

Catalysis By Some Pillared Montmorillonites

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By

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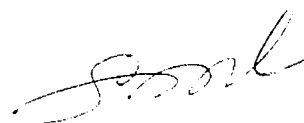
*Remembering each and every one who stood with me
in times of shine and shade throughout
my research period.....*

...to my loving ikka and moloos

CERTIFICATE

This is to certify that the thesis herewith is an authentic record of research work carried out by Ms. Rahna K. Shamsudeen under my supervision, in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

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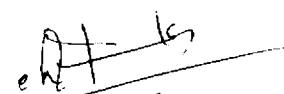


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DECLARATION

I hereby declare that the work presented in this thesis entitled “**Catalysis by Some Pillared Montmorillonites**” is entirely original and was carried out by me independently under the supervision of Dr. S. Sugunan, Professor in Physical Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-22, Kerala, India, and has not been included in any other thesis submitted previously for the award of any degree.

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Rahna K. Shamsudeen

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" I bow before the sovereign Alchemist that in a trice transmutes life's leaden metal into gold"

- Omar Khayyam

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PREFACE

Heterogeneous catalysis is an interdisciplinary area since it is based on solid state chemistry and physics, materials chemistry and engineering, surface science, analytical chemistry, theoretical chemistry, reaction kinetics and mechanisms and reaction engineering. It has not only become the basis of industrial and environmental chemistry during this century, but also its scientific foundation has been developing with ever increasing speed. Because of the great importance of acid catalysts in the petrochemical industry, extensive research work has been carried out during the last three decades concerning the fundamental and applied aspects of catalysis by acids. There is now renewed interest in the field of pillared clays since they are microporous materials with high surface area and they have a close resemblance with zeolites. The interesting architecture of pillared clays can be tuned by varying the interlayer distance. In addition, the chemical functions such as Brønsted and Lewis acidity can be modified by various techniques. By virtue of their acidic properties, they can be promising catalysts in acid catalysed reactions.

In the present study, we have prepared and evaluated the physical and chemical properties and catalytic activities of various single, mixed and modified pillared montmorillonites. The single oxide pillared clays include Al-, Fe- and Cr-pillared montmorillonites. The mixed oxide pillared montmorillonites such as Fe-Al and Cr-Al pillared systems with various Fe(Cr)/Al ratios are also prepared. Modification of iron-pillared system is done by vanadia impregnation. Characterisation using various physico-chemical techniques and a detailed study of acidic properties are also carried out. Major part of our work is oriented to evaluate the catalytic activity of the pillared systems towards certain important catalytic reactions. Our samples are found to be excellent catalysts for the reactions namely Friedel-Crafts benzoylation and benzylation, methylation of aniline and catalytic wet peroxide oxidation of phenol.

The thesis is organised into six chapters. The first chapter deals with the brief introduction and literature survey on pillared clays and their catalysis. Second chapter expounds the materials and methods employed in the work. Results and discussion regarding the characterisation and activity studies are described in subsequent chapters. Last chapter includes the summary of the investigation and the conclusions drawn from the work.

Introduction And Literature Survey

1.0 Introduction

Catalysis has a profound beneficial impact on industry and more importantly on society in the 21st century. It is the most important technology in environmental protection. The successful exploration of a material as a catalyst eliminates or minimises the use and release of environmentally hazardous substances, which are responsible for environmental pollution. Furthermore, catalysis plays a vital role in providing fuels, commodity/fine chemicals and pharmaceuticals. Today, more than 60% of all chemical products and almost 90% of chemical processes are based on catalysis, attesting to the pervasive presence and necessity of this discipline throughout the chemical industry.

The term catalysis was introduced as early as 1836 by J.J. Berzelius in which he assumed that catalysis possesses special powers that can influence the affinity of chemical substances. A definition that is valid still today was proposed by Ostwald in 1895. He defined a catalyst as a substance that accelerates a chemical reaction without affecting the position of equilibrium. This definition includes the possibility of small loss of catalyst or its activity during the course of the reaction. However, the catalyst affects only the rate of the reaction, it changes neither the thermodynamics of the reaction nor the equilibrium position.

