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SHORT COMMUNICATION

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Cleaving of muscovite powder by molten lithium nitrate

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Abstract Muscovite powder was cleaved along the (0 0 1) planes in molten lithium nitrate. The condition for optimal cleavage was 1 g muscovite with 17 g lithium nitrate at 350 °C for 12 h. The specific surface area of muscovite increased from 3.5 to 170 m^2/g. IR spectroscopy and XRD confirmed that the structure of muscovite did not change. Reaction with some other alkaline nitrates did not markedly increase the specific surface area.

Keywords Muscovite

Introduction

Nanocomposites may be synthesized by the combination of polymers with muscovite [1–5]. Muscovite is used as a reinforcing agent. Reducing the particle size of the muscovite can significantly increase the tensile modulus and strength. Mica is also a popular substrate for surface investigations due to its well-defined and flat surface [6, 7]. Micas with ultra high specific surface area can provide a unique chance for surface studies.

The commercial method to cleave muscovite includes heating to 800 °C, dispersing it immediately in Na_2CO_3 or $NaHCO_3$ saturated aqueous solutions and neutralizing by HCl [8]. The muscovite prepared by this method has a low specific surface area of 2–5 m^2/g. Also, ultrasound was applied to cleave mica [1, 5]. However, its efficiency is as low as with the commercial method. Caseri et al. [9] proposed another method. In typical experiments, 0.2 g muscovite and 33 ml lithium nitrate solution (containing ca. 57 g lithium nitrate) were stirred for 46 h at 130 °C. The specific surface area of muscovite was increased to 135 m^2/g. The disadvantage of this method is that it demands great amounts of lithium nitrate (the mass ratio of lithium nitrate to muscovite is about 285) and long reaction times to obtain small amounts of muscovite. In a later report [10], the authors used twice the cleavage process to get mica with specific surface areas of 100–110 m^2/g. Although they used less lithium nitrate (the mass ratio of lithium nitrate to muscovite was about 34), this process took much longer time (2 weeks). Therefore, we propose a more effective method to cleave muscovite.

Experimental

Five hundred milligram muscovite powder and excessive amounts of $LiNO_3$ were mixed and heated in a muffle furnace at specified temperatures. After being cooled to room temperature, the sample was dispersed in 100 ml deionized water and vacuum filtered. The process of washing and filtering was repeated three times to remove

