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Original Paper

Research Progress on the Modification Methods of Clay Minerals

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Abstract

Clay minerals are widely distributed in nature, and their applications have been rapidly developed in the last decade or so due to their unique physical and chemical properties. Since the most researched is the modification of clay minerals, this paper introduces the types of clay, basic structural characteristics and common modification methods. The methods of modified clay include high-temperature excitation and acid-base excitation methods to stimulate the activity of clay minerals, as well as interlayer ion exchange modification methods, clay surface grafting techniques such as sol-gel method, surface hydroxyl grafting modification and other methods, and also introduces the intercalation methods, including solution intercalation method, In situ polymerization intercalation method, etc. The applications and developments of clay minerals are summarized, from traditional industrial applications to environmental protection and high-tech nanomaterials, mainly in the automotive industry, environment-friendly materials and catalysts.

Keywords

clay mineral modification, review, clay/polymer nanocomposites, surface grafting, intercalation

1. Introduction

Clay and clay minerals have been used for a long time, and the earliest application put into use would be for the treatment of diseases. With the rapid development of science and technology, there is an increasing demand for high performance materials, not only for their quantity, but also for their high performance. The properties of clay polymer nanocomposites are superior to both clay and polymer, and their airtightness and water permeability as well as thermal and mechanical properties can meet the needs of industrial material properties, which have been developed from traditional industrial applications to environmental protection and human health as well as high-tech nanomaterials. For environmental treatment, it can adsorb antibiotics in the environment. Aiqin Wang et al. invented a method to prepare a biochar-loaded concave bumpstone nanocomposite using antibiotic wastewater to achieve the treatment of antibiotic-contaminated water bodies (Wang, Tang, Mou, et al., 2018). Clay minerals have been widely studied due to their excellent properties, and a large number of researchers have modified them to improve their properties. This paper focuses on the basic structure of clays and the main modification methods in recent years.

2. Basic Structural Units and Classification of Clay Minerals

Clay minerals are widely distributed in nature, and most of them are silicates with a layered structure. Each silicon atom in the crystal is often surrounded by four oxygen atoms, thus forming a silica-oxygen tetrahedron. Multiple tetrahedra are connected in sequence and extended indefinitely to obtain a silica-oxygen tetrahedral sheet. The octahedral sheet is formed by the close packing of two layers of hydroxide ions or cations, with the large cation in the middle. Two basic structural layers, tetrahedral and octahedral sheets, form the majority of layered silicate crystals. The structural unit layers consist of tetrahedral and octahedral sheets connected to each other. Due to the different coordination ratios of the two basic structural layers, there are 1:1-layer types (e.g., kaolinite group) and 2:1 layer types (e.g., mica group) of layered silicate structural unit layers. There are many types of clay minerals and each has different structures and properties. The clay minerals involved in the current study are montmorillonite, kaolinite, seafoam, vermiculite, pozzolanite, etc. (Xu, Zhou, Yan, et al., 2020; Santos, Laihinen, Rodrigues, et al., 2018; Tsai, Bunekar, Wu, et al., 2017; Chen, Yang, & Wang, 2019; Liu, Wang, & Pan, 2018; Cortés, Scott, Pereira-Almao, et al., 2019).

