10 to 20 Å. The most common smectite, with a general chemical formula of montmorillonite, is $(\frac{1}{2}\text{Ca,Na})(\text{Al,Mg,Fe})_4(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$. Smectite clays normally occur as extremely small crystals (less than 1 μm), so the identification is usually based on X-ray diffraction technique.

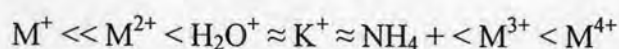
2.3.1 Bentonite clay [31]

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 Properties of clay

2.4.1 Ion exchange [27]

Clays have the ability to adsorb and exchange cations from solution. In most clays, the ideal neutral structure is disrupted by introduction of charged imbalance into the clay sheets. Two main causes of these charged imbalance are (1) isomorphous substitution of cations in the lattice by lower valent ions, such as the substitution of aluminum cation for silicon in the tetrahedral layer, magnesium for aluminum or sometimes lithium for magnesium cations in the octahedral layer and (2) crystal defects. The layers have an overall negative charge which is balanced by adsorption of metal cations into the interlayer of the clay minerals. These balance cations can be readily replaced by other cations in aqueous solution. The property of ion exchange is great fundamental and practical importance in the investigation of clay minerals. In the application of clay mineralogy, it is important because the nature of the exchangeable ion may influence substantially the physical properties of the material. When a solution of a metal cation is used to exchange the interlayer cations of clay, it has been observed that the smaller the size and the higher the charge of the exchange cation, the more powerful that cation at replacing the interlayer exchangeable cations. Similarly the ease of replacement of interlayer cations follows the reverse trend. The following series can be constructed:



increasing exchange power
(decreasing ease of exchange)

Scheme 2.1 The exchange properties of cations with clays.

For the swelling clay minerals, such as smectites, the interlayer cations can be exchanged with cations from external solutions.

The concentration of exchangeable cations (CEC) is measured in milliequivalents per 100 g of dried clay. CEC is often measured by uptake and release of ammonium ions from 1 M ammonium acetate solution, although other cations are sometimes used in place of NH_4^+ . Since smectites have the highest concentration of interlayer cations, they have the highest cation exchange capacities (typically 70-120 mequiv/100 g). Structural defects at layer edges give rise to an additional CEC and a small amount of anion exchange capacity [23].

2.4.2 Swelling [23]

Many clay minerals adsorb water between their layers, which move apart and the clay swells. The energy is released by the attractive forces, such as hydrogen bonding, between the adjacent layers from cations and/or layer solvation. Thus water forms strong hydrogen bonds with hydroxyl groups on hydrophilic octahedral layers in 1:1 clay minerals (kaolinite), allowing the swelling to occur.

With 2:1 clay minerals, the ability to swell depends on the solvation of interlayer cation and the 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 charge (*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.

2.4.3 Acidity of clays [27]

Clay minerals show both Brønsted and Lewis 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 Brønsted acidity. The higher electronegativity of a cation, the stronger acidic sites generated. Brønsted 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 Brønsted and/or Lewis acidity, generally at low concentrations.

A further source of acidity is associated with the $-\text{OH}$ groups of the octahedral layer which protrude into the interlayer region *via* the holes of the ring. The incidence of these protons may be increased by preparing a 'proton-exchanged' clay. This is achieved either a simply exchanging the clay with dilute acid, or less destructively to exchanging the clay with ammonium ions and calcining at 200-300°C to expel ammonia. The exchanged proton can migrate into vacancies on the octahedral layer where they protonate bridging oxygen.

2.5 Intercalation [32]

The insertion of a guest species into the interlayer region of a layered solid is called intercalation, and consequently the layered structure still remains. Intercalation compound can be observed by the XRD pattern, which must unambiguously show an increase in the spacing between adjacent layers, *i.e.* a change in the basal spacing.

2.6 Pillaring [32]

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

2.7 Pillared clay

Pillared clays, a family of microporous materials, were prepared by the exchange of cations and polyoxocations bulk inorganic into the interlayer of swellable clay, leading to the intercalated clays. The intercalated clays are calcined, in order to transfer polyoxocations into pillars, thus leading to the pillared solids. The possibility

of controlling the properties of the pillared solids are performed by changing the natural clay (montmorillonite, bentonite, hectorite, *etc.*) and of intercalating species (polycations based on Al^{3+} , Si^{4+} , Ti^{4+} , Zr^{4+} , Cr^{3+} , Fe^{3+} or Ca^{2+} , *etc.*) [33]. 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. [34]

