Crystal chemistry characteristics and dispersion performance of Ca-montmorillonite with different layer charge density

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Keywords: Ca-montmorillonite, layer charge density, crystal chemistry, dispersion performance

Abstract

The correlation between crystal chemistry characteristics and dispersion performance of Ca-montmorillonite with different layer charge density was studied. The four kinds of purified montmorillonite were characterized by XRD, XRF, FTIR, SEM, TEM, BET, TG-DTG, Zeta potential, and Molecular dynamics simulation (MD). The XRD analysis results show that the d001 value of the four kinds of Ca-montmorillonite are 1.51 nm, 1.51 nm, 1.53 nm, and 1.50 nm, respectively, and the calculation results of layer charge density show that the semi-unit cell charge density are 0.38, 0.53, 0.61, and 0.69, respectively. The charge density is positively correlated with the mass content of MgO. The FTIR analysis results show that with the increase of layer charge density, the couple vibration wave number of Si–O–Mg and Mg–O move towards the high frequency region, from 464.70 cm⁻¹ to 466.36 cm⁻¹ and from 517.12 cm⁻¹ to 520.41 cm⁻¹. The SEM analysis results show that the higher layer charge density of montmorillonite, the worse exfoliation between layers and the thicker layer thickness, The images of TEM show that montmorillonites are mainly composed of a clearly layered structure. The results of BET show that with the increase of layer charge density, the BET surface area, micropore area and total pore volume gradually increase from 32.69 m² g⁻¹ to 64.50 m² g⁻¹, from 4.87 m² g⁻¹ to 18.24 m² g⁻¹, and from 0.06 cm³ g⁻¹ to 0.12 cm³ g⁻¹, respectively, while PSDs and pore diameter decrease from 7.88 nm to 1.74 nm, and from 7.65 nm to 5.47 nm. The results of TG and DTG show that with the increase of charge density, the removal temperature of free water and interlayer water increase from 80 °C to 100 °C and 139 °C to 155 °C, respectively. The simulation results of MD show that with the increase of layer charge density, the number of hydrogen bonds increase from 186 to 271 and the adsorption energy increases from −1467.11 to −1874.32 kcal mol⁻¹. The particle size increases from 701 nm(Mt1) to 1576 nm(Mt4) with the layer charge density, and the absolute value of Zeta potential, colloidal value and expansion capacity of montmorillonites suspension decrease with the increase of the layer charge density, which further indicates that the dispersion of montmorillonites decrease with the increase of layer charge density.

1. Introduction

Montmorillonite clay mineral is composed of two tetrahedral layers sandwiching an aluminum octahedral layer [1]. Layer charge density is an important crystal chemistry property of montmorillonite, and which is a main reason for the difference of application properties of montmorillonite. In nature, montmorillonite obtains electric charge mainly through two ways [2]. Firstly, the isomorphism substitution in the crystal structure of montmorillonite results in the permanent negative charge of montmorillonite on the layer surface.
ions Si<sup>4+</sup> in the tetrahedron can be replaced by Al<sup>3+</sup>, and the central ions Al<sup>3+</sup> in the octahedron can be replaced by a certain number of divalent cations, such as Mg<sup>2+</sup>, Fe<sup>2+</sup>, etc. The results of infrared spectrum analysis can also prove that the phenomenon of mass isomorphism exists widely in montmorillonite. The research result of Tsiantos and Wumei Lin et al. [3] indicates that due to the isomorphic substitution between divalent cations and Al<sup>3+</sup> in alumina octahedron of montmorillonites, the M–O characteristic peak of 470 cm<sup>-1</sup> wavelength moves to the high-frequency region [4]. On the other hand, the end face of the montmorillonite is charged because of the breaking Al–O and Si–O bond at the edge of the montmorillonite lamellar layer. Previous research results show that the edge charge of montmorillonite varies with the pH value of the solution and has little effect on the hydration properties of montmorillonite [5, 6]. By comparison, layer charge density of montmorillonite has an important impact on the application performance of montmorillonite. Many researcher put forward that the hydration properties of montmorillonite are closely related to the layer charge density of montmorillonite [5, 7]. Gouy–Chapman [8] pointed out that the hydration properties of montmorillonite, especially the swelling of montmorillonite, were related to the charge density of montmorillonite. Ana Luisa et al. [9, 10] found that with the increase of layer charge density, the expansion capacity and adsorption capacity of montmorillonite tended to decrease. This conclusion is consistent with that of Hao Yi et al. [11].