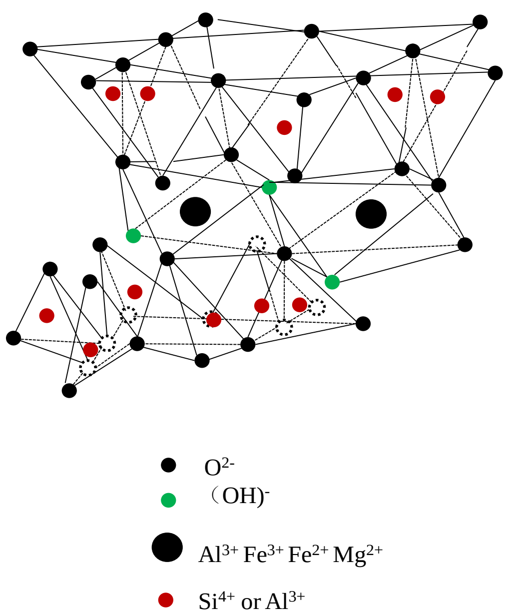

Figure 1. Schematic Diagram of the Crystal Structure of Monazite - vermiculite

3. Study on the Modification Method of Clay

3.1 Active Excitation of Clay Minerals

Activation techniques for clay minerals include high-temperature excitation and acid-base excitation. High-temperature excitation, such as treatment at temperatures above 100 ℃ (usually 200-1000 ℃) for a certain period of time (usually 2-4 h), has a significant effect on the distribution of hydrate species on the surface of clay minerals and at key reaction sites, affecting various surface reactions, including adsorption. Layer spacing and swelling properties are also affected by heat treatment, with montmorillonite layer spacing decreasing with increasing temperature and swelling properties decreasing with increasing temperature (Lu, 2015). However, this calcination process is energy costly, so researchers have invested heavily in the study of alternative methods of clay activation. Acid and alkali excitation is a commonly used means of clay activation. Acid activation usually takes hydrochloric acid or sulfuric acid to treat clay, which is a traditional method of clay chemical treatment. After acid treatment, the surface properties of the clay material are improved and thus suitable for new applications. Sulfuric acid is often used to activate calcium-based bentonite clays, thereby removing calcium ions from the surface or edges of the bentonite layer and increasing its total negative charge, resulting in an increase in the number of acid active sites in the original clay.

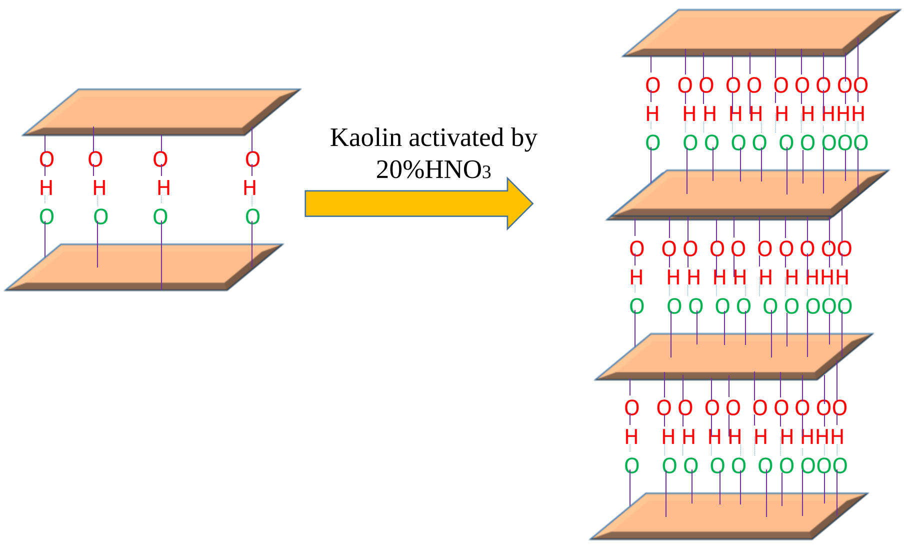

Figure 2. Schematic Diagram of the Crystal Structure of HNO_3 Activated Kaolinite

In contrast, alkali activation is the conversion of an aluminosilicate precursor into an alkali aluminosilicate phase by adding an alkali activation solution, which is then mixed and cured. The composition and processing of the dissolved precursors are the two main influencing factors of the process, with the silica-alumina ratio of the dissolved precursors being the most important one. Crystalline products are more likely to form at lower silica-alumina ratios, and higher is more likely to form geopolymer phases (Marsh, Heath, Patureau, et al., 2019). Alkali activation of metakaolinite can be prepared to obtain geopolymer, which is a commonly used building material, and high alkalinity, although it helps the geopolymer reaction, increases the risk of alkali flooding on the surface of the building material. High pH will accelerate the alkali-excited metakaolin reaction, but when the pH is too high, the alkali-excited reaction is intense and gives off a large amount of reaction heat, and the geopolymer body will form a large temperature stress, which will lead to a decrease in its compressive strength (Fang, Peng, Wei, et al., 2020). In recent years, many researchers have investigated geopolymers and the interest of researchers in geopolymers has been increasing.