1.1 Homogeneous and Heterogeneous Catalysis

In chemical industry, two major catalytic processes namely homogeneous and heterogeneous, have been widely employed. Each of these catalytic processes possesses its own advantages and disadvantages. Homogeneous systems often perform better selectivity, activity and reproducibility. However, they are more vulnerable to extraneous materials. The cost of production is very high owing to their low thermal stability and shorter catalyst lifetime, which is a serious drawback from an industrial point of view. The advantages of heterogeneous catalytic processes include the easy separation of the final reaction mass from the catalyst, reusability of

the catalyst and the possibility of continuous operation in a reactor without interruption. Also, heterogeneous processes are more environmentally benign and have little disposal problems, in comparison with homogeneous catalysis. Thus there is a strong impetus for the synthesis of new heterogeneous systems to replace the existing homogeneous systems and this has become a challenging task in the catalytic field.

1.2 Heterogeneous Catalysis

The field of heterogeneous catalysis is one of the most rapidly expanding areas in chemistry. In heterogeneous catalysis, the reactants and catalysts are present in different phases. Usually, the catalyst is a solid and the reactants are either liquids or gases. The heterogeneous catalyst provides an alternate reaction path with a lower energy of activation. The process of heterogeneous catalysis involves the following steps:

- (i) Diffusion of the reactants to the surface of the catalyst,
- (ii) Adsorption of the reactants on the surface,
- (iii) Reaction on the surface,
- (iv) Desorption of the products from the surface and
- (v) Diffusion of the products away from the catalyst.

Of these, (ii) and (iii) are the most important steps. A catalyst can be effective only when the adsorption of the reactant(s) on the surface of the catalyst is not very strong and the desorption of the product(s) is fast. Very strong interaction of the reactants and products on the surface only 'poisons' the catalyst. Adsorption generally is not uniform across a solid surface. Adsorption and therefore catalysis occurs primarily at certain favourable locations called 'active sites'.

The properties of a heterogeneous catalyst for industrial use may be classified into two categories [1].

- (i) Properties that determine directly the catalytic activity and reactivity. Here factors such as bulk and surface chemical composition, local microstructure and phase composition are important.

(ii) Properties that ensure their successful implementation in the catalytic process. These include thermal and mechanical stability, porosity, shapes and dimension of catalyst particles.

In short, a commercial heterogeneous catalyst should be stable, active and selective and should have sufficiently high surface area, good porosity and stable mechanical strength.

1.3 Classification of Heterogeneous Catalysts

Heterogeneous catalysts are classified into several ways. Based on their physicochemical nature, they are generally classified as

- a) Metal oxides: Simple, mixed, supported and modified metal oxides
- b) Supported metals/bimetallic catalysts
- c) Zeolites/molecular sieves
- d) Clays and hydrotalcites
- e) Solid supported heteropolyacids

They are also classified on the basis of their function as

- a) Shape selective catalysts
- b) Phase transfer catalysts
- c) Redox catalysts
- d) Acid-base catalysts

Apart from these two classifications, heterogeneous catalysts are also described as structure sensitive and structure insensitive, based on their behaviour in a particular reaction. Rates of structure sensitive catalytic reactions alter markedly when the crystallite size of the system is changed, whereas rate is independent of crystallite size in structure insensitive reactions.

1.4 Solid Acid-Base Concept in Heterogeneous Catalysis

A major part of the industrial chemical reactions such as catalytic cracking, hydration, dehydration, hydrolysis, isomerisation, etc. come under the acid-base reaction category. These types of reactions are accelerated under the influence of an acid or a base. The elementary step in these reactions is the characteristic transfer of proton or the production of heteropolar donor-acceptor pair [2]. Acid-base property

of a heterogeneous surface is thus an important factor in determining the catalytic efficiencies for these reactions.

