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RESEARCH ARTICLE

Exfoliation of kaolinite by urea-intercalation precursor and microwave irradiation assistance process

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Abstract A type of exfoliated kaolinite was produced by urea-intercalation and original microwave irradiation assisted method. The product was investigated by Fourier transformation infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electronic microscopy (SEM), Brunauer-Emmett-Teller (BET) and laser particle analysis techniques. FT-IR spectra show that NHCO molecule exists in the intercalated kaolinite. XRD analyses indicate that the kaolinite sheet-like structure was disordered after microwave irradiation. The urea decomposition process and explosion effect between the sheet-like structures of kaolinite under microwave irradiation were discussed. The SEM and BET analyses reveal that the end product is exfoliated kaolinite with thin particles and increased surface area. Size and zeta potential analyses show that the particle size distribution is between 250 nm and 550 nm with normal distribution and the particle is negatively charged. In comparison with the conventional grind method, the process adopted appears to be economic and the exfoliated kaolinite end product may display a significantly enhanced performance in industrial applications.

Keywords exfoliated kaolinite, microwave irradiation, intercalation

1 Introduction

Kaolinite is an important industrial mineral, which has many uses, including paper coating, plastic filler, adhesives, ink extender, enamels, and molecular sieves. Many factors have influenced kaolin's industrial use, including the geological conditions under which the kaolin formed, the total mineralogical composition of the kaolin deposit, and its physical and chemical properties (Murray, 2000). The morphology and size of kaolinite particles are considered to influence its surface area and plasticity, which are important indexes for its industrial application (Tsunematsu et al., 1992).

A kaolinite platelet, with an ideal chemical composition of $Al_2Si_2O_5(OH)_4$, comprises two alternating layers: one octahedral-oxygen layer and one octahedral aluminum-oxygen layer. Commonly, kaolinites for industrial use are mechanically ground to cause destruction in the crystal structure by the rupture of the O-H, Al-OH, Al-O-Si, and Si-O bonds. However, this process is time-consuming, usually lasting about 10 h (Frost et al., 2001, 2003). For economical and many other considerations (Zeng et al., 2001; Michalková et al., 2002; Dong et al., 2003; Patakfalvi and Dékány, 2004), intercalation processes were introduced with strong polar molecules, which can expand the layer space. In recent years, scientists have made a great effort on the intercalation of kaolinite, and molecules such as acetamide, formamide, potassium acetate, urea, dimethyl sulphoxide, and polystyrene have been investigated as intercalators (Tsunematsu et al., 1995, 1997; Frost et al., 1999; Fang et al., 2005; Elboke and Detellier, 2006).

In the present work, we used urea-intercalated kaolinite as a precursor followed by microwave irradiation treatment, to produce an exfoliated kaolinite with a markedly increased surface area and decreased particle size. Its potential industrial value is discussed.

2 Experiment

2.1 The exfoliated kaolinite

The kaolinite used in this work came from the Guangdong Fotao Corporation. The raw material was selected and sieved to a particle size distribution of 5–20 μm before use due to minor illite and quartz impurities. The chemical compositions of this kaolinite are shown in Table 1.

In a typical process the kaolinite was intercalated by mixing 5 g of kaolinite with 20wt-% of urea and uniformly

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Table 1 The chemical compositions of the raw kaolinite

Composition	MgO	CaO	SiO_2	Fe_2O_3	K_2O	Al_2O_3	TiO_2
%	0.057	0.120	67.100	0.800	2.600	20.000	0.400

mechanically ground. The product was then treated under 2 450 MHz microwave irradiation for 5 min. We designated this intermediate product urea-kaolinite complex (UKC). After further irradiation for 5, 25 and 40 min, the intermediate was boiled in water (100°C) and washed six times by centrifuging. The final product was obtained by drying at 120°C in vacuum.