3.2 Interlayer Ion Exchange Modification

Ion exchange is one of the ways to chemically modify clays, usually using cationic surfactants with reactive end groups. Covalent modification of clays is also possible using silane coupling agents. Surface and interfacial modification of clays by covalent or non-covalent routes is an important step towards materials suitable for many applications (Djouani, Herbst, Chehimi, et al., 2010; Mazeyar, Parvinzadeh, Gashti, et al., 2015). The presence of many inorganic metal particles between clay lamellae usually makes the clay less compatible with organic polymer matrix and often requires organic salts to exchange the metal ions between the layers for organic modification. The organic chains enter into the interlayer of the clay and make the lamellae to be propped up. At the same time, the introduction of organic matter between the layers makes it easier for the polymer to enter between the clay lamellae to achieve a better dispersion. Clay modification by cation exchange using quaternary ammonium salts is a well known and accepted method to increase the interlayer distance and more importantly to introduce reactive and functional molecules and macromolecular species. Zhang Liang et al. obtained hydroxybismuth ion modified montmorillonite by ion exchange of sodium ions with hydroxybismuth ions between layers of sodium based montmorillonite, which dissolved Bi_2O_3 into a certain amount of $HClO_4$, added ultrapure water and then removed the undissolved Bi_2O_3 by centrifugal filtration before adding the montmorillonite, the process should be well stirred. The removal efficiency of the modified clay on I^- in water was investigated and it was found that the removal of I^- by the modified material should occur by chemisorption and increase the efficiency of bismuth utilization (Zhang, Li, Gao, et al., 2018).

3.3 Surface Grafting Technology of Clay Minerals

3.3.1 One-step Synthesis by Sol-gel Method

Sol-gel method can be used to prepare different forms of nanomaterials and its main advantage is the mild synthesis conditions. Under suitable reaction conditions, synthetic clays with structures similar to natural clays can be obtained by the sol-gel method.Kamal et al. prepared sol-gel silica/nanoclay composites by adding potassium-based montmorillonite clay and trimethyl stearyl ammonium modified montmorillonite to tetraethyl proto-silicate precursor and formic acid catalyst in certain proportions, respectively, using the sol-gel technique. It was found that the dispersion of nanoclay in the silica composites led to the improvement of the thermal stability of silica. And the surface of the coating became more hydrophobic with increasing clay content, which implies its moisture-proof property

(Meera, Sankar, Murali, et al., 2012).

3.3.2 Surface Hydroxyl Grafting Modification

The surface of montmorillonite has a large number of hydroxyl groups, and in the preparation of polymer nanocomposites, the intercalation of polymer molecular chains is difficult due to the hydrophilic nature of the hydroxyl groups on the clay surface, and modification of the hydroxyl groups on the clay surface is often required. Some researchers then used 3-mercaptopropyltrimethoxysilane (MPS) with sulfhydryl groups to modify bentonite in the presence of sodium silicate to form siloxane bonds, and successfully introduced sulfhydryl groups into the interlayer and surface of bentonite, the mechanism of which is shown in Figure 3 (Dong & Xia, 2020). Ma et al. further proposed the reaction of the terminal triethoxy groups of triethoxymethylsilyl ligands with the hydroxyl groups on the clay surface by reacting the lanthanide A method for covalent grafting of lanthanide complexes onto clays was further proposed by Ma, Yang, Song, et al. (2019). Table 1 summarizes the reagents and methods commonly used for surface hydroxyl grafting modification of montmorillonite.