Many materials possess inherent acid-base centres. An exhaustive list of various solid acids and bases is tabulated by Tanabe [3] who defined a solid acid as one on which the colour of a basic indicator changes concomitant with its chemisorption and a solid base as one on which the colour of an acidic indicator changes as a result of chemisorption. Various solid acids include the naturally occurring clay minerals, zeolites, silica-alumina and various metal oxides, sulphates, sulphides, phosphates and halides. These solid acids have usually been employed as catalysts on various acid catalysed reactions. Surface hydroxyl groups and co-ordinatively unsaturated metal cations are responsible for the surface acidity. Surface hydroxyl groups originating from incomplete dehydration act as Brönsted acid sites. They may dissociate to protonate an adsorbed base. Brönsted acid sites are present only when surface hydroxyl groups are available. Exposed co-ordinatively unsaturated (CUS) cations may act as Lewis acid sites. The strength of these acid sites depends on the charge and size of the cations.

Extensive studies on heterogeneous cracking catalysts undertaken during 1950s revealed that the essential feature of cracking catalysts is acidity, and therefore, generation of acidic sites on the solids was extensively studied. As a result, amorphous silica-alumina was utilised as a cracking catalyst for a long time. Presently, zeolites have replaced almost all kinds of catalysts in cracking. Good correlation between the total amount of acid (Lewis+Brönsted) and catalytic activities has been found in many cases. For example, the rates of both catalytic decomposition of cumene [4] and polymerisation of propylene [5] over $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts were found to increase with increasing acid amounts.

In contrast to the extensive studies of heterogeneous acidic catalysts, fewer efforts have been given to the study of heterogeneous basic catalysts. Pines *et al.* first reported the study of heterogeneous basic catalysts [6]; sodium metal dispersed on alumina acted as an effective catalyst for double bond migration of alkenes.

The various types of heterogeneous basic catalysts [7] are,
a) single component metal oxides such as oxides of alkali, alkaline earth and rare earth metals.

- b) alkali ion-exchanged and alkali ion added zeolites
- c) alkali metal ions supported on alumina, silica or alkaline earth oxide
- d) clay minerals such as hydrotalcites, sepiolite and chrysotile
- e) non-oxides such as KF supported on alumina, lanthanide imide and nitride on zeolite.

In addition to the above mentioned catalysts, a number of materials have been reported to act as heterogeneous base catalysts. Except for non-oxide catalysts, the basic sites are believed to be surface oxygen atoms. These oxygen atoms can interact with a proton. Apart from the double bond migration of 1-butene as reported by Pines *et al.* [6], several other reactions such as alcohol dehydrogenation to aldehydes or ketones, hydrogenation of olefins, amination of conjugated dienes, Meerwin-Ponndorf-Verley (MPV) reduction, side chain alkylation of aromatics, aldol condensation, etc. also come under the base catalysed reactions.

In our investigation, clay based systems are chosen as heterogeneous catalysts. Thus, it is now the turn of clay catalysts that are to be discussed in detail. A detailed discussion on clays is given below.

1.5 Clays

Clays are a group of silicate minerals composed of aluminium and/or magnesium hydroxides along with silica. Clay minerals are loosely described as aluminosilicates. They are usually produced as a result of the process of weathering, hydrothermal alteration or diagenesis.

Majority of these minerals have layer structures and are therefore called phyllosilicates. But some clay minerals have chain or ribbon structures and are called inosilicates (for example, pyroxenes). Disorder in one or two dimensions and interlayering produce many clay mineral species which are intermediate between the wholly crystalline and amorphous forms. Owing to their weak tendency to crystallise, clay minerals are usually of colloidal grain size. These are widespread in both continental and marine clays in soils and in hydrothermal products.

1.5.1 Structure of Clays

In clay minerals, the layer silicates, the extremely stable SiO_4 tetrahedral structural unit has polymerised to form two-dimensional sheets. These

