

Montmorillonite: Natural Origin Reusable Catalysis

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Abstract: Montmorillonite is a member of the general mineral groups, the clays. It typically forms microscopic or at least very small platy micaceous crystals. The water content is variable, and in fact when water is absorbed by the crystals they tend to swell to several times their original volume. This makes montmorillonite a useful mineral for several purposes. It is the main constituent in a volcanic ash called bentonite, which is used in drilling muds. The bentonite gives the water greater viscosity ("thickness" of flow), which is very important in keeping a drill head cool during drilling and facilitating removal of rock and dirt from within a drill hole. Another important use of montmorillonite is as an additive to soils and rocks. As a mineral specimen, montmorillonite does not get much consideration. Usually, pure samples of montmorillonite are massive, dull and not very attractive. However, as with all minerals, there are those exceptional specimens that defy the norm. Montmorillonite has been found as attractive pink inclusions in quartz crystals and these make for interesting specimens. Montmorillonite is widely used in pharmacy for a variety of applications such as stabilization of suspensions, emulsions, viscosizing, adhesion to the skin and tablet making. It is also used as drug carrier or as a part of drug delivery systems, such as for controlled drug release, including for gene delivery, and for drug targeting to specific tissues. It is also used for stability enhancement in drug and nutrient application. There are also other similar uses. Montmorillonite is used as a reusable catalyst in production of pharmaceuticals.

Keywords: Montmorillonite, Catalysis, Mineral Clays, heterogeneous solid clay catalysts

1. INTRODUCTION [1, 2]

The production of most industrially important chemicals involves catalysis. Similarly, most biochemically significant processes are also catalyzed. Research into catalysis is a major field in applied science and involves many areas of chemistry, notably in organometallic chemistry and material science. Catalysis is relevant to many aspects of environmental science, e.g. the catalytic converter in automobiles. Catalytic reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated as opposed to stoichiometric reactions in which all the reactants are consumed and more side products are formed. The most common catalyst is the proton (H⁺). Many transition metals and transition metal complexes are used in catalysis as well. Enzymes act as important catalysts in biology. A catalyst works by providing an alternative reaction pathway to the reaction product. The rate of the reaction is increased as this alternative route has lower activation energy than the reaction route, not mediated by the catalyst.

Activated montmorillonites are used to catalyze various chemical reactions. The activation process is similar to that used for the bleaching clays. An early example of their use was for the catalytic cracking of petroleum. This process, which is used for increasing the yield and quality of gasoline from petroleum, involves splitting the heavier molecular weight hydrocarbons into lighter ones with lower boiling points. The catalyst used must promote rupture of the carbon to carbon bond near the middle of the hydrocarbon chain. The first cracking catalysts were montmorillonite but synthetic catalysts have now mainly replaced them. Present uses of activated clays are as alkylation catalysts, particularly for the alkylation of phenols. These alkylated phenols have many uses and are intermediaries in the formation of detergents. Clays are also used to promote polymerization, dehydration and various other chemical reactions. In addition, the activated clays are used as delicate pH adjusters where the last traces of alkalinity have to be removed from organic liquids. The natural clay is similarly used for the removal of traces of acidity

Advantages of Montmorillonite: [3, 4]

- Montmorillonite clay is an excellent soil conditioner that is proven to grow better, more nutritious garden produce. It's not a nitrogen-type fertilizer; Montmorillonite has a nutrient delivery system and buffer for fertilizers and humus. it is perfect for organic gardens growing exotic plants.
- Just as it feeds your garden, groves and plants, Montmorillonite clay feeds you. It contains vital trace minerals that are depleted from our soils and our food chain. Find one that contains the 50 plus minerals that show high likelihood of contributing to human and animal health, and in the right ratios. Here you want to be sure your product is powdered Premium Calcium Montmorillonite, the best Montmorillonite clay for this application..
- It is a fine water purifier; it removes heavy metals and pollutants from water, like a filter. Use it to polish tap water or wells. Montmorillonite also disinfects water of many bacteria.
- This is why it is perfect for ponds, aquariums and wells as an all-natural additive that helps detoxify and purify water environments.
- This incredible clay is an unbelievable body detox supplement for the colon and to help blood and lymph. Ingesting it or bathing in it can be very health-promoting for removing chemicals and heavy metals, as well as parasites, molds, yeast and toxins.