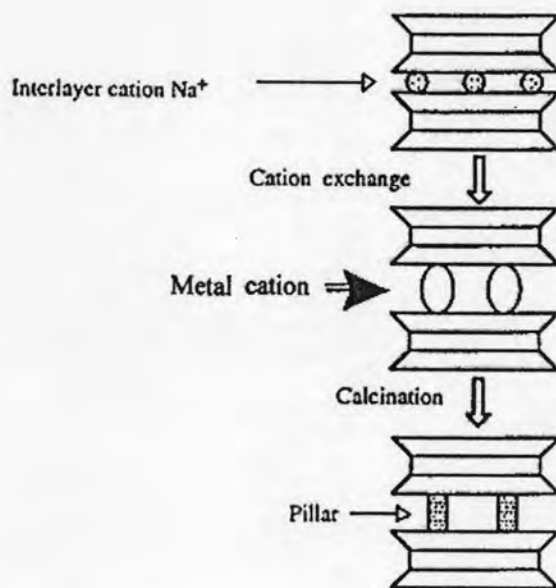


Figure 2.6 Diagram for the preparation of pillared clay compounds [35].

2.7.1 Pillaring agent [32]

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

2.8 Characterization of clays and clay catalysts

2.8.1 Powder X-ray diffraction (XRD) [29]

X-ray powder diffraction (XRD) is an instrumental technique that is used to identify minerals, as well as other crystalline materials. XRD is a technique in which a collimated beam of nearly monochromatic X-rays is directed onto the flat surface of a relatively thin layer of finely ground material. XRD can provide additional information beyond basic identification. Fig. 2.7 shows a monochromatic beam of X-

ray incident on the surface of crystal at an angle θ . The scattered intensity can be measured as a function of scattering angle 2θ . The resulting XRD pattern efficiently determines the different phases present in the sample.

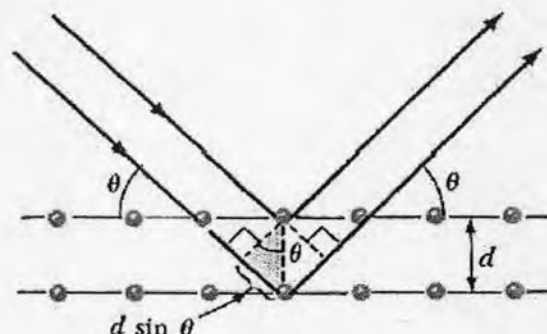


Figure 2.7 Diffraction of X-ray by regular planes of atoms.

Bragg diffraction occurs when a grating (crystal plane) scatters radiation "in phase". This happens when the exit beam is retarded by an integral number of wavelengths. This is known as the Bragg Equation

$$n\lambda = 2 d \sin\theta$$

Where the integer n is the order of the diffracted beam, λ is the wavelength, d is the distance between adjacent planes of atoms (the d -spacings) and θ is the angle of between the incident beam and these planes.

2.8.2 Nitrogen adsorption-desorption isotherm

The N_2 adsorption technique is used to determine the physical properties of mesoporous molecular sieves, such as the surface area, pore volume, pore diameter and pore-size distribution of solid catalysts.

Adsorption of gas by a porous material is described by an adsorption isotherm, the amount of adsorbed gas by the material at a fixed temperature as a function of pressure. Porous materials are frequently characterized in terms of pore sizes derived from gas sorption data. IUPAC conventions have been proposed for classifying pore sizes and gas sorption isotherms that reflect the relationship between porosity and sorption. The IUPAC classification of adsorption isotherms is illustrated in Fig. 2.8. Six types of isotherms are the characteristics of adsorbents that are microporous (type

I), nonporous or macroporous (types II, III, and VI) or mesoporous (types IV and V) [36].

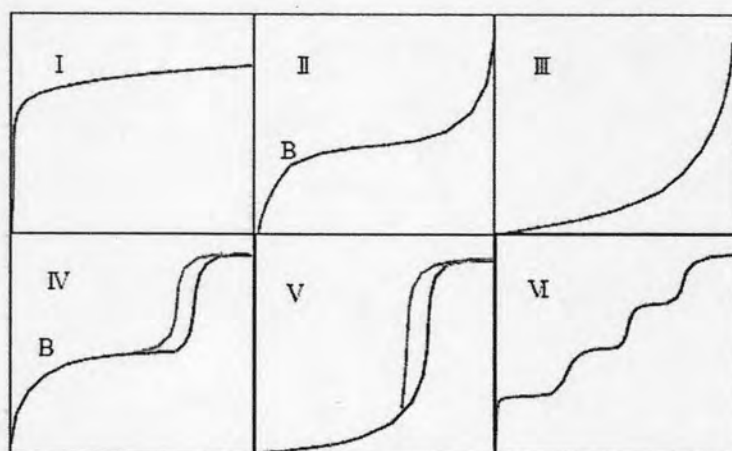


Figure 2.8 The IUPAC classification of adsorption isotherms.