two-dimensional tetrahedral sheets of composition T_2O_5 (T-tetrahedral cation) are formed by the linkage of individual tetrahedral unit with neighbouring tetrahedron by sharing three of the oxygens (basal oxygen) at the corners of the tetrahedra [8] as illustrated in Figure 1.1(a). The continuous linkage through these basal oxygen results in a hexagonal mesh pattern as shown in Figure 1.1(b). It should be noted that SiO_4 is also capable of polymerising one dimensionally using only two oxygens to form chains or ribbons as in the case of inosilicates, and even by sharing all its corner oxygen to form a three-dimensional structure such as quartz which is a tectosilicate. So far as clay minerals are concerned, it is the fact that each tetrahedron has a spare oxygen, unshared in the sheet, which is of importance. This fourth oxygen, called apical oxygen, of course points normally away from the tetrahedral sheet. These oxygens are linked to the other main structural element involved in the crystal. This element is an octahedral sheet formed from oxygen and metal ions, as shown in Figure 1.1(c). Most often, the latter are Al or Mg. Like tetrahedra, octahedra too can polymerise in two dimensions (Figure 1.1 (c)), in this case, by the sharing of four oxygens. Apart from aluminium and magnesium, Fe^{2+} and Fe^{3+} are also commonly found in naturally occurring clays, but other appropriately sized cations such as Ti, V, Mn, Li, Co, Ni and Zn are present in individual minerals.

The tetrahedral sheet (Tet) of polymerised SiO_4 units and the octahedral sheet (Oct) are the basic building blocks of most clay minerals. It turns out to be geometrically possible for oxygens to be shared between the two types of sheets lying one on top of the other. However, there is a degree of distortion and strain in the resulting lattice since the octahedral sheet unit is commonly smaller than the tetrahedral sheet unit. The oxygen involved are the apical from the tetrahedral sheet and those unshared octahedral ions normal to the octahedral sheet; the result is that the oxygen of the Si-O becomes the oxygen of the Al-OH, producing the link Si-O-Al, as shown in Figure 1.2. It can be seen from this structure that the tetrahedral sheet has no further spare apical oxygen, so it is not possible for another octahedral sheet to come under the tetrahedral sheet in order to form Oct-Tet-Oct sandwich. However, it is clearly possible for another tetrahedral sheet to condense on the top of the octahedral sheet, as the latter has spare OH groups, to form Tet-Oct-Tet layers. This is shown schematically in Figure 1.3. Tet-Oct-Tet is now a

completed layer structure, a lamella about 1nm thick, incapable of further growth by condensation in the 'c' plane.

Perhaps the best known fact about clays is that the majority of these carry a net negative charge due to isomorphous substitution of lower valency cations for the higher, within the structure. This often comes about during their formation in 'dirty' geochemical environments, when ion size, rather than either valency or even chemical identity determines substitution in either tetrahedral or octahedral spaces in the oxygen framework. The resulting negative charge in the lattice is electrically balanced in the natural state by adsorption at the surface of various positively