2.2 Measurements

The Fourier transformation infrared (FT-IR) spectrum was obtained using an Avatar370 FTIR spectrometer, measured by KBr pellet technique. X-ray diffraction (XRD) patterns of the kaolinites were obtained with an MXP18AHF X-ray diffractometer using graphite-monochromatized CuKα radiation. The scanning electron microscopy (SEM) images were taken using a JSM-35CF instrument. The nitrogen adsorption was measured at 78 K using Micrometrics ASAP 2010 constant-volume adsorption equipment, and the surface area was calculated using either Brunauer-Emmett-Teller (BET) or Langmuir methodology, depending on the type of isotherm. The particle size and zeta potential were measured by a Nano ZS90 Malvern Laser Particle Analyzer with DTS1060-Disposable Zeta cell, the viscosity and refractive values were set as 0.887 2 and 1.33, respectively.

3 Results and discussion

3.1 FT-IR analyses

The FT-IR of the raw kaolinite and the mixture of kaolinite with 20wt-% urea after microwave irradiation for 5 min are shown in Fig. 1. There were obvious differences between the two curves from 1 400 cm^{-1} to 2 500 cm^{-1}. The molecule

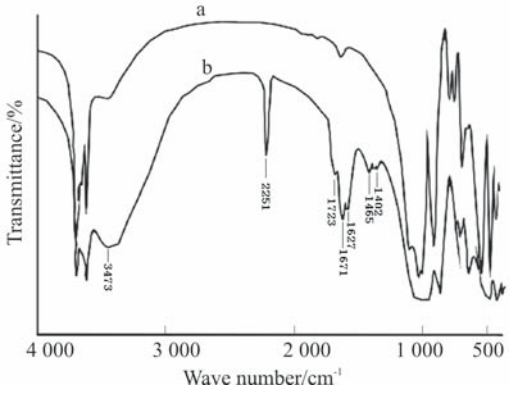

Fig. 1 (a) FT-IR of the raw kaolinite; (b) FT-IR of the urea-kaolinite complex

intercalated into kaolinite can be confirmed from IR (Infrared) absorption spectra to be NHCO. The frequencies at 3 573 cm^{-1}, 1 971 cm^{-1}, 1 402 cm^{-1} were assigned as N-H, C-O, and C-N stretching vibrations, respectively, based on the urea-kaolinite complex.

3.2 XRD analyses

For comparison, the XRD patterns of raw kaolinite and exfoliated kaolinite end products prepared under different irradiation times (0, 5, 25, 40 min) are shown in Fig. 2. The 001 reflection of the raw kaolinite (Fig. 2a) at 7.2 Å shows a very sharp profile. In contrast, there is a broad 001 reflection for the end product with 5 min microwave irradiation (Fig. 2c). We also found that the *hkl* reflections of the raw kaolinite are sharper than those of the end products. The results indicate that microwave irradiation causes disorder of the sheet-like structure of kaolinite. The basal spacing of the sample with no further irradiation (0 min) was larger than that of the raw kaolinite (7.2 Å), indicating that the molecules which have been decomposed from urea remain settled in the kaolinite layer structure. This process can be confirmed by FT-IR as shown in Fig. 1. Based on this conclusion, the kaolinite particles that received further microwave irradiation may be smaller than those of kaolinite without urea intercalation.

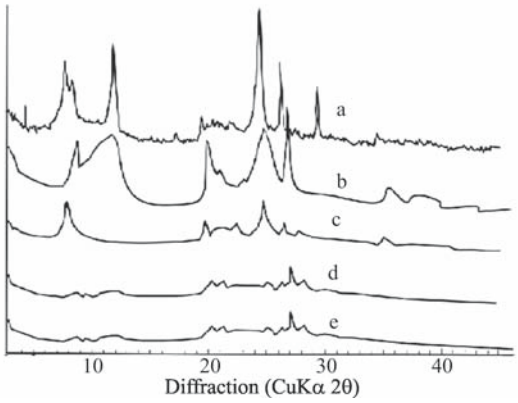

Fig. 2 XRD patterns of raw kaolinite (a) and exfoliated kaolinite end products prepared with different irradiation times; (b) 0 min; (c) 5 min; (d) 25 min; (e) 40 min