Table 1. Reagents and Methods Commonly Used for Surface Hydroxyl Graft Modification of Montmorillonite

Functional grouping type	Combination method	Reagents	Results	References
Amino-functionalization		γ-aminopropyltriethoxysilane (APTES)		Lai, Li, Wang, et al., 2020; Kostenko, Artiushenko, Kovalchuk, et al., 2019; Altaf, Batool, Gill, et al., 2021
		[3(2-aminoethyl)]propyltrimethoxysilane (AEP-TMS)	Introduction of Amino	Dongmo, Pecheu, Jiokeng, et al., 2020
	Covalent bonds	γ-aminopropyltriethoxysilane (APTES)		Asgari & Sundararaj, 2018
		Triethoxyvinylsilane (VTMS)	Formation of siloxane bonds	Raji, Bouhfid, Qaiss, et al., 2018
Silicone alkylation		Octyltriethoxysilane (OS)		Mbokana, Dedzo, & Ngameni, 2020
		Ethyltrimethoxysilane (ETMS). Dimethylethoxyvinylsilane (DMEVS). Allyltrimethoxysilane (ATMS)		Shin, Park, & Kim, 2019

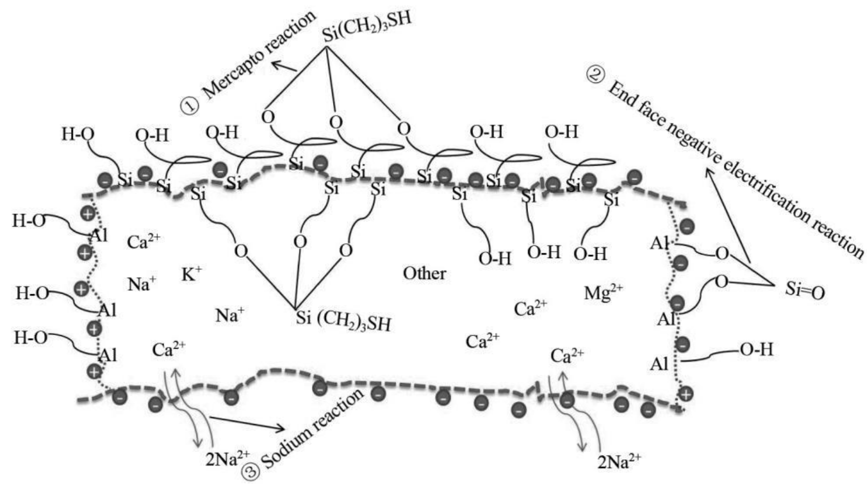

Figure 3. Mechanism of Synergistic Modification of Bentonite by Mercaptopropyltrimethoxysilane and Sodium Silicate (Dong & Xia, 2020)

3.4 Modification by Intercalation Method

3.4.1 Solution Intercalation Method

The solution intercalation method is to dissolve the organic material in a suitable solvent, then add the clay, and make the organic material enter the clay interlayer under the action of the solvent, and then remove the solvent by appropriate means such as evaporation to obtain the intercalated modified clay composite. Therefore, the key is to choose a suitable solvent. The solution intercalation method mainly includes polymer emulsion intercalation method and aqueous solution intercalation method.

Cheng Hongfei et al. used the intercalation method to insert CTAC into the interlayer of kaolinite, sodic montmorillonite and vermiculite, respectively. Among them, kaolinite was inserted several times, and it was found that the hydrogen bonds between kaolinite layers were broken, thus providing sufficient space for CTAC molecules to enter the interlayer. For vermiculite and montmorillonite, clay mineral-CTAC intercalation complexes can be obtained directly by ion exchange entirely. The layer spacing of the intercalated complexes is about 4 nm, and the schematic diagram of the intercalation of the three clays is shown in Figure 5 (Cheng, Jia, Haorilva, et al., 2018). The composites produced by the solution intercalation method are more stable, easy to operate and simple to control, but they are usually difficult to operate because of the inability to find solvents that provide better dissolution and dispersion of the clays. The commonly used intercalation polymers are: alkene homopolymers or copolymers, polyphthalamides, polyethers, polyesters, elastomers (Chen, Gou, Cao, Wu, Ran, Peng, Li, & 2019).

