Study on the ball milling modification of attapulgite

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Abstract

In order to improve the dispersion of attapulgite (ATP), the surface of ATP was modified by conventional ball milling, chemical modification and ball milling modification methods. The ATP samples were studied by XRD, FTIR, TG, TEM, etc. The research results show that the resulting ATP modified by conventional ball milling still has the secondary agglomeration phenomenon and partial damage phenomenon of its rod-like crystal. The surface of ATP can be effectively modified by silane coupling agent KH-550 using chemical modification and ball milling modification methods and their rod-like crystal cannot be damaged. The ball milling modification and dispersion effects for ATP was the best. The contact angle of the resulting ATP was increased by 189\%, its specific surface area was increased by 218\%, and the volume of the bundles and the sedimentation rate were decreased.

1. Introduction

Sample Attapulgite (ATP), also known as palygorskite, is a hydrous magnesium-rich aluminosilicate clay mineral containing layer-chain structures. Generally, the molecular formula of ATP can be expressed as $\text{Mg}_x\text{Si}_y\text{O}_{2x}[(\text{OH})_2]_y\cdot\text{H}_2\text{O}$ [1]. In natural state, ATP presents aggregates composed of a cluster of the rod crystals. The diameter of the rod-like crystals varies in the range from tens to dozens of nanometers, with the length ranging between tens to dozens of microns.

ATP has been widely used in various fields, such as food and pharmaceuticals, agriculture, building materials, environmental protection, mining and metallurgy. In the chemical industry, ATP has been widely used as a filling material which is added to polymers to prepare composite materials. The introduction of ATP improves the mechanical properties and flame retardancy of the polymer matrices [2]. However, the dispersion of ATP is poor due to its susceptibility to agglomeration [3]. Further, ATP has poor compatibility with polymers due to its high hydrophilicity [4]. As a result, it is unable to take the full advantages of ATP in the preparation of composite materials [5]. Therefore, it is of vital importance to improve the dispersion of ATP and its compatibility with polymers.

Numerous research studies have been carried out for the chemical modification of ATP to overcome the agglomeration of ATP as well as to improve its compatibility with polymers. For instance, (3-aminopropyl) triethoxysilane (APTES) have been grafted on the ATP surface to improve the compatibility of ATP with polyvinylidene fluoride (PVDF) matrix [6]. 3-(trimethoxysilyl) propyl methacrylate (MPS) have been grafted on the ATP surface, which made ATP suitable for the facile \textit{in situ} bulk polymerization with polystyrene [7]. Poly(methyl methacrylate) (PMMA) have been grafted on the ATP surface to improve the compatibility of ATP with polylactide (PLA) matrix [8]. Acrylic acid and (3-mercaptopropyl) trimethoxysilane have been simultaneously used for the modification of ATP to enhance its adhesion with the cotton fabric [9]. Ethylenediamine has been used in the modification of ATP to improve its adsorption properties [10]. However, the chemical modification methods, are cumbersome and require strict process conditions and preparation techniques [11]. Due to the advantages such as simple processing and high efficiency, ball milling has received widespread application in industrial production [12, 13]. Specifically, the ball milling method has been
employed worldwide to treat diverse particles. Typical cases include ball milling of multi-walled carbon nanotubes to improve their dispersion, dispersion of TiO₂ in polymers via ball milling, improved dispersion of ATP via ball milling treatment [14–16]. However, the nanoparticles treated by the conventional ball milling method are prone to secondary agglomeration, which can offset the effect of improving dispersion. Besides, ball milling does not affect the hydrophilicity of ATP. Thus, in summary, both chemical modification and conventional ball milling methods have specific limitations. To eliminate these limitations, ball milling modification methods have been developed. In ball milling modification, the modifiers are incorporated in the conventional ball milling processes to treat the particles in order to achieve superior properties. For instance, improved dispersion of SnO₂ nanoparticles and modification of silica particles have been reported by employing the ball milling modification method [12, 17].

In order to improve the dispersion of ATP and to study the effects of surface modification methods on the crystal structure, surface chemical composition, hydrophilicity, pore structure, dispersion of ATP, the ATP samples was treated by pickling, conventional ball milling, chemical modification and ball milling modification. Further, the properties of ATP samples prepared by these methods have been compared.

2. Materials and methods

2.1. Materials and reagents

ATP powder (nanoscale) was purchased from Shandong Nano Technology Co., Ltd. and designated as o-ATP. Analytical grade anhydrous ethanol, concentrated sulfuric acid and acetic acid were purchased from Tianjin Fuyu Chemical Co., Ltd. Analytical grade silane coupling agent KH-550 was purchased from Sinopharm Chemical Reagent Co., Ltd. The deionized water used in this study was produced in the laboratory.