The basal space of kaolinite increases from 7.2 Å to 10.8 Å as the intercalation of urea into the interlayer sheets increases. The cohesive energy between kaolinite layers is primarily electrostatic. There is also a certain degree of Van der Waals attraction and hydrogen bonding between the hydroxyl groups of the gibbsite layer and the oxygen atoms of the adjoining silica layer. The intercalation of urea into the kaolinite structure seems to weaken the interaction force between the layers. Under further irradiation, urea can be decomposed quickly because of its strong polar movement. Contributing to the quickly heating up particularity of microwave irradiation, the decomposition process can be

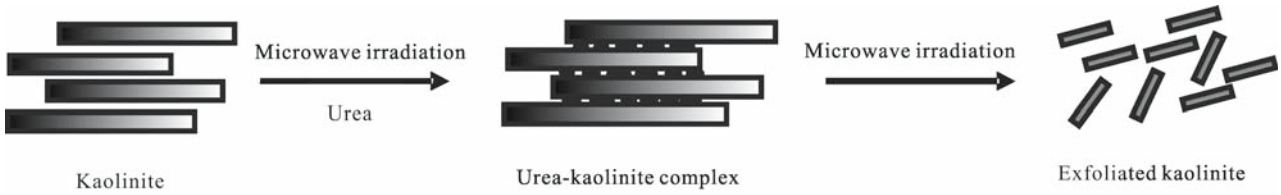

Fig. 3 Sketch of exfoliation process of kaolinite with microwave irradiation assistance

completed in so short a time that it produces a very strong pressure, like an explosion between the sheet-like structures of kaolinite, so that the silicate layers between urea molecules become fragments because of the weak interaction force between the silicate layers. Therefore, kaolinite can be easily exfoliated and shattered by microwave irradiation. When compared with the data of relative references (Frost et al., 2001, 2003), the time for exfoliation under microwave assistance was 1/20 that of the simple mechanical method under the same conditions. The mechanism is illustrated in Fig. 3.

3.3 Morphology analyses

Images of kaolinite and the end products after microwave irradiation for 25 min were observed via SEM (shown in Fig. 4). Figure 4a shows that the raw kaolinite was a mixture of large sheet-like and fine-grain particles. By comparing these two SEM micrographs we can see that the kaolinite was exfoliated and shattered into 500 nm diameter particles by the urea explosion (Fig. 4b).

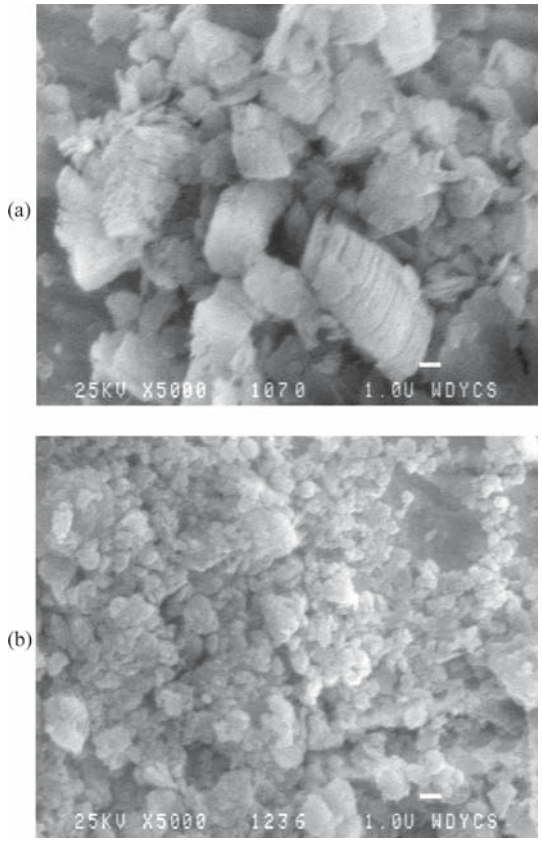

Fig. 4 (a) SEM image of raw kaolinite; (b) SEM image of urea-kaolinite complex after 25 min microwave irradiation

3.4 BET analyses

According to related works (Frost et al., 2001, 2003), in the case of kaolinite ground without urea, the surface area was slightly increased. In contrast, the surface area of the end products increased from 18–98 m^2/g when irradiation time was increased from 0–25 min. From a technical view, we can markedly save production time and reduce energy consumption during the process of exfoliation and shattering of the kaolinite.