- Clean with it...it is a natural disinfectant and antiseptic. Premium Montmorillonite makes a fantastic tooth powder, and its detox and mineral properties help fight tooth and gum problems.
- Montmorillonite clay is great as a pet supplement. Many of our pets suffer from the same environmental and dietary chronic health problems that we do. This inexpensive material is a simple and potent dietary supplement..
- As if all that weren't enough, Premium Montmorillonite clay functions as an unbelievable poison antidote and can be used as a poultice to relieve the pain of bee stings, bites, cuts, scrapes, burns, etc. Its ionic electrostatic charge interacts with the nerves to instantly relieve topical pain for humans and animals alike.

2. DISCOVERY[5, 6]

Montmorillonite was discovered in 1847 in Montmorillon in the Vienne prefecture of France, more than 50 years before the discovery of bentonite in the US. It is found in many locations worldwide and is known by various names like sodium montmorillonite, sodium bentonite [Wyoming bentonite (US)], sodium activated bentonite [Bentonite (UK)], calcium montmorillonite, calcium bentonite [Mississippi bentonite (US)] and sub-bentonite [Texas bentonite (US)].

Bentonite is an important source of montmorillonite in nature. It is a rock formed from highly colloidal and plastic clays mainly composed of montmorillonite. Bentonite particles are indistinguishable from kaolin-clay minerals viewed under scanning electron micro-scope (SEM); however, the main difference indicated is thickness. Sodium or potassium salts of bentonite exfoliate into thin plates that could be 1 nm in thickness, theoretically.

3. TYPES OF MONTMORILLONITE[7]

Montmorillonite belongs to the smectite group of clays. There are two types of montmorillonite, sodium and calcium. Sodium montmorillonite is commonly known as bentonite; the name is derived from the location of the first commercial deposit mined at Fort Benton, Wyoming USA.

3.1 Calcium montmorillonite [8, 9]

the second type of montmorillonite, is also known as "living clay" for it principally consists of minerals that enhance the production of enzymes in all living organisms. California Earth Minerals calcium montmorillonite is the preferred choice to use for soil, plants, animals and humans, especially when ingested, hence "edible clays." Benefits of calcium montmorillonite minerals have been documented in research conducted by many scientists and leading universities.

The benefits of calcium montmorillonite clay are due to the mineral content or trace elements which are vital to the cellular functions of all forms of living creatures. Perfect health can only be obtained by a diet which supplies a proper balance of essential nutrients. Trace mineral elements are necessary for vitamins and enzymes to function. Without enzymes the body can not activate certain chemical processes like digestion or the synthesis of proteins within cells. For example:

- A trace of Copper is needed for the synthesis of hemoglobin.
- A trace of Cobalt is needed to make vitamin B 12.
- A trace of Zinc is needed by the pancreas to manufacture insulin.

However, modern agricultural practices jeopardize our health. Our farming techniques use the soil over and over for high yield mass production, depleting the soil and the crops of vital essential elements. As soil health declines, crop health falters and farmers become increasingly reliant upon synthetic petroleum-based fertilizers to artificially replenish the soil with nitrogen, phosphorous, and potassium (NPK); only three essential elements.

The trade off for adding synthetic enhancers is that the living soil remains deprived of naturally occurring bacteria that produce nitrogen, thus the soil is dying and crops actually become dependent on artificial fertilizer to sustain life. Aquifers are now contaminated with nitrates that were leached from farmlands. The combination of leaching from rain and irrigation, overuse of the land, and chemical fertilizers deteriorates the level of nutrients in our soil. As a result, most of the food grown is deficient in trace mineral elements. The few trace mineral elements that remain are removed during processing, e.g., the milling of wheat.