In order to further study the influence of layer charge density of montmorillonite on its hydration characteristics at the molecular and atomic level, molecular simulation has been widely used in the study of the hydration characteristics of montmorillonite. Our recent findings indicated that the layer charge density of montmorillonite had a significant effect on hydration properties, the higher layer charge density, the lower self-diffusion coefficient of water molecules in inter-layer and the worse hydration performance of montmorillonite [12]. We also found that the more −OH bonds formed between layers of montmorillonite and water molecular in inter-layer, the higher the removal temperature of inter-layer water [13], which is consistent well with the conclusions of Jianxi Zhu et al. Jian Fei Peng et al. [14] and Zhongxin, Luo et al [15] found that there might be a negative correlation between the charge density of montmorillonite and its hydration performance, the higher charge density of montmorillonite, the worse dispersion in aqueous solution, the worse colloidal stability, and the lower the absolute value of Zeta potential.

However some researchers don’t think so, they believe that the hydration properties of montmorillonite are only related to water content and crystal structure of montmorillonite, but not related to layer charge [16, 17]. Philip F Low [18] thought that the expansibility of montmorillonite was more related to the proportion of collapse versus expansion layer than to the layer charge density. Christidis and Chiou et al. [19] found that the lamellar structure of montmorillonite made it easier to disperse in water. The thinner lamellar of montmorillonite, the greater hydration properties of montmorillonites in water, and thus the well swelling performance of montmorillonite. This finding is consistent with that of Kaufhold et al. [4], who reported that the swelling process was regulated by multiple factors, such as the composition of the minerals and crystal structure.

It can be seen from above that there have been many studies about the relationship between charge density and hydration properties of montmorillonite, it is generally believed that the hydration characteristics of montmorillonite are both related to its layer charge and crystal structure. In fact, the layer charge density of montmorillonite is closely related to its crystal structure, however, both the charge density and crystal structure of montmorillonite depend on its mineralogical properties, therefore, the author thinks that the crystal chemistry properties of montmorillonite are the most important factors determining its hydration properties or other application properties. In this paper, four kinds of montmorillonite with different charge density from different regions in China were used as the research materials, the crystal chemistry properties of four kinds of montmorillonite were systematically studied by XRD, XRF, FTIR, SEM, TEM, BET, TG–DTG, MD and Zeta potential analysis, on this basis, the correlation between crystal chemistry properties and hydration properties of montmorillonite was studied.

### 2. Experiment

#### 2.1. Materials

The four kinds of raw bentonite ore are from Weifang (Mt1), Liaoning (Mt3) and Inner Mongolia (Mt2, Mt4) of China, respectively. The four kinds of raw bentonite ore used in this work were first purified by natural sedimentation in laboratory, the −2 μm fraction in the suspension was collected and dried at 90 °C in a drying oven. The four kinds of purified montmorillonite clay mineral were marked as Mt1, Mt2, Mt3, and Mt4, respectively. All the four purified montmorillonite clay mineral were ground in a vibrating ball mill and sieved through 200 mesh.
2.2. Measurements
The mineral and chemical composition, crystal chemistry characteristics and dispersion properties were comprehensively studied by XRD, XRF, FTIR, SEM, TEM, BET, TG-DTG, Zeta potential and MD. The mineral composition of montmorillonite can be determined by XRD, according to the analysis results of XRF, the chemical composition of montmorillonite can be obtained, the charge density of semi-unit cell is calculated by using the structural inference algorithm, the difference of isomorphism of montmorillonite with different charge density are analyzed by FTIR, the difference of exfoliation properties, morphology features and particle size of different montmorillonite can be separately studied by SEM, TEM and nano particle analyzer, the specific surface area and pore structure of four kinds of montmorillonite studied by BET, the mechanism of difference in hydration properties of montmorillonite with different layer charge density are simulated by MD. The swelling capacity, colloid valence, Zeta potential of the four kinds of montmorillonite are analyzed by experiments.