2.2. Treatment of ATP

Pre-treatment of o-ATP was conducted by washing the powder with acid solution. The concentrated sulfuric acid was added into deionized water to prepare the dilute sulfuric acid solution with a concentration of 1 M. 10 g of o-ATP powder was added into 100 ml dilute sulfuric acid solution, treated for 0.5 h, then the mixed solution was repeatedly rinsed with deionized water until the filtrate pH = 7. The filtered sample was dried at 100 °C for 8 h, then, collected and designated as p-ATP. Further, the so-obtained p-ATP sample was subjected to conventional ball milling. For this, 3 g p-ATP powder, 16 ml deionized water and 10 ml anhydrous ethanol were added to a planetary ball milling machine. The intermittent ball milling procedure, in which the ball mill operates for 6 min with a pause of 3 min, was employed. The ball milling was carried out for total 9 h at a rotational speed of 400 r min⁻¹. The suspension was subsequently filtered out and dried. The so-obtained ATP sample was collected and designated as bp-ATP. In the second method, the p-ATP sample was treated via the chemical modification method. The γ - aminopropyl triethoxysilane also named KH-550, is a glass fiber treatment agent with strong versatility, which structural formula is NH₂CH₂CH₂Si(OC₂H₅)₃ [18]. For this, anhydrous acetic acid was added into deionized water to prepare acetic acid solution with a pH = 3. 50 ml of anhydrous ethanol was added to 100 ml of the dilute acetic acid solution. Afterwards, 10 g of p-ATP and 0.3 g of silane coupling agent KH-550 were subsequently added to the mixed solution. The contents of the mixture were heated in a water bath at a constant temperature of 70 °C under magnetic stirring for 6 h. The solid obtained after the chemical modification was repeatedly washed and dried, followed by its designation as cp-ATP. In the ball milling modification, 3 g p-ATP and 0.09 g silane coupling agent KH-550 were added to the sample container of the planetary ball milling machine. 16 ml deionized water and 10 ml anhydrous ethanol were subsequently added to the container. The intermittent ball milling procedure, in which the ball milling machine operates for 6 min followed by a pause for 3 min, was employed for total 9 h with the rotational speed of 250 r min⁻¹. The solid attained after filtering the suspension was repeatedly washed and dried, followed by its designation as mp-ATP. The summaries of the treatment procedures of ATP samples showed in table 1.

2.3. Characterization

The crystal structure and phase composition of the ATP samples were analyzed using an X-ray diffractometer (Ultima IV, Japan Science Corporation). The working voltage, working current and scanning speed were 40 kV, 40 mA and 4 °/min, respectively. The scanning of the samples was carried out in the 2θ range from 5° to 60° at room temperature. The chemical composition of the ATP samples was characterized using a Fourier transform infrared spectrometer (NEXUS-670, American Thermal Power Company). The samples were incorporated in the KBr (1 mg sample and 200 mg KBr) and pressed disks (YP-20, Henchld Science Technology Development Co., Ltd.). The scanning wavenumber range was 4000 to 500 cm⁻¹, with a step size of 4 cm⁻¹ at room temperature. TGA of the ATP samples with the weight of around 6 mg was performed on TGA thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ from 30 °C to 850 °C under a nitrogen atmosphere.
| Sample name | o-ATP | p-ATP | bp-ATP | cp-ATP | mp-ATP |
|-------------|-------|-------|--------|--------|--------|
| Treatment method | raw materials | pickling | ball milling | chemical modification | ball milling modification |
| Process parameters | — | 10 g o-ATP, 100 ml 1 M acid solution, treated 0.5 h. | 3 g p-ATP, 26 ml ethanol solution, ball material ratio 1:24, rotational speed 400 r min$^{-1}$, ball milling 6 h. | 10 g p-ATP, 0.3 g KH-550, 150 ml ethanol solution, magnetic stirring 6 h, 70°C. | 3 g p-ATP, 0.09 g KH-550, 26 ml ethanol solution, ball material ratio 1:24, rotational speed 250 r min$^{-1}$, ball milling 6 h. |
The Zeta potential of the ATP samples was measured using JS94H electrophoresis analyzer (Shanghai Zhongchen Digital Technology Equipment Co., Ltd.) with an accuracy of ± 0.3 mV. For this, the samples were dispersed in anhydrous ethanol under ultrasonic agitation at room temperature, followed by injected into the sample cell. The wettability of the ATP samples was characterized by employing a JGW-360A optical contact angle analyzer (Xiamen Chongda Intelligent Technology Co., Ltd.) with an accuracy of ± 2°. The sample powders were pressed into 2 mm thick disks with smooth surface, and the deionized water was dropped on the surface of the disks at 1 atm with room temperature. The contact angles between the water droplet and disk surface were subsequently measured. The micro-morphology and dispersion of the ATP samples were characterized with a transmission electron microscope (JEM-210, Japanese Electronics Company). The specimens were prepared in the film form by dispersing ATP in anhydrous ethanol under ultrasonic agitation and immersing a copper mesh carrier in the suspension, followed by drying in air at room temperature. The samples were characterized at an accelerating voltage of 120 kV. The specific surface areas (with an accuracy of ± 0.5 m² g⁻¹) of the ATP samples were determined by N₂ adsorption and desorption isotherms at 77 K temperature with a surface area and pore size analyzer (NOVA 4000e, Quantachrome, America). Prior to the tests, the obtained samples were dried in vacuum under 100 °C for 24 h and the total surface areas were calculated from N₂ physisorption by Brunauer-Emmett-Teller (BET) equation. The dispersion of the ATP samples was observed at macroscopic scale by using the sedimentation observation method. For this, the samples were dispersed in anhydrous ethanol under ultrasonic agitation and immersed in a copper mesh carrier in the suspension, followed by observation of the suspensions at regular time intervals. The dispersion of the samples was characterized using a UV–vis spectrophotometer (UV-5100, Shanghai Precision Instrument Co., Ltd.) with an accuracy of ± 3.5%. The absorbance of the sample was measured at the wavelength of 350 nm.