Adsorption isotherms are described as shown in Table 2.1 based on the strength of the interaction between the sample surface and gas adsorbate, and the existence or absence of pores. Pore types are classified as shown in Table 2.2. [37]

Table 2.1 Features of adsorption isotherms

Type	Features	
	Intercalation between sample surface and gas adsorbate	Porosity
I	Relatively strong	Micropores
II	Relatively strong	Nonporous
III	Weak	Nonporous
IV	Relatively strong	Mesopore
V	Weak	Micropores or Mesopore
VI	Relatively strong sample surface has an even distribution of energy	Nonporous

Table 2.2 IUPAC classification of pores

Pore Type	Pore diameter (nm)
Micropore	Up to 2
Mesopore	2 to 50
Macropore	20 to up

Pore size distribution is measured by the use of nitrogen adsorption/desorption isotherm at liquid nitrogen temperature and relative pressures (P/P_0) ranging from 0.05-0.1. The large uptake of nitrogen at low P/P_0 indicates filling of the micropores (<20 Å) in the adsorbent. The linear portion of the curve represents multilayer adsorption of nitrogen on the surface of the sample, and the concave upward portion of the curve represents filling of mesopores and macropores.

The multipoint Brunauer, Emmett and Teller (BET) method is commonly used to measure total surface area.

$$\frac{1}{W[(P_0/P)]-1} = \frac{1}{W_m C} + \frac{C-1}{W_m C} (P_0/P)$$

Where W is the weight of nitrogen adsorbed at a given P/P_0 , and W_m is the weight of gas to give monolayer coverage, and C is a constant that is related to the heat of adsorption. A linear relationship between $1/W[(P_0/P)-1]$ and P/P_0 is required to obtain the quantity of nitrogen adsorbed. This linear portion of the curve is restricted to a limited portion of the isotherm, generally between 0.05-0.30. The slope and intercept are used to determine the quantity of nitrogen adsorbed in the monolayer and calculate the surface area. For a single point method, the intercept is taken as zero or a small positive value, and the slope from the BET plot is used to calculate the surface area. The surface area reported depends upon the method used, as well as the partial pressures at which the data are collected.

2.8.3 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) [38]

The inductively coupled plasma is a type of plasma source in which the energy is supplied by electromagnetic induction as shown in Fig. 2.9. The sample is nebulized and entrained in the flow of plasma support gas and break up into their

respective atoms. The plasma torch consists of concentric quartz tubes. The inner tube contains the sample aerosol and Ar support gas and the outer tube contains flowing gas to keep the tubes cool. A radiofrequency (RF) generator (typically 1-5 kW at 27 MHz) produces an oscillating current in an induction coil that wraps around the tubes. The induction coil creates an oscillating magnetic field. The Ar gas is ionized in those fields. A stable high temperature plasma at about 7000 K is then generated as the results of the inelastic collisions between neutral Ar atoms, created ions and free electrons.

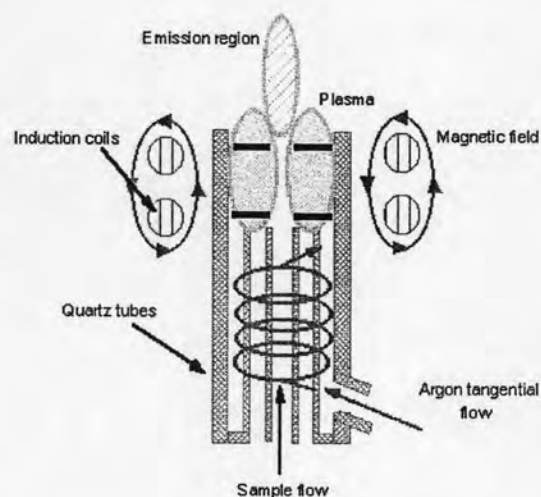


Figure 2.9 A typical plasma source [38].

ICP-AES is an emission spectrophotometric technique, exploiting the fact that excited electrons emit energy at a given wavelength as they return to ground state. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its chemical character. Although each element emits energy at multiple wavelengths, in the ICP-AES technique it is most common to select a single wavelength for a given element. The intensity of the energy emitted at the chosen wavelength is proportional to the amount of that element in the analyzed sample. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can quantify the elemental composition of the given sample relative to a reference standard.