2.3. Characterization techniques
XRD data were recorded with a RigaKu D/max-rB diffractometer using CuKα radiation at 40 Kv and 100 mA (Rigaku Corporation, Akishima-shi, Japan). The diffraction angle of the patterns was recorded from 3° to 70° with a scanning speed of 8°/min.

The chemical composition analysis of the purified montmorillonite was carried out using the Axios advanced x-ray fluorescence spectrometer manufactured with rhodium target and pressed powder for 20 min (PANalytical B.V, Almelo, Netherlands).

The functional groups present in the montmorillonite were identified by using the Nicolet i550 FT-IR Fourier infrared spectrometer (Thermo Fisher Scientific, USA) with the KBr pellet method and the wavelength range was 450 cm\(^{-1}\)–4000 cm\(^{-1}\). SEM images were collected using an APREO instrument (FEI, Hillsboro, Oregon, USA).

The microstructure of montmorillonite with different layer charge density were investigated by the TEM on the FEI Tecnai G2 F20 device. The acceleration voltage of the experiment was 2000 kV, the amplification factor was 200 000, and the sample size was 20 nm (FEI, Tecnai, USA).

The BET specific surface area, pore volume, average pore diameter, and nitrogen adsorption/desorption isotherms of different montmorillonites were determined using the Mike ASAP2460 series volumetric gas adsorption instrument, which is a USA automated gas adsorption system using nitrogen as the adsorbive. The determination is based on measuring the nitrogen adsorption. Experiment for adsorption isotherms were performed at 77.3 K and at the relative pressure up to P/P0 ~ 1 (micrometerics, Mike company, USA).

The TG analysis was carried out using a TG/SDTA851ethermogravimetric/differential thermal synchronizer. The TG and DTG analysis were conducted under nitrogen atmosphere and raising the temperature from 30 °C to 350 °C at the rate of 5 °C min\(^{-1}\) and the weight of each sample should be controlled at 8 ± 0.05 mg (Mettler-Toledo, Zurich, Switzerland).

Particle size was measured by ZEN1690-nano90 nano particle analyzer and the suspension concentration was 0.05% (Malvern Panalytical, Malvern, England). Zeta potential was measured by a JS94H microelectrophoresis instrument at room temperature with 10 voltage, the suspension concentration was 0.01% and the pH value was 7 (ZhongChen, Shanghai, China).

MD simulation was performed by Materials Studio 7.0 software (Accelrys, San Diego, CA, America) to further investigate the microscopic mechanism of the hydration properties of four kinds of montmorillonite with different layer charge. In the experiment of molecular simulation, according to the atomic coordinates of the montmorillonite, the 8a × 4b × 1c super-cell models of four kinds of montmorillonite were established in the first step. In the next experiment, the four kinds of montmorillonite models were optimized and simulated. The molecular dynamics simulation used the NPT and NVT ensembles in Forcite module. The temperature was 298.0 K, the step length was 1.0 fs, the total simulation time was 2 ns. The number of steps was 2 \times 10^8 and the output was every 200 steps. The universal force field (UFF) was used for simulation in this work [20]. The atomic coordinates of montmorillonite were shown in table 1.

3. Results and discussion

3.1. Mineral composition analysis
XRD analysis results of four kinds of raw bentonite and four kinds of –2 μm purified montmorillonite are shown in figure 1.

It can be seen from figure 1(a) that all the four kinds of raw bentonite contain a certain number of impurity minerals, such as quartz, cristobalite and feldspar. The d\(_{\text{001}}\) of montmorillonites are 1.51 nm, 1.51 nm, 1.55 nm, and 1.50 nm, respectively, which are all typical Ca-montmorillonites. After purification, it can be seen from figure 1(b) that the four kinds of purified montmorillonite only contain a small number of cristobalite
impurity minerals, which indicates that the purity of 2 μm montmorillonite can meet the technical requirements of the subsequent XRF test and charge density calculation.