3. Results and Discussions

3.1. Properties of the modified ATP

The spectrum of α-ATP exhibits the characteristic diffraction peaks at 2θ = 8.3°, 26.6° and 30.9° corresponding to the (110) plane of ATP, (011) plane of SiO₂ and (104) plane of CaCO₃, respectively (figure 1). These peaks confirm the presence of CaCO₃ and quartz impurities in α-ATP. The spectrum of p-ATP demonstrates the characteristic diffraction peaks at 2θ = 8.3°, 20.8° and 26.6° corresponding to the (110) plane of ATP, (1(−)21) plane of CaSO₄ and (011) plane of SiO₂, respectively. It indicates that the pickling treatment led to the removal of the most of the CaCO₃ impurity in α-ATP and a small portion of the CaCO₃ impurity was converted into CaSO₄. The spectrum of bp-ATP exhibits the characteristic diffraction peaks at 2θ = 44.8° corresponding to the (110) plane of iron, which is due to the iron element shedding in the mill pot caused by the high speed in conventional ball milling. The three treated ATP samples bp-ATP, cp-ATP and mp-ATP are observed to exhibit similar
spectra (figure 1). The peaks at $2\theta = 8.3^\circ$, $19.9^\circ$ and $26.6^\circ$ correspond to the (110) and (040) planes of ATP as well as the (011) plane of SiO$_2$, respectively. Among the spectra, the intensity of the diffraction peaks in the bp-ATP sample is noted to be lower than cp-ATP and mp-ATP. The decline in the peak intensity can be mainly attributed to the partially damaged crystal structures in ATP owing to the conventional ball milling treatment performed at a relatively high rotational speed. Thus, it can be concluded from the similar peak intensities of p-ATP, cp-ATP and mp-ATP that no damage to the crystal structure of ATP took place during the pickling treatment, chemical modification and ball milling modification.

Figure 2 shows the FTIR spectra of the silane coupling agent KH-550 and ATP samples. The $\text{–OH}$ vibration peaks are observed in the FTIR spectra at 3549 cm$^{-1}$, 3398 cm$^{-1}$ and 1645 cm$^{-1}$. Among these peaks, the signals at 3549 cm$^{-1}$ correspond to the stretching vibration absorption peak of the hydroxyl groups in the crystalline water. The peaks at 3398 cm$^{-1}$ can be attributed to the stretching vibration absorption peak of the zeolite water and the water adsorbed on the surface of the ATP particles. On the other hand, the peaks at 1645 cm$^{-1}$ correspond to the anti-symmetric stretching vibration absorption peak of the hydroxyl groups in the zeolite water and the water adsorbed on the surface of the ATP particles. An anti-symmetric stretching vibration peak absorption peak of the carbonate ions can be observed at 1450 cm$^{-1}$ in the FTIR spectrum of o-ATP. However, the peak is noted to disappear in the spectrum of p-ATP, thus, indicating that a large extent of the carbonate impurities in o-ATP is removed after the pickling treatment. The observed finding is consistent with the XRD observations. The Si–$\text{O}$ stretching vibrations at 1086 cm$^{-1}$ and 777 cm$^{-1}$ are observed in the FTIR spectrum of KH-550. Though the wavenumbers for the Si–$\text{O}$ peaks are noted to shift to 1033 cm$^{-1}$ and 788 cm$^{-1}$ in cp-ATP and mp-ATP, however, differences among the intensity of these peaks are observed. The observed differences can be attributed to the presence of Si–O in ATP and silane coupling agent KH-550, which leads to high peak intensity. In addition, the stretching vibrations absorption peak of the methylene groups at 2973 cm$^{-1}$ and 2891 cm$^{-1}$ can be observed in the FTIR spectrum of KH-550, while the wavenumber of these peaks in the cp-ATP and mp-ATP samples is noted to shift to 2974 cm$^{-1}$ and 2903 cm$^{-1}$ respectively. However, these peaks are observed to be absent in the FTIR spectra of o-ATP, p-ATP and bp-ATP, which is consistent with the fact that there is no KH-550 during the preparation of o-ATP, p-ATP and bp-ATP. The observed finding indicates that KH-550 has been coupled with cp-ATP and mp-ATP.