3.5 Particle size distribution and zeta potential of the exfoliated kaolinite

Particle size and particle size distribution (PSD) are very important in determining the industrial uses of kaolinite. A coarse particle kaolinite has very different physical and optical properties relative to a fine particle size kaolinite (Murray, 2000). Zeta potential represents the electric potential at the shear plane between a particle and the surrounding liquid when the charged particle moves in an electric field (Brady et al., 1996; Hu and Liu, 2003). It is a very important surface chemical property which has a relation to viscosity. A relatively low viscosity of kaolinite at high solid concentrations is particularly important in paper coating and paint applications (Murray, 2000).

3.5.1 Particle size distribution of the exfoliated kaolinite

The statistical results of the particle size of typical exfoliated kaolinite are shown in Fig. 5. We can see that the PSD of the exfoliated kaolinite is fine. Most of the particles are between 250 and 550 nm with normal distribution. The average size of the exfoliated kaolinite is about 450 nm and agrees with the SEM image (Fig. 4b) very well.

3.5.2 The zeta potential of the exfoliated kaolinite

The zeta potentials of typical exfoliated kaolinite and raw kaolinite are shown in Fig. 6 as a function of pH value. From the two curves we can see that owing to the layer structure of the destroyed kaolinite, the isoelectric point moved

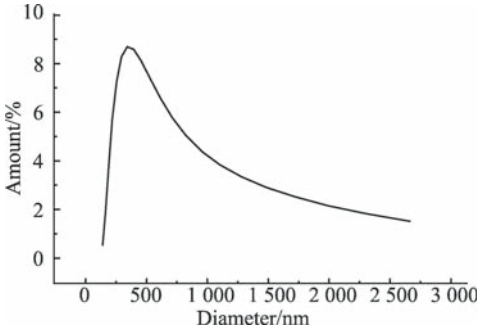

Fig. 5 The statistical results of the particle size of exfoliated kaolinite

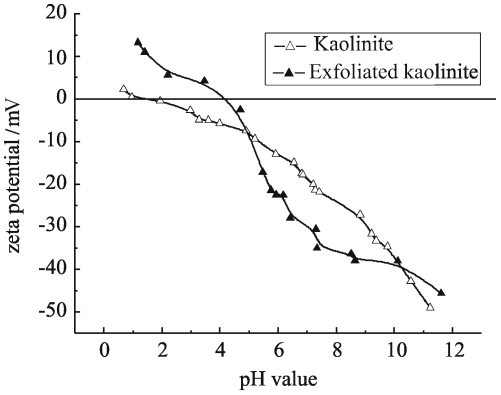

Fig. 6 The zeta potential of exfoliated kaolinite and raw kaolinite

positively. This shows that the isoelectric point of exfoliated kaolinite is about 4.2. We can estimate from the curve that the exfoliated kaolinite dispersed in neutral water is negatively charged by about −30 mV. This means that the particles can be dispersed and stable in water with low viscosity (Gao et al., 2003), which is significant for kaolinite's industrial application such as paper coating and paint applications.

4 Summary

The basal spacing of kaolinite expanded with the intercalation of urea into the interlayer sheets of kaolinite. After microwave irradiation for 25 min, the urea-kaolinite complex was exfoliated and shattered completely, which indicates that kaolinite was easily exfoliated by microwave irradiation with urea present. The BET analyses show that the specific surface area of kaolinite can be markedly increased to 98 m^2/g after exfoliation. Compared to the traditional mechanical motor grinding method, it is evidently more economical and efficient to reach this point. The average particle size of the exfoliated kaolinite is about 450 nm and the PSD is fine. The isoelectric point is 4.2. We infer from these results that this exfoliated kaolinite may display improved performance in industrial applications compared to its counterparts.

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