3.2. Calculation of layer charge density
The results of chemical composition of the four kinds of purified montmorillonite measured by XRF are shown in the table 2.

It can be seen from table 2 that the mass content of SiO$_2$ and Al$_2$O$_3$ in the four kinds of purified montmorillonite are all above 63% and 17%. The content of MgO in four kinds of montmorillonite increases from 4.15% to 6.44%, which shows that the substitution of Mg$^{2+}$ for Al$^{3+}$ in octahedron increases gradually from Mt1 to Mt4. The content of CaO in the four kinds of montmorillonite is obviously higher than that of Na$_2$O, which further indicates that all the purified montmorillonite are Ca-montmorillonites. The results are consistent well with the XRD analysis results.

According to the crystal structure characteristics of montmorillonite and the occupancy rule of cations in crystal structure [21], the Si$^{4+}$ in tetrahedron is usually replaced by Al$^{3+}$, and Al$^{3+}$ in octahedron is usually replaced by Mg$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, the structural formulas and charge density of four kinds of montmorillonite were calculated according to the calculation method of 11(O) [22] in semi-unit cell of montmorillonite. The calculation results of crystallochemical formula are as follows:

$$\text{(Ca}_{0.17}\text{K}_{0.02}\text{Mg}_{8.98})\text{Si}_{0.38} [(\text{Al}_{3.63}\text{Fe}_{0.01}\text{Mg}_{0.36})\text{2.00}][(\text{Si}_{9.08}\text{Al}_{0.02})\text{4.00}\text{O}_{10}]\text{OH}_{2}]$$  (Mt1)

$$\text{(Ca}_{0.25}\text{K}_{0.03})\text{Si}_{0.53} [(\text{Al}_{4.44}\text{Fe}_{0.03}\text{Ti}_{0.02}\text{Mg}_{8.53})\text{2.00}][(\text{Si}_{9.06}\text{Al}_{0.04})\text{4.00}\text{O}_{10}]\text{OH}_{2}]$$  (Mt2)
Ca Na K Mg Al Fe Ti Mg Si Al O OH
Mt30.27 0.02 0.03 0.01 0.61 1.34 0.05 0.03 0.58 2.00 3.94 0.06 4.00 10 2
Ca Na K Mg Al Fe Ti Mg Si Al O OH
ag Mt 40.29 0.03 0.04 0.02 0.69 1.27 0.04 0.03 0.66 2.00 3.94 0.06 4.00 10 2

It is clear that the charge density of four kinds of montmorillonite are 0.38, 0.53, 0.61, and 0.69, respectively.

According to the results, the proportion of layer charge density generated in tetrahedrons of the four kinds of montmorillonite accounts for about 5.3%–9.8% of the total charge density, and the proportion of charge generated in the octahedron accounts for about 90.2%–94.7%. Therefore, the charge density of montmorillonite depends mainly on the amount of charge generated in the octahedron.

The layer charge in the octahedron is mainly due to the substitution of Mg\(^{2+}\) for the Al\(^{3+}\). Usually, the Mg\(^{2+}\) in the montmorillonite is present in the octahedron, so the content of MgO in the chemical composition of montmorillonite has a corresponding impact on the magnitude of the charge density. Generally, the higher the content of MgO in montmorillonite, the higher the charge density of montmorillonite. The relationship between MgO content and layer charge density is shown in figure 2.

3.3. FTIR Analysis of Montmorillonites

Pre-treatments were completed before the experiment. The \(2 \mu\)m purified montmorillonite and KBr drug were placed in a constant temperature drying oven and dried at 90 °C for 12 h to ensure that the water on the surface of the montmorillonite did not affect the results of the experimental test. Four kinds of montmorillonite were analyzed by infrared spectroscopy at room temperature with KBr as the background value. The results are shown in figure 3.