Figure 3 shows the thermogravimetric curves (TG) and the differential thermogravimetric curves (DTG) of ATP samples. The relevant data of TG (figure 3(a) and DTG (figure 3(b) are listed in table 2. There are four steps of weightlessness in each TG courses of the ATP samples, which indicates there are four stages during ATP weightlessness. It is generally believed that in the four processes of TG, the weight loss of ATP at 50 °C–170 °C is attributed to degradation of water adsorbed on the surface of the ATP particles, the weight loss at 180 °C–300 °C is attributed to degradation of crystallization water in ATP, the weight loss at 300 °C–550 °C is attributed to degradation of crystallization water and structure water in ATP, the weight loss at 550 °C–800 °C is attributed to degradation of structure water in ATP [19, 20]. The weight loss rate of o-ATP at 550 °C–800 °C is the largest among the five groups of ATP samples (figures 3(a) and 3(b)), and the extra mass loss is attribute to decomposition of carbonate salts in o-ATP. The weight loss rate of p-ATP at 50 °C–170 °C is the highest among the five groups of ATP samples, which is attributed to the adsorption of larger quantities water after the impurities are removed by acid pickling treatment. The weight loss rate of cp-ATP and mp-ATP at 50 °C–170 °C
is lower than that of p-ATP and bp-ATP, which is attributed to the addition of KH-550, which reduces the amount of absorbed water in cp-ATP and mp-ATP. The weight loss rate of cp-ATP and mp-ATP at 350 °C–500 °C is higher than that of other groups of ATP samples, and the extra mass loss is attributed to the decomposition of KH-550 modified on ATP surface [21]. The weight loss rate of mp-ATP at 350 °C–500 °C is higher than that of cp-ATP, which indicates that the quantity of KH-550 modified on mp-ATP is greater than that of cp-ATP.

Table 3 shows the Zeta potential results of the ATP samples. ATP is negatively charged due to the proportion of Si4+ in the silicon-oxygen tetrahedron replaced by Al3+, thus, generating excess negative charges. Besides, exposed hydroxyl groups are present on the surface of ATP [22]. As seen from Table 3, the absolute values of the Zeta potential of the ATP samples exhibit an initial increase, followed by a decrease. Specifically, the absolute value of the Zeta potential of p-ATP is higher than that of o-ATP. This value is also noted to be the largest among the five samples. The reason is that most of the impurities filled in the pores of ATP were removed during the pickling treatment, which is consistent with the result that there is no carbonate decomposition process of p-ATP in TG and DTG curves. As a result, more negative charges are carried by the p-ATP structure, and a proportion of H+ in the ATP crystals is dissolved during the second dissolution process. The absolute value of the Zeta potential of bp-ATP is noted to be smaller than that of p-ATP. The reason is that the mechanical force in the conventional ball milling process will destroy certain percentage of crystal structures in ATP, thus, resulting in the decrease in the amount of structure and number of hydroxyl groups on the ATP surface. Further, the absolute value of the Zeta potential of cp-ATP is smaller than that of bp-ATP. The observed difference can be attributed to the fact that the surface of the ATP rod crystals is modified by the silane coupling agents during the chemical modification, and the silane coupling agents form interactions with the hydroxyl groups on the ATP surface. That is, the decrease in the absolute potential value of Zeta in cp-ATP indicates that KH-550 is successfully modified on ATP, which is consistent with the result that

Table 2. Thermal weight loss data of the ATP samples.

| Sample | First stage | Second stage | Third stage | Forth stage |
|--------|-------------|--------------|-------------|-------------|
|        | $T_{\text{max}1}$ (°C) | $E_1$ (%) | $T_{\text{max}2}$ (°C) | $E_2$ (%) | $T_{\text{max}3}$ (°C) | $E_3$ (%) | $T_{\text{max}4}$ (°C) | $E_4$ (%) |
| o-ATP  | 77.7        | 4.0          | 198.7       | 1.5         | 458.0        | 3.6         | 692.8        | 7.3         |
| p-ATP  | 111.8       | 7.4          | 187.7       | 1.8         | 412.5        | 3.4         | 773.3        | 2.0         |
| bp-ATP | 87.2        | 4.8          | 186.0       | 1.9         | 333.9        | 3.5         | 762.4        | 0.1         |
| cp-ATP | 80.7        | 4.2          | 176.5       | 1.7         | 420.0        | 4.2         | 759.7        | 0.4         |
| mp-ATP | 75.0        | 3.1          | 177.7       | 2.8         | 437.4        | 5.1         | 647.7        | 1.1         |

Table 3. Zeta potentials of the ATP samples.