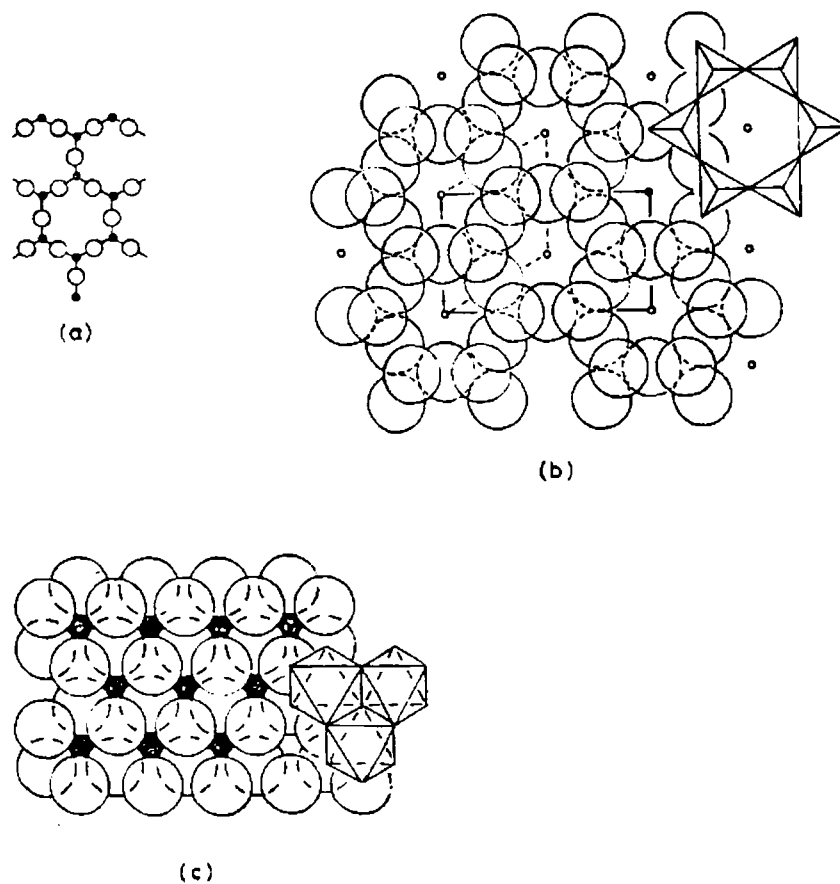


Figure 1.1 (a) Hexagonal mesh pattern formed by the linkage of basal oxygens of silicon tetrahedral (b) plan view of ideally hexagonal tetrahedral sheet. Alternative hexagonal (dashed line) and orthogonal cells (full lines) are shown connecting lattice points and (c) octahedral sheet

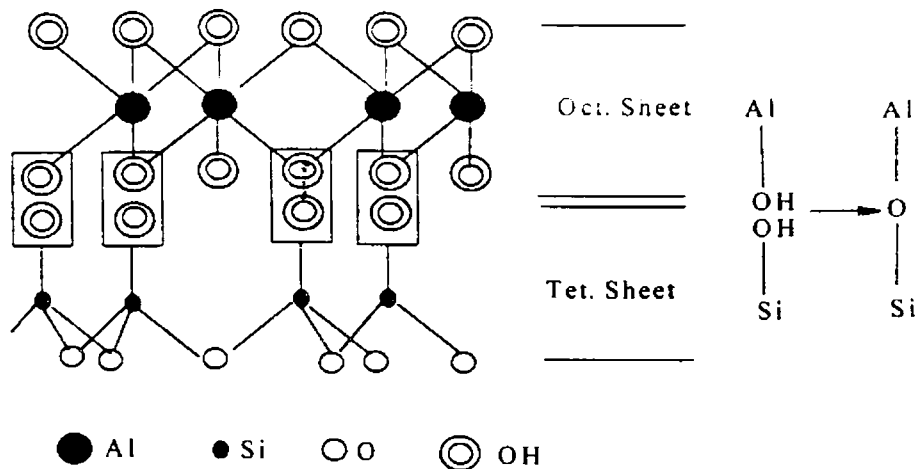


Figure 1.2 Diagrammatic representation of condensation of octahedral and tetrahedral sheets

charged species from the solution. In other words, the two-dimensional oxy anions are separated by layers of cations which are either hydrated or unhydrated. These interlayer cations are capable, in the right conditions, of holding the individual lamellae face to face, so that assemblages of them act together, either chemically and/or physically. Hence, even a suspension of a clay mineral in water may consist of a wide range of crystal sizes, depending upon the history of the sample and the strength of the links provided by the hydrated cation. The presence of water molecules forces the lamellae apart, and this weakens the net forces of attraction compared to the situation in which a bare (small) cation balances the charge close to both surfaces. Thus we can say that as the hydration of the cation in the interlayer increases, the net force of keeping the lamellae together becomes weaker. When this is a bare and small cation, the lamellae will be tightly held together. The best example of a cation, which does not hydrate easily and can balance charge in this way, is potassium and this is found most exclusively in the mica group of minerals.

1.5.2 Classification of Clay Minerals

The phyllosilicate clay minerals can be conveniently classified on the basis of layer type, layer charge per unit cell and types of inter layer [9]. Based on the charge possessed by the clay layers, the clay minerals can be classified into 8 major groups, as shown in Table 1.1. The layer charge can vary from zero to as large as four and the clay groups are accordingly named. On the basis of layer types, clay minerals can be classified into two as 1:1 clays and 2:1 clays. In 1:1 clays, one clay layer is

formed by the assemblage of one tetrahedral sheet with one octahedral sheet to form a double layer. In such clays, the uppermost unshared plane of anions in the octahedral sheets consists only of OH groups (Fig. 1.2). In 2:1 clays, an octahedral sheet is sandwiched between two tetrahedral sheets facing each other to form a three sheet complex (Fig. 1.3). In order to accomplish this linkage, the upper tetrahedral layer must be inverted so that its apical oxygen points down and can be shared with the octahedral layer below (Fig. 1.3). Both octahedral anion planes are then of the same O and OH composition.