It can be seen from figure 3 that the main infrared spectra of the four kinds of montmorillonite have little difference in overall. In the high-frequency absorption, there are two obvious absorption bands, namely 3620 cm\(^{-1}\) and 3390 cm\(^{-1}\), in which the characteristic peak near 3620 cm\(^{-1}\) is caused by the stretching vibration of Al–O–H. The characteristic peak near the mid-band 920 cm\(^{-1}\) is also related to the stretching vibration of the Al–OH bond. The appearance of absorption bands of 1032 cm\(^{-1}\) and 790 cm\(^{-1}\) in the IR spectrum are caused by the stretching vibrations of Si–O–Si in tetrahedron (figure 3(a)). Moreover, the appearance of absorption of 460 cm\(^{-1}\) and 520 cm\(^{-1}\) in the IR spectrum (figure 3(a)) may be caused by the presence of coupled vibration of Si–O–Mg and Mg–O [3, 23]. While with the increase of the substitute of Mg\(^{2+}\) for Al\(^{3+}\), the absorption band gradually moves to the high frequency region, from 464.70 cm\(^{-1}\) to 466.36 cm\(^{-1}\) and from 517.12 cm\(^{-1}\) to 520.41 cm\(^{-1}\) (figure 3(b)), respectively. The characteristic band strongly depends on the different occupancy of Mg\(^{2+}\) in octahedron of different montmorillonites [6]. The higher the content of MgO in montmorillonite, the higher the number of occupied Mg\(^{2+}\) in octahedron, the higher the charge density, and the more obvious the coupling vibration of Si–O–Mg and Mg–O in the high frequency zone. This research result fits well with the conclusions obtained in section 3.2.

3.4. Morphology analysis of montmorillonites

In order to further study the difference of exfoliation properties of montmorillonite with different layer charge density, the micromorphology of the four kinds of montmorillonite were analyzed by SEM, and TEM. The test results of SEM are shown in figure 4, respectively. The test results of TEM are shown in figure 5.
As shown in figure 4, the morphology of montmorillonite with different layer charge density varies greatly from Mt1 to Mt4, with the increase of the layer charge of montmorillonite, the exfoliability of montmorillonite becomes worse and worse, the higher the layer charge density of montmorillonite, the thicker the lamellar layers of montmorillonite. The reason is that the higher the layer charge density of the montmorillonite, the greater the electrostatic attraction between the layers, so the worse the peel property between the layers, resulting in the thicker the layer thickness.

The TEM micrographs of montmorillonite with different layer charge density are presented in figure 5. The images indicate that the four kinds of montmorillonite are mainly composed of a layered structure with a slight difference in the inter-layer distance. The basal spacing of four kinds of montmorillonite is in the range of 1.49–1.51 nm, which is in good agreement with the value obtained by the XRD analysis.
3.5. BET analysis of montmorillonites
In order to explore the differences of surface area and pore structure of four kinds of montmorillonite, BET test was performed. The test results of N2 adsorption/desorption isotherms are shown in figure 6. The results of pore size distributions of montmorillonite with different layer charge density are shown in figure 7. The results of surface area, pore volume, and pore diameter of four kinds of montmorillonite are shown in table 3.

It can be seen from figure 6 that the nitrogen adsorption–desorption isotherms of the four kinds of montmorillonite are all IV adsorption isotherm, indicating that the four kinds of montmorillonite are all mesoporous materials. It can be also seen that the monolayer adsorption capacity, that is the BET surface area, increases in the following order: Mt1 < Mt2 < Mt3 < Mt4. It can be seen from table 3 that with the increase of
layer charge density, the BET surface area increases from 32.6945 m$^2$ g$^{-1}$ (Mt1) to 64.5017 m$^2$ g$^{-1}$ (Mt4), the micropore area increases from 4.8716 m$^2$ g$^{-1}$ (Mt1) to 18.2493 m$^2$ g$^{-1}$ (Mt4), and pore volume increases from 0.0575 cm$^3$ g$^{-1}$ (Mt1) to 0.1234 cm$^3$ g$^{-1}$ (Mt4), respectively, while the pore diameter gradually decreases from 7.6534 nm (Mt1) to 5.4700 nm (Mt4).