These same crops are used in turn to feed the animals we use for food. Mass production robs these animals of their natural grazing habits, so animal feeds are needed to supplement or replace their natural food sources. The plant life used to create animal feed is deficient of naturally occurring trace elements, therefore, the animals are robbed of these life giving nutrients.

Studies have shown that there is a relationship between human malnutrition and the depletion of trace elements in soil. According to the USDA, we would have to eat 75 bowls spinach in order to get the same amount of iron as one bowl eaten in 1948. As a result, malnutrition exists in 57% of US citizens over the age of 65! To slow (and eventually reverse) this malnutrition trend, we need to look more closely at nature and learn a more complete picture of health.

3.2 Sodium montmorillonite[10, 11]

Montmorillonites are three-layer minerals consisting of two tetrahedral layers sandwiched around a central octahedral layer. Oxide anions at the apices of the tetrahedral subunits are directed inward where they surround interior aluminum, iron and magnesium cations, thereby forming the octahedral subunits of the octahedral layer. Bonding, between the shared interior oxide anions and the cations in both the tetrahedral and the octahedral layers, links the layers together and yields the unique sheet structure characteristic of clay minerals. For montmorillonite, the total negative charge contributed to the structure by the sum of all the oxide anions (O^{2-}) is somewhat in excess of the total positive charge contributed by the sum of all the structural cations (Si^{+4} , Al^{+3} , Fe^{+2} , Fe^{+3} , Mg^{+2}) and imparts a slight overall negative charge to the surfaces of the clay sheets. This slight excess negative charge on the sheets is counterbalanced by free-moving (exchangeable) cations which exist between them. These three layers in each sheet

comprise individual bentonite platelets which are typically 1 nm in thickness and 0.2-2 microns in diameter. Dry platelets of sodium bentonite are most commonly grouped together in a face-to-face arrangement, with exchangeable cations and small amounts of adsorbed water in an interlayer region between each platelet. The thickness of the interlayer region is variable depending on the amount of water adsorbed between the platelets.

4. PROPERTIES MONTMORILLONITES[12]

Chemical formula: $(\text{Ca}_{0.14}\text{Na}_{0.02})\text{P}=0.16(\text{Al}_{1.66}\text{Mg}_{0.36}\text{Fe}_{0.04})\text{P}=2.08(\text{Si}_{3.90}\text{Al}_{0.10})\text{P}=4.00\text{O}_{10}(\text{OH})_2 \cdot 1.02\text{H}_2\text{O}$

Physical Properties of Montmorillonite

- Color : white, gray white, yellow, brownish yellow, greenish yellow, pink with yellow or green tints also exists
- Cleavage perfect: perfect in one direction.
- Fracture: uneven to lamellar claylike fracture
- Hardness : 1.5 to 2.0 Talc-Gypsum
- Density : 2.0 to 2.7 average 2.35
- Crystal system: monoclinic tiny scaly crystals, lamellar microcrystalline aggregates, compact, crystals expand to several times the original volume
- on water absorption
- Luster: Dull
- Streak: White
- Luminescence: None
- Transparency : Translucent Crystals Are Translucent And Masses Are Opaque

5. CATALYTIC PROPERTIES[13]

Activated montmorillonites are used to catalyze various chemical reactions. The activation process is similar to that used for the bleaching clays. An early example of their use was for the catalytic cracking of petroleum. This process, which is used for increasing the yield and quality of gasoline from petroleum, involves splitting the heavier molecular weight hydrocarbons into lighter ones with lower boiling points. The catalyst used must promote rupture of the carbon to carbon bond near the middle of the hydrocarbon chain. The first cracking catalysts were montmorillonite but synthetic catalysts have now mainly replaced them. Present uses of activated clays are as alkylation catalysts, particularly for the alkylation of phenols. These alkylated phenols have many uses and are intermediaries in the formation of detergents. Clays are also used to promote polymerization, dehydration and various other chemical reactions. In addition, the activated clays are used as delicate pH adjusters where the last traces of alkalinity have to be removed from organic liquids. The natural clay is similarly used for the removal of traces of acidity.