On the basis of the octahedral sheet type, each of the eight major groups can be subdivided into two sub-groups, namely dioctahedral and trioctahedral clay minerals. The various individual clay minerals coming under each subgroup are described in Table 1.1. In a unit cell formed from 20 oxygens and 4 hydroxyl groups, there are eight tetrahedral sites and six octahedral sites. When two-thirds of the octahedral sites (i.e., 4 sites) are occupied by cations, the mineral is classified as a dioctahedral phyllosilicate. When all the octahedral sites are occupied by cations, the clay mineral is called a trioctahedral phyllosilicate.

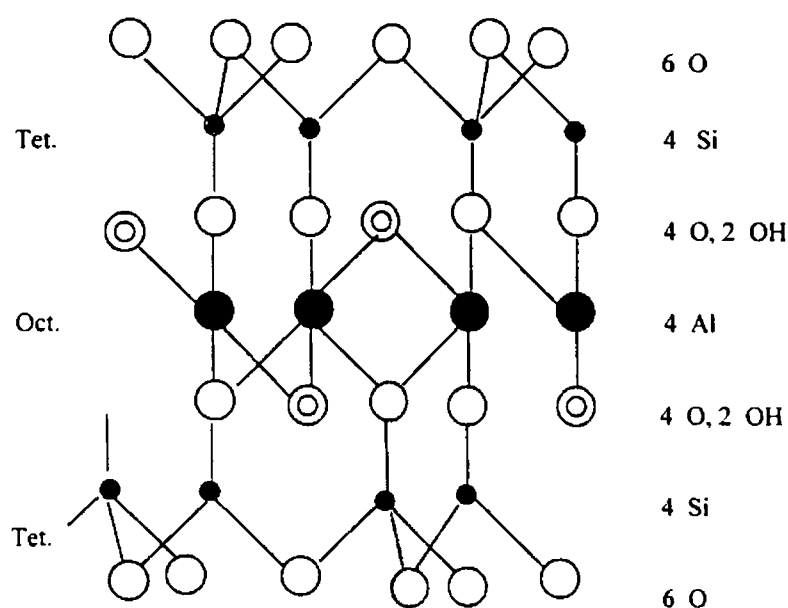


Figure 1.3 Diagrammatic representation of a 2:1 Tet.-Oct.-Tet. clay structure

Table 1.1 Classification and nomenclature of clay types (phyllosilicates)

Group name	Layer charge (x)	Layer type	Octahedral occupancy	Sub-group	Species
Serpentine-Kaolin	Very low or zero	1:1	Tri-	Serpentines	Chrysotile
			Di-	Kaolins	Kaolinite, dickite
Talc-Pyrophyllite	zero	2:1	Tri-	Talcs	Talc
			Di-	Pyrophyllites	Pyrophyllite
Smectites	Low ($0.6 < x < 1.2$)	2:1	Tri-	Saponites	Saponite, hectorite
			Di-	Montmorillonites	Montmorillonite, biedillite
Vermiculite	Medium ($1.2 < x < 1.8$)	2:1	Tri-	Trioctahedral Vermiculites	Trioctahedral Vermiculites
			Di-	Diocahedral Vermiculites	Diocahedral Vermiculites
Mica	High ($x \approx 2$)	2:1	Tri-	Trioctahedral micas	Phlogopite, biotite
			Di-	Diocahedral micas	Muscovite, illite
Brittle mica	Very high ($x \approx 4$)	2:1	Tri-	Trioctahedral brittle micas	Clintonite
			Di-	Diocahedral brittle micas	Margarite
Chlorite	Variable	2:1	Tri-	Trioctahedral chlorites	Chlinochlore
			Di-	Diocahedral chlorites	Dondassite
Sepiolite-Palygorskite	Variable	2:1	Tri-	Sepiolites	Sepiolite
			Di-	Palygorskites	Palygorskite