It can be seen from figure 7 that the pore size distributions (PSDs) of four kinds of montmorillonite are slight differences in character. The PSDs of Mt3 and Mt4 are both less than 2 nm, 1.7412 nm and 1.7404 nm, respectively. It can be seen that the PSDs of the Mt3 and Mt4 are very close, mainly because the layer charge density of the two kinds of montmorillonite is also close. The PSDs of Mt1 and Mt2 are both more than 6 nm, 6.7972 nm and 7.8789 nm, respectively. Obviously, the layer charge density of montmorillonite is directly related to the pore structure and specific surface area. The increase of layer charge density of montmorillonite results in the simultaneous increase of PSDs, pore volume, and pore connectivity.

The main reason for these experimental phenomenon is that with the increase of the layer charge density, the layer of montmorillonite becomes thicker and thicker, which is in good agreement with the results of SEM, TEM, and analysis results of particle size (figure 11). With the increase of the thickness of montmorillonite layer, the montmorillonites are more likely to accumulate, which results in the mean pores diameter of montmorillonite becomes smaller, and the BET becomes greater. Therefore the higher layer charge density of montmorillonite, the higher BET surface area, micropore area, and total pore volume, the lower PSDs and pore diameter.

### 3.6. TG and DTG analysis of montmorillonites

In order to further explore the different dehydration temperatures of free water and inter-layer water with different charge density, TG and DTG analyses were carried out in this paper. The combination of the TG and DTG could be used to study the thermal stability of montmorillonites and further study the effect of charge density on the dehydration temperature. The TG and DTG curves of four kinds of montmorillonite are shown in figures 8(a) and (b), respectively.
As shown in figure 8 (b), from Mt1 to Mt4, the removal temperature of the free water was 80 °C, 90 °C, 92 °C, and 100 °C and the inter-layer water was 139 °C, 142 °C, 150 °C, and 158 °C, respectively. The DTG curves showed two endothermic peaks, the first peak appears between 50 °C–100 °C, and the second appears between 100 °C–200 °C. The mass losses of montmorillonite at first peak may be attributed to the losses of free water. The second peak is caused by the removal of inter-layer water from the montmorillonite. According to our previous research result, the removal of inter-layer water requires a higher temperature because of the –OH bonds formed by hydrogen atom of water molecules and oxygen atoms in the Si–O surface [24]. In the process of removing inter-layer water, high energy is needed to break the H–O bond so that inter-layer water can be removed from the montmorillonite. Therefore, the higher the amount of O–H bond and the bond energy between the water and montmorillonite layer surface, the higher the temperature of water removal. The number of O–H bonds and adsorption energy increase with the increase of charge density which therefore leads to increase of dehydration temperature of montmorillonite [25].

3.7. Molecular dynamics simulation of hydration properties of montmorillonites

According to the calculation results of crystal chemical formula, 8a × 4b × 1c super-cell models were established for simulation study. According to our previous research methods [26], the microscopic mechanism of the hydration properties of four kinds of montmorillonite with different layer charge was deeply studied at the atomic level by means of molecular dynamics simulation. The research results are shown in table 4 and figure 9.

It can be seen from table 4 and figure 9, with the increase of layer charge density of montmorillonites, the number of hydrogen bonds formed by hydrogen atoms (Hw) in the water molecules and oxygen atoms (Ot) in the siloxane surface in the inter-layer of montmorillonite increases from 186 to 271, and the adsorption energy increases from −1467.11 to −1874.32 kcal mol⁻¹. The reason is that with the layer charge density of montmorillonites increase, the electronegativity of the montmorillonite siloxane surface increases, with the increase of electronegativity of montmorillonite siloxane surface, more and more water molecules are adsorbed to the siloxane surface, both the number of hydrogen bonds formed by hydrogen in water molecules and oxygen in siloxane surface and adsorption energy are also increasing, as a result, the hydration performance of montmorillonite decreases with the increase of layer charge density.