Catalytic Evaluation Method

Catalytic evaluation was performed using a microactivity test (MAT) similar to the one described by Ciapetta and Anderson (1967). The weight hourly space velocity was 15, with an 80-sec catalyst-contact time at 480~ A catalyst-to-oil ratio of 2.5 was used. The charge stock was a Kuwait gas oil having a 260~176 boiling range. The results show that the ACH-bentonite retained its high conversion ability and activity up to 540~ Its catalytic activity is comparable to that of a clay-based commercial cracking catalyst containing about 15% of a zeolite of the faujasite type.

Prior to testing, the catalysts were heated at 540~ for 10 hr with 10% steam. However, although the activity of the commercial catalyst was practically independent of the pretreatment temperature below 760~ between 540 ~ and 650~ a progressive collapse of the pillared structure occurred with a corresponding decrease in surface area and cracking activity. Similar conversion results on West Texas gas oil were published by Vaughan et al. (1979), and Shabtai et al. (1980) discussed the catalytic activity of interlayered clays for cumene and 1-isopropylnaphthalene dealkylation.

5. MECHANISM OF MONTMORILLONITE: [14]

Montmorillonite-based products are indicated to work immediately on the digestive channel and bind the toxic substances, resulting ultimately in their removal from the body through the stool. Use of montmorillonite by astronauts in the NASA space program was noted for its highly absorptive calcium content. Montmorillonite is hydrophilic like most other clay minerals. It swells with the absorption of water, which greatly increases its volume. Water penetrates the interlayer molecular spaces, and the variation in the level of swelling is possible in various grades. Montmorillonite typically exhibits a gradual dehydration and phase change to stronger nonexpandable clay, illite, under increasing temperature and pressure. These two clay minerals coexist as a mix-layer phase at intermediate states. The temperature and pressure at which the transition begins depends on various factors, i.e., original composition of montmorillonite, chemistry of available fluids, porosity, and geological environment. The interlayer cations are exchangeable, and the amount of expansion as a result of water absorption largely depends upon the type of exchangeable cation. When sodium is present as the predominant exchangeable cation, the increase in montmorillonite volume is several times the original amount. This characteristic had been made sodium montmorillonite a major constituent in nonexplosive agents for splitting rock with reduced waste. Various chemical formulas known for montmorillonite are the result of its modifiable structure. Moreover, the cation substitution creates a charge imbalance that allows the chemical composition to vary. The exact theoretical formula is never seen in nature; [13] therefore, it is also shown without the structural substitution as $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20} \cdot n\text{H}_2\text{O}$. However, the occurrence in nature in any form consists of water molecules.

6. RECENT APPLICATION OF MONTMORILLONITE [15, 16]

For the past several centuries, clays have been used for a variety of applications. Therefore, with the recent introduction of montmorillonite clay as a functional filler in thermoplastic and thermoset polymers, the clay minerals, or montmorillonite, have been studied for various applications and performance including the use as a catalyst in organic synthesis as a food additive for health and stamina, for antibacterial activity against tooth and gum decay, for the assessment of frictional and sliding behavior or the study of mineralogical attributes and as a sorbent for nonionic, anionic, and cationic dyes. More recently the interest and volume in the investigation of the use of clay minerals, particularly montmorillonite clays, have significantly increased. The research has concentrated on the development of nanoclays through modifications in physical and chemical structures and on the study of the effects of nanoclays on the thermal-mechanical properties of polymers.

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