1.5.3 Structural Formula for Clays

The composition of a 1:1 mineral like kaolinite could be written relative to the proportion of oxides, i.e., as $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, but this is virtually devoid of structural information. It is better to take the unit cell as the basic quantity, then express the formula as $(\text{Si}_4)^{\text{IV}}(\text{Al}_4)^{\text{VI}}\text{O}_{10}(\text{OH})_8$. This tells us at once about the cation occupancy of the tetrahedral sheet (superscript IV) and the octahedral sheet (superscript VI). All the 1:1 clay mineral will have the same anion group, $\text{O}_{10}(\text{OH})_8$. Similarly, the anion group is invariant for 2:1 mineral and is $\text{O}_{20}(\text{OH})_4$. A unit cell representation such as $(\text{Si}_8)^{\text{IV}}(\text{Al}_4)^{\text{VI}}\text{O}_{20}(\text{OH})_4$ reveals that the clay mineral is a dioctahedral 2:1 type. Out of the six octahedral sites, only four are occupied and it is by Al. A unit cell representation such as $(\text{Si}_8)^{\text{IV}}(\text{Mg}_6)^{\text{VI}}\text{O}_{20}(\text{OH})_4$ tells that the clay is of a 2:1 trioctahedral type in which tetrahedral cations are Si^{4+} and octahedral cations are Mg^{2+} . Idealised structural formula for some dioctahedral and trioctahedral 2:1 phyllosilicates [10] along with the isomorphous substitutions are given in Table 1.2.

Table 1.2 Idealised structural formulae for some dioctahedral and trioctahedral 2:1 phyllosilicates

Mineral group	Dioctahedral	Trioctahedral
Pyrophyllite -Talc	Pyrophyllite: $[\text{Al}_4\text{O}](\text{Si}_8\text{O})\text{O}_{20}(\text{OH})_4$	Talc: $[\text{Mg}_6\text{O}](\text{Si}_8\text{O})\text{O}_{20}(\text{OH})_4$
Smectites	Montmorillonite: $\text{M}^{n+}_{x/n} \cdot y\text{H}_2\text{O}(\text{Si}_8\text{O})[\text{Al}_{4-0-x}\text{Mg}_x]\text{O}_{20}(\text{OH})_4$ Biedillite: $\text{M}^{n+}_{x/n} \cdot y\text{H}_2\text{O}(\text{Si}_{8-0-x}\text{Al}_x)[\text{Al}_4\text{O}]\text{O}_{20}(\text{OH})_4$ Nontronite $\text{M}^{n+}_{x/n} \cdot y\text{H}_2\text{O}(\text{Si}_{8-0-x}\text{Al}_x)[\text{Fe}_{4\text{O}}]\text{O}_{20}(\text{OH})_4$	Hectorite: $\text{M}^{n+}_{x/n} \cdot y\text{H}_2\text{O}(\text{Si}_8\text{O})[\text{Mg}_{6-0-x}\text{Li}_x]\text{O}_{20}(\text{OH.F})_4$ Saponite: $\text{M}^{n+}_{x/n} \cdot y\text{H}_2\text{O}(\text{Si}_{8-0-x}\text{Al}_x)[\text{Mg}_6\text{O}]\text{O}_{20}(\text{OH})_4$
Micas	Muscovite: $\text{K}_2(\text{Si}_{6\text{O}}\text{Al}_{2\text{O}})[\text{Al}_4\text{O}]\text{O}_{20}(\text{OH})_4$	Phlogopite: $\text{K}_2(\text{Si}_{6\text{O}}\text{Al}_{2\text{O}})[\text{Mg}_6\text{O}]\text{O}_{20}(\text{OH})_4$

Pyrophyllite and talc (Table 1.2) are made up of neutral clay layers, so that no exchangeable cations (M^{n+}) can be accommodated in the interlamellar region. Separate clay layers are therefore rather loosely bound via weak dipolar and van Der Waals forces. The five other sheet silicates, collectively known as smectites, listed in the table bear a net negative charge on the Tet-Oct-Tet framework, as a result of isomorphous substitution. In montmorillonite, some of the Al^{3+} in the octahedral sub-lattice are replaced by Mg^{2+} ions; in hectorite, some of the Mg^{2+} in the octahedral