| Sample | o-ATP | p-ATP | bp-ATP | cp-ATP | mp-ATP |
|--------|-------|-------|--------|--------|--------|
| Zeta potential (mV) | −9.7 ± 0.3 | −19.7 ± 0.3 | −13.2 ± 0.3 | −8.1 ± 0.3 | −7.1 ± 0.3 |
Table 4. Contact angle of the ATP samples.

| Sample | o-ATP | p-ATP | bp-ATP | cp-ATP | mp-ATP |
|--------|-------|-------|--------|--------|--------|
| Contact angle (°) | 18 ± 2 | 22 ± 2 | 26 ± 2 | 33 ± 2 | 52 ± 2 |

the weight loss rate of cp-ATP and mp-ATP at 50 °C–170 °C is lower than that of p-ATP and bp-ATP and the weight loss rate of cp-ATP and mp-ATP at 350 °C–500 °C is higher than that of other samples in TG and DTG curves. Comparing mp-ATP and cp-ATP, the absolute value of the Zeta potential of mp-ATP is observed to be less than that of cp-ATP due to a large number of more KH-550 molecules bonded to the ATP surface of ATP owing to the ball milling modification, which is consistent with the result that the weight loss rate of mp-ATP at 50 °C–170 °C is lower than that of cp-ATP and the weight loss rate of mp-ATP at 350 °C–500 °C is higher than that of cp-ATP in TG and DTG curves.

Table 4 shows the contact angle analysis of the ATP samples. An increase in the contact angle of a sample indicates a shift in sample’s wettability from hydrophilicity to hydrophobicity. In addition, it also indicates that an optimal surface modification has been achieved. It can be seen from table 4 that the contact angle values of o-ATP (18° ± 2°), p-ATP (22° ± 2°) and bp-ATP (26° ± 2°) are relatively low, thus, indicating that these ATP samples exhibit a relatively high hydrophilicity. Thus, it can be concluded that pickling or conventional ball milling slightly affect the chemical composition of the ATP surface, thereby, slightly altering the surface hydrophilicity. It can be seen from table 4 that the contact angle of cp-ATP is increased to 33° ± 2°, which can be attributed to the successful coupling of the rod-like ATP crystals with KH-550 via chemical modification. Thus, the introduction of KH-550 is observed to enhance the contact angle of cp-ATP. It can be seen from table 4, mp-ATP exhibits the largest contact angle (52° ± 2°) among the five samples. The reason for the observed phenomenon is the effective dispersion of ATP due to the mechanical forces involved in the ball milling process. This facilitates an effective contact between the rod-like ATP crystals and KH-550. Besides, the mechanical forces in ball milling modification process provide higher energy than that in chemical modification process, thus, guaranteeing that a higher extent of KH-550 molecules are coupled with the mp-ATP surface, leading to the largest increase in the contact angle. Overall, the observed results indicate that the ball milling modification is more beneficial for decreasing the hydrophilicity of ATP.

3.2 Effects of surface modification method on the dispersion of ATP

A large number of rod-like ATP crystals and impurities among these crystals, as well as aggregates formed by the agglomeration of the rod-like crystals and impurities are observed in the TEM image of o-ATP (figure 4(a)). On the other hand, figure 4(b) shows the TEM image of p-ATP. It can be seen from figure 4(b) that the extent of impurities in p-ATP is significantly reduced. The aggregates are observed to mainly contain the rod-like crystals and clusters formed by the rod-like crystals. This indicates that a significant extent of the impurities in the o-ATP sample can be removed by the pickling treatment. Though the size of p-ATP aggregates is noted to be smaller than that of o-ATP, the agglomeration of the rod-like crystals has not been significantly mitigated. The reason is that the short-term pickling treatment has an insignificant effect on the hydroxyl groups on the ATP surface and van der Waals force between the ATP rod-like crystals, thus, no inhibition of the particle agglomeration [20]. The TEM image of the bp-ATP sample is presented in figure 4(c), where a proportion of the rod-like ATP crystals in the bp-ATP sample is observed to be damaged. Specifically, the length of the rod-like crystals becomes shorter, along with the presence of the damaged ATP particles. As a result, the rod-like crystals formed agglomerates and crystal bundles. The distance between the crystal bundles in bp-ATP is observed to be longer than that of p-ATP, indicating that the agglomeration of the rod-like crystals in bp-ATP is mitigated. The reason can be attributed to the fact that the distance between the ATP rod-like crystals increases under the action of mechanical force in the conventional ball milling process. Besides, the strong mechanical force damages the structure of the rod-like ATP crystals, thus, shortening their length. Figure 4(d) corresponds to the TEM image of cp-ATP, where the agglomeration of the rod-like ATP crystals can be observed to have further mitigated as compared to bp-ATP. The distance between the crystal bundles is also increased. The structure of the rod-like crystal structure is also noted to be more complete as compared to bp-ATP. These observations indicate that the agglomeration of the rod-like ATP crystals is inhibited in the chemical modification method, and the structure of the rod-like ATP crystals is retained. Figure 4(e) presents the TEM image of mp-ATP, where the size of the crystal bundles formed by the rod-like crystals is noted to be the smallest among the five ATP samples, while the distance between the crystal bundles is the largest. Besides, the rod-like ATP crystals with relatively complete structure are observed. These observations suggest that compared with chemical modification, the ball milling...
modification leads to an effective dispersion of ATP, with no damage to the structure of the rod-like ATP crystals occurring.