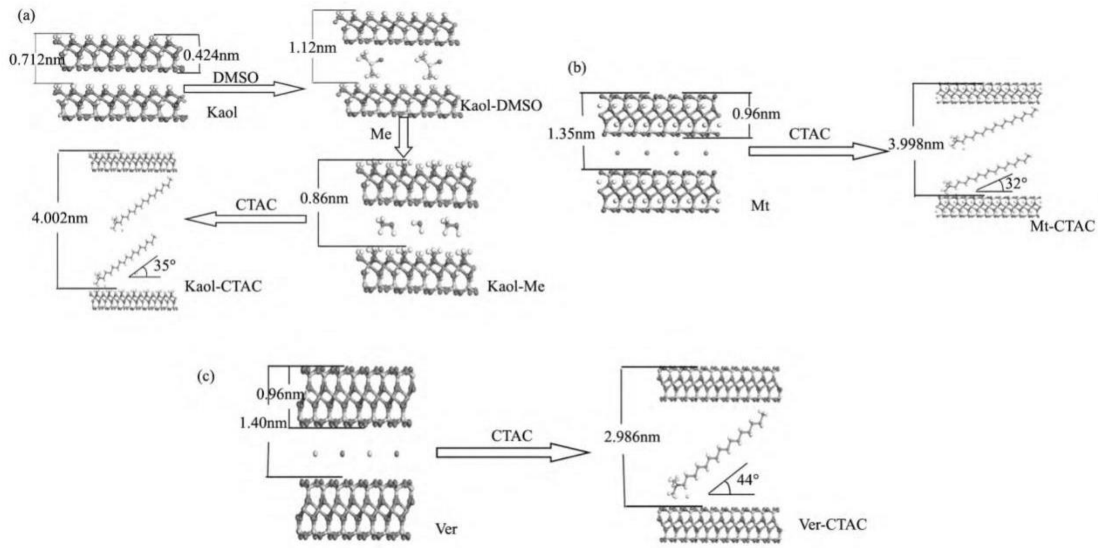

Figure 5. Structural Sketch of Kaolinite, Sodium-based Montmorillonite, Vermiculite and Their Intercalation Complexes (Cheng, Jia, Haorilva, et al., 2018)

3.4.2 In Situ Polymerization Interpolation Method

In situ polymerization intercalation method is used to insert some monomers such as acryl or vinyl into the organically modified clay layer, which makes the clay swell in the monomers, and add suitable polymerization initiator to make the monomers polymerize into polymer, thus breaking the force between the clay layers and making the clay layer dispersed in the matrix. Rongqun Li et al. invented a method for the preparation of in situ polymerized styrene/modified montmorillonite composites. The styrene monomer was introduced into the interlayer of montmorillonite, which was then polymerized into polystyrene, and the montmorillonite was dispersed in the polystyrene at the nano-scale. The resulting composites have high ductility and high flame retardancy (Li, Zhou, & Xu, 2015). A two-step in situ polymerization intercalation method was used to produce organic montmorillonite/polycarbonate diol-based TPU elastomer composites by Bai Jingjing et al. The layer spacing of organically modified montmorillonite was found to increase to 1.856 nm, while the layer spacing of the composites prepared by two-step in situ polymerization intercalation increased to 3.425 nm (Bai, Wang, Lei, & Li, 2017). The composites produced using in situ polymerization intercalation have excellent properties, but it is difficult to operate in practical production because of difficulties in controlling the organic reactions and the volatility of organic reagents, among other difficulties.

4. Conclusion and Outlook

The clay is stable and has excellent properties, such as cation exchange, adsorption, swellability, etc. Moreover, clay is widely distributed in nature, easy to obtain and inexpensive, so it has a wide range of applications. Although nanoclay has been well used in many fields, there are still many problems to be solved in the actual industrial production.

(1) The clay is generally not well dispersed and uniform enough in the process.

(2) The quantum and surface effects of nanoclay particles have not been further investigated in depth.

(3) It is difficult to guarantee the quality of clay from different sources and batches. And.

In response to the above problems, I think the research on clay minerals should be inclined to the following aspects, optimize the separation and purification technology of clay, and try to make the quality of clay from different batches of different mineral sources similar. Improve the modification technology and explore more efficient and economical modification methods.

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