3.8. The dispersion performance of montmorillonites

In order to further explore the differences of dispersion properties of montmorillonite with different charge density, the particle size, Zeta potential, the swelling capacity and colloid valence of four kinds of montmorillonite were separately tested. The particle size analysis of four kinds of montmorillonite are shown in Figure 8.
The results of Zeta potential, swelling capacity and colloid valence ofmontmorillonites are shown in table 5 and figure 11. It can be seen from figure 10. That the particle size of montmorillonites gradually increases with the increase of the layer charge density of four kinds of montmorillonite, the particle size of four kinds of montmorillonite gradually increases from 701 nm (Mt1) to 1576 nm (Mt4). As we all known, Zeta potential is an important index to characterize the stability of colloidal dispersion system, the higher the absolute value of Zeta potential, the more stable the system is. It can be seen from table 5 and figure 11. That the Zeta potential, swelling capacity, and colloid valence of montmorillonite all decrease with the increase of charge density. The absolute value of Zeta potential decreases from 21.92 mv to 17.92 mv, the swelling capacity decreases from 15.99 ml g$^{-1}$ to 6.99 ml g$^{-1}$, and the colloidal valence decrease from 5.60 ml g$^{-1}$ to 2.93 ml g$^{-1}$. The experimental results are also in good agreement with the MD simulation results of figure 9 and table 4. The reason is that the lower layer charge density of montmorillonites (Mt1), the less number of hydrogen bonds and the lower adsorption energy, the more easily dispersed and peeled of under the action of polar water molecules. And another reason is that montmorillonite easily forming a stable card-house structure due to the montmorillonite with negatively charge on inter-layer surface and with positively charge on end face. This can also explain the phenomenon that the particle size of montmorillonites increases with the increase of the layer charge density of four kinds of montmorillonite. Therefore, as the layer charge density increases, the particle size of montmorillonites increases, the Zeta potential, expansion capacity and colloidal valence decreases.

4. Conclusions

In this study, it is found that due to the differences in the crystal chemical characteristics of the four kinds of montmorillonite, their corresponding chemical composition characteristics, FTIR characteristics, SEM morphology, BET nitrogen adsorption/desorption isotherms, TG and DTG curve characteristics, MD simulation result, Zeta potential value, and dispersion properties are also significantly different. Four kinds of montmorillonite all with obvious layered structure are reflected in the TEM image, and the results are in good agreement with the value obtained by the XRD analysis. The higher the layer charge density of montmorillonite, the higher the content of magnesium in their chemical composition, the more obvious the couple vibration wave number of Si–O–Mg and Mg–O move towards the high frequency region in the FTIR spectrum, the more easily layer of montmorillonite aggregate, the thicker layer thickness reflected in the SEM image, the higher value of
BET surface area, micropore area and pore volume, the smaller value of PSDs and pore diameter, the worse the exfoliation between layers and the thicker the layer thickness, the higher the removal temperature of water molecules in inter-layers. With the layer charge density increase, the number of hydrogen bonds formed by hydrogen atoms in the water molecules and oxygen atoms in the siloxane surface and the higher adsorption energy gradually increase. The simulation results are in good agreement with the experimental results, according to the results of the dispersion performance analysis of montmorillonite, the higher layer charge density, the larger particle size, the lower the absolute value of Zeta potential, colloidal value and expansion capacity of montmorillonite suspension, and the worse the dispersion of montmorillonite.

Acknowledgments

This work was supported by a grant from National Natural Science Foundation of China—‘Design of structure and gelling performance of Montmorillonite/Alkylammonium based on the adsorption properties of Alkylammonium on Montmorillonite (No:51774200)’, and ‘Study on the immobilization effect and mechanism of heavy metal in sulfide-mine tailings by chelating agent modified bentonite (No:51764003)’.
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icts of interest

We declare that we have no conflicts of interest.

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Figure 11. The Zeta potential, swelling capacity and colloid valence of montmorillonites.
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