Figure 5 shows the nitrogen adsorption-desorption and pore size distribution curves of the ATP samples. It can be observed that the adsorption-desorption curves of the ATP samples match the Type IV isotherm behavior, thus, indicating the presence of micropores and mesopores in the ATP samples. Besides, a low adsorption capacity is observed in the low-pressure area of the curves, and higher adsorption capacity and distinct hysteresis loops appear in the high-pressure area of the curves. These results indicate that the pores in the ATP samples mainly contain mesopores, along with a few micropores [23]. The hysteresis loops

Figure 4. TEM images of ATP samples: (a) α-ATP, (b) β-ATP, (c) β′-ATP, (d) cp-ATP and (e) mp-ATP.

Figure 5. Nitrogen adsorption-desorption and pore size distribution curves of the ATP samples.
observed in the high-pressure area of the adsorption-desorption curves are noted to be H3 type hysteresis loops, thus, indicating that the slit pores are formed by the agglomeration of the ATP particles in the samples [23]. The pores with diameters between 2–7 nm present in the pore size distribution curves in figure 5 can be assigned to the fine mesopores in the internal gaps of ATP. On the other hand, the pores with diameters between 12–22 nm can be attributed to the slit pores formed among the rod-like ATP crystals. Thus, the larger is the peak intensity, the greater is the number of pores in the ATP sample [24].

The pore size distribution curve of o-ATP in figure 5 features a single peak distribution between 2–7 nm and a relatively low peak intensity. The reason for the observed findings is the presence of impurities and large aggregates formed by the agglomeration of the impurities and rod-like ATP crystals. The presence of impurities and aggregates leads to a reduction in the number of slit pores formed by the rod-like crystals and mesopores within the rod-like crystals. The pore size distribution curves of p-ATP, bp-ATP, cp-ATP and mp-ATP both feature a bimodal distribution with a primary peak between 12–22 nm and a secondary peak between 2–7 nm. In addition, the peak intensities in the 2–7 nm in p-ATP, bp-ATP, cp-ATP and mp-ATP are observed to be larger than those of o-ATP. The observed difference in the peak intensities can be attributed to the dissolution of the impurities in ATP after pickling treatment, which leads to the appearance of the pores in the gaps between the ATP particles as well as the slit pores among the rod-like crystals. Moreover, the intensities of the secondary peaks in cp-ATP primary and secondary peaks in bp-ATP and mp-ATP are noted to be larger than those of p-ATP. The difference in the peak intensities can be attributed to the improvement in the dispersion of ATP via the conventional ball milling, chemical modification and ball milling modification. As a result, more slit pores are formed among the rod-like ATP crystals. The intensities of the secondary peaks in cp-ATP and primary, secondary peaks in mp-ATP are noted to be higher than those of bp-ATP. The observed The observed difference in peak intensities can be attributed to the addition of silane coupling agent in the chemical modification and ball milling modification, which leads to a better improvement of dispersion of rod like ATP crystals compared with the conventional ball milling. As a result, an increased number of slit pores are formed among the rod-like crystals in cp-ATP and mp-ATP as compared to bp-ATP. The intensity of the primary and secondary peaks of mp-ATP are noted to be larger than that of cp-ATP. In addition, the intensities of the two peaks in mp-ATP are also observed to be the largest among the five samples. The observed phenomenon can be attributed to the fact that the rod-like crystals in mp-ATP modified via ball milling modification have the most optimal dispersion among the five samples. Therefore, the number of micropores appearing in the rod-like crystals and slit pores forming among the rod-like crystals in mp-ATP are also the highest among the samples.

Table 5 shows the specific surface areas of the ATP samples. As can be seen that the specific surface area of o-ATP is $51 \pm 0.5$ m$^2$ g$^{-1}$, while the surface area of p-ATP reaches up to $102 \pm 0.5$ m$^2$ g$^{-1}$. A large extent of impurities are present in the mesopores of the rod-like crystals in o-ATP, along with significant agglomeration of the rod-like crystals. Thus, the increase in the specific surface area in p-ATP can be attributed to the removal of the impurities in the pores and in the gaps among the rod-like crystals during the pickling treatment. The specific surface area of bp-ATP is noted to reach $142 \pm 0.5$ m$^2$ g$^{-1}$, which is larger than that of p-ATP. The improvement of specific surface area is mainly attributed to the improved ATP dispersion and shortening of the length of the rod-like ATP crystals after the conventional ball milling treatment. The specific surface area of cp-ATP is noted to reach up to $160 \pm 0.5$ m$^2$ g$^{-1}$, which is even higher than that of bp-ATP. The observed improvement of specific surface area can be attributed to the fact that the addition of KH-550 brings better improvement of dispersion of rod like crystals in cp-ATP than that in bp-ATP. As a result, more slit pores are formed by the rod-like crystals in cp-ATP as compared to bp-ATP. Moreover, the specific surface area of mp-ATP is noted to be $162 \pm 0.5$ m$^2$ g$^{-1}$, which is the highest number among the five ATP samples. As both primary and secondary peaks in figure 5 exhibit the highest intensities among the five samples, the improved specific surface area and peak intensities can be attributed to the improved dispersion of ATP due to the addition of the silane coupling agent and mechanical forces involved during the ball milling process. In addition, due to a higher extent of silane coupling agent loaded on the surface of the rod-like crystals in mp-ATP as compared to cp-ATP, the amount of the slit pores formed by the rod-like crystals in mp-ATP as well as the amount of mesopores appearing on the surface are observed to be the highest among the five samples.

Figure 6 shows the findings from the sedimentation analysis of the ATP samples. Figure 7 shows the results of UV absorbance spectra in the sedimentation observation of ATP. As observed from figure 6, during the time period 0–70 min, the sedimentation rate of Sample 2 is slower than Sample 1, while the former becomes faster than the latter during the time period 70–280 min, which is consistent with the result that the absorbance

| Sample | o-ATP | p-ATP | bp-ATP | cp-ATP | mp-ATP |
|--------|-------|-------|-------|-------|-------|
| Specific surface area (m$^2$ g$^{-1}$) | $51 \pm 0.5$ | $102 \pm 0.5$ | $142 \pm 0.5$ | $160 \pm 0.5$ | $162 \pm 0.5$ |

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**Table 5.** Specific surface area of the ATP samples.
Figure 6. Settlement results of the ATP samples. Marks 1° to 5° correspond to o-ATP, p-ATP, bp-ATP, cp-ATP and mp-ATP, respectively.

Figure 7. UV absorbance spectra of the ATP samples as a function of time.
of p-ATP is observed to be higher than o-ATP during the time period 0–70 min and lower during the time period 70–280 min shown in figure 7. The observed changes in the sedimentation behavior between Sample 1# and Sample 2# can be attributed to the rapid sedimentation rate of Sample 1# owing to the significant agglomeration of the rod-like ATP crystals and impurities. In addition, after the pickling treatment, the volume of the aggregates in Sample 2# is noted to be smaller than Sample 1#. However, during the time period 70–280 min, the smaller carbonate impurities in Sample 1# detach from the rod-like ATP crystals and dispersed in the solution due to the ultrasonic agitation of Sample 1#, which sedimentation rate is noted to be slower than that of the ATP aggregates in Sample 2#. As observed from figure 6, the sedimentation rates of Samples 3#, 4# and 5# are slower than those of Samples 1# and 2#, which is consistent with the result that the absorbance of bp-ATP, cp-ATP and mp-ATP is noted to be higher than that of o-ATP and p-ATP shown in figure 7. The observed difference in the sedimentation rates of the samples can be attributed to the fact that the conventional ball milling, chemical modification and ball milling modification methods result in the improved dispersion of the rod-like ATP crystals and facilitate the formation of the crystal bundles composed of the rod-like ATP crystals, thus, leading to a slow sedimentation rate. Moreover, the sedimentation rates of Samples 4# and 5# are observed to be slower than that of Sample 3#, which is consistent with the result that the absorbance of cp-ATP and mp-ATP are observed to be higher than that of bp-ATP shown in figure 7. The differences in the sedimentation rate between them can be attributed to the addition of KH-550 to Sample 4# and 5#, the agglomeration rates of the ATP particles as well as the volume of the rod-like crystal bundles in the two samples are lower than those of Sample 3#. Between Sample 4# and Sample 5#, the sedimentation rate of Sample 5# is noted to be slower than that of Sample 4#, which is consistent with the result that the absorbance of mp-ATP is noted to be higher than that of cp-ATP shown in figure 7. In addition, the sedimentation rate of Sample 5# is also observed to be the slowest among the five samples. This is owing to the fact that Sample 5# has the slowest secondary agglomeration rate and the smallest volume of the crystal bundles among the five samples via ball milling modification.

3.2. Mechanism of ATP modification and dispersion of ATP

Figure 8 shows the mechanism of ATP modification and dispersion of ATP via the chemical modification and ball milling modification. As seen from figure 8, the ethoxy group on the surface of the silane coupling agent KH-550 is unstable. During the process, KH-550 is likely to undergo hydrolysis to form a silanol compound. The silanol is noted to have strong reactivity and is prone to dehydration polymerization, thus, resulting in the self-polymerization of KH-550 after hydrolysis. In normal conditions, ATP is extremely prone to agglomeration due to the presence of a large number of hydroxyl groups on its surface. The hydroxyl groups on the surface of the rod-like ATP crystals form hydrogen bonds with each other. Together with the van der Waals force between the rod-like crystals, the presence of hydrogen bonds, thus, leads to a significant agglomeration of the ATP particles. On addition of p-ATP to the solution containing KH-550, a small proportion of the agglomerated rod-like crystals are separated owing to stirring of the suspension using a glass rod. Due to the presence of hydrogen bonds, the hydroxyl groups on the surface of p-ATP are absorbed by the exposed silanol groups in KH-550 generated via hydrolysis and polymerization after the dispersion of the agglomerated ATP particles. As the chemical modification process presented in figure 8, on stirring the mixed solution of p-ATP with hydrolytically self-polymerized KH-550 absorbed on its surface in a thermostat magnetic stirring container at a constant temperature of 70 °C, the agglomerated rod-like crystals are partially dispersed. Subsequently, the p-ATP particles dispersed in the suspension undergo hydrolytic condensation with KH-550 molecules on the p-ATP surface. As a result, the interaction between p-ATP and KH-550 shifts from hydrogen bonding to silicon-oxygen bonds. After proceeding with the modification process for six hours, the p-ATP particles are dried and collected. The successful modification of cp-ATP with KH-550 improves the dispersion and dispersion stability of the rod-like ATP crystals. Moreover, the carbon chains in the KH-550 molecules decreasing the hydrophilicity of ATP. The chemical modification of ATP is realized.

As shown in the ball mill modification process presented in figure 8, the mixed solution of the p-ATP sample with hydrolytically self-polymerized KH-550 absorbed on its surface are added to the container of the ball mill. The container is subsequently loaded into the planetary ball milling machine. Owing to the abrasion between the grinding balls and container, the agglomerated rod-like ATP crystals are dispersed in the suspension. During the ball milling modification process, the rotational speed of the machine is lower than that of conventional ball milling process. Based on the fact that compared with p-ATP, the crystal structure in mp-ATP is not altered, and the micro-morphology of p-ATP is not damaged, it can be concluded that the crystal structure and the rod-like crystals in ATP have not been damaged. In addition, the mechanical forces provided by the grinding balls in the ball milling modification process are greater than the stirring force exerted in the chemical modification process. Therefore, the agglomerated ATP rod crystals are better dispersed under the action of the mechanical forces generated by the abrasion between the grinding balls and container in the ball mill machine. In addition, the
dispersed p-ATP particles can absorb a high extent of the silane coupling agent. During the ball milling modification process, p-ATP and KH-550 adsorbed on the surface undergo hydrolytic condensation. The mechanical forces generated by the collision of the grinding balls provide high energy and result in enhanced local temperature, thereby, improving the rate and efficiency of the hydrolytic condensation reaction in the ball milling modification process to the levels higher than the chemical modification process. After hydrolytic condensation, the interaction between p-ATP and KH-550 shifts from hydrogen bonding between the hydroxyl groups to silicon-oxygen bonds. Consequently, the mp-ATP sample is obtained after drying with successful bonding of KH-550 to the surface of the rod-like ATP crystals. The amount of bonded KH-550 on the surface of mp-ATP is observed to be higher than that of cp-ATP, which is consistent with the result that the weight loss rate of mp-ATP at 350 °C–500 °C is higher than that of cp-ATP in TG and DTG curves. As a result, the ball milling modification provides better effect than chemical modification on improving the dispersion and dispersion stability of the rod-like ATP crystals, which is consistent with the result that the size of the crystal bundles formed by the mp-ATP rod-like crystals is noted to be smaller than cp-ATP, while the distance between the mp-ATP crystal bundles is larger than cp-ATP. Moreover, ball milling modification also has a more efficient results than chemical modification in an decreasing of ATP hydrophilicity. Based on the observed findings, the ball milling modification and dispersion effects for ATP was the best.

Figure 8. Schematic diagram of the mechanism of chemical modification, ball milling modification and dispersion of ATP.
4. Conclusions

(1) Compared with the conventional ball milling and chemical modification methods, the ball milling modification method has the best modification and dispersion effects for attapulgite (ATP), which was modify by silane coupling agent KH-550 under certain ball milling conditions.

(2) During the ball milling modification process, the mechanical force can provide effectively dispersing effects on ATP, which can decrease the volume of the bundles of ATP. Meanwhile, the mechanical force can provide higher energy to promote coupling effect between silane coupling agent KH-550 and ATP, resulting in that ATP can be effectively coated by KH-550 and the weight loss of resulting ATP in 437 °C increased by 50%.

(3) For the resulting ATP modified by ball milling modification method, silane coupling agent KH-550 can decrease the hydrophilicity and increase the bundles distance, resulting in improving dispersion effect of ATP. The contact angle of the resulting ATP was increased by 189% along with a lower sedimentation rate. The specific surface area of the resulting ATP was increased by 218% along with the proportion of quantity at 17 nm increased by 283%.

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