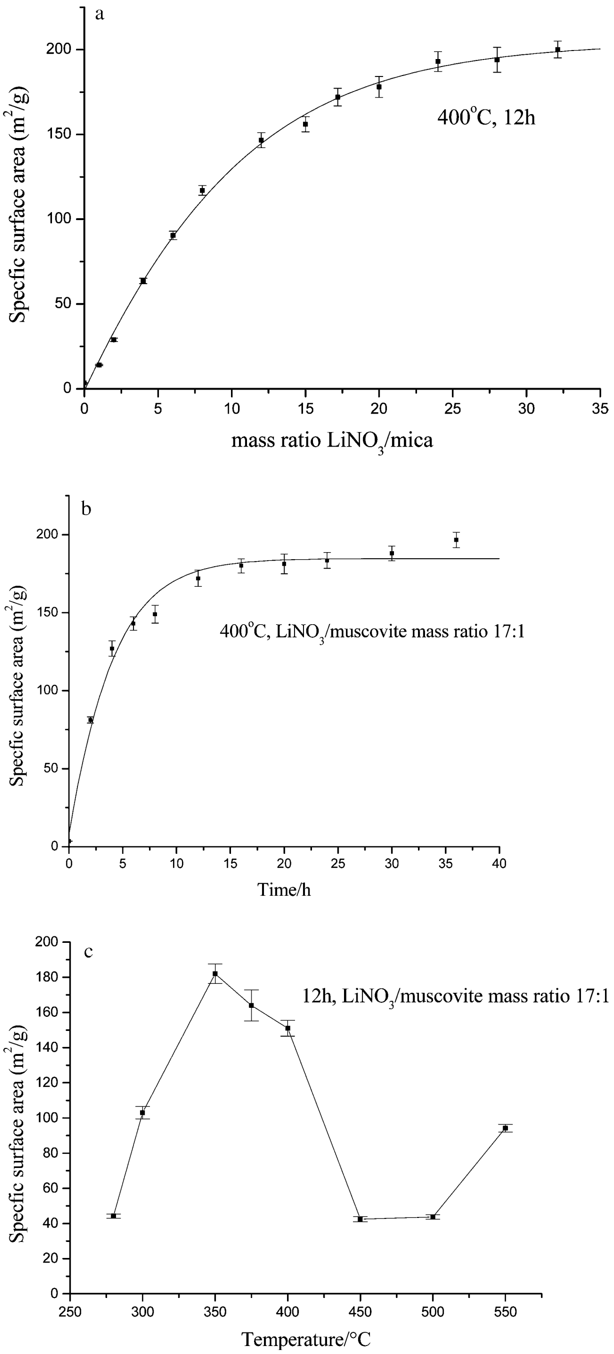

Fig. 1 Specific surface area of muscovite as a function of **a** LiNO$_3$/muscovite mass ratio; **b** cleavage time; **c** cleavage temperature

the excess LiNO$_3$. The sample was dried at 120 °C and hand ground in an agate mortar. The LiNO$_3$/muscovite mass ratio, time and temperature were varied to find the best condition for muscovite cleavage.

The specific surface area of muscovite was measured by methylene blue adsorption [11–13]. An amount of 100 or 200 mg muscovite was dispersed in 10 or 20 ml water. The methylene blue solution (1 or 2 mmol/l) was added to it until the color of the suspension became dark blue, which is usually, at the final concentration of methylene blue > 0.1 mmol/l. The dispersion was then stirred for an hour and allowed to stand for 12 h to reach adsorption equilibrium. The supernatant solution was diluted for UV-Vis measurement at 664 nm in a Cary-1E spectrometer.

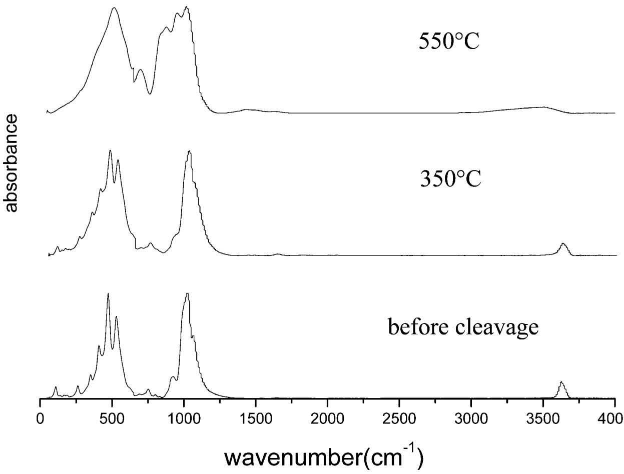

Fig. 2 Infrared spectra of untreated muscovite and muscovite cleaved at 350 and 550 °C

For calculation of the specific surface area, the apparent area of methylene blue cations was taken as 66 Å^2 [14]. The IR spectra were recorded in the 50–4,000 cm^{-1} range (Nicolet 750 FTIR). XRD was carried out with a Rigaku Rotaflex X-ray powder diffractometer (Cu Kα, Ni-filter, 40 kV, 100 mA). ICP data were acquired by the ICAP-9000 SP instrument of JARRELL-Ash Company.

The DTG and DTA diagrams were recorded on an SDT2960 apparatus of Thermal Analysis Company with α-Al_2O_3 as the reference substance. The sample was heated (10 °C min^{-1}) from room temperature to 900 °C in a flowing N_2 atmosphere.

Results and discussion

The specific surface area of muscovite increased with the mass ratio LiNO$_3$/mica, and approximated a plateau when LiNO$_3$/muscovite mass ratios > 10 (Fig. 1a). The error in special surface area determination is mainly related to the UV-Vis spectroscopic measurements. Within the first 4 h, the specific surface area of muscovite increased strongly (Fig. 1b). As a function of temperature, the specific surface area increased to a maximum around 350 °C (Fig. 1c). Above 400 °C, the specific surface area decreased sharply. The IR spectra and XRD results reveal that the structure of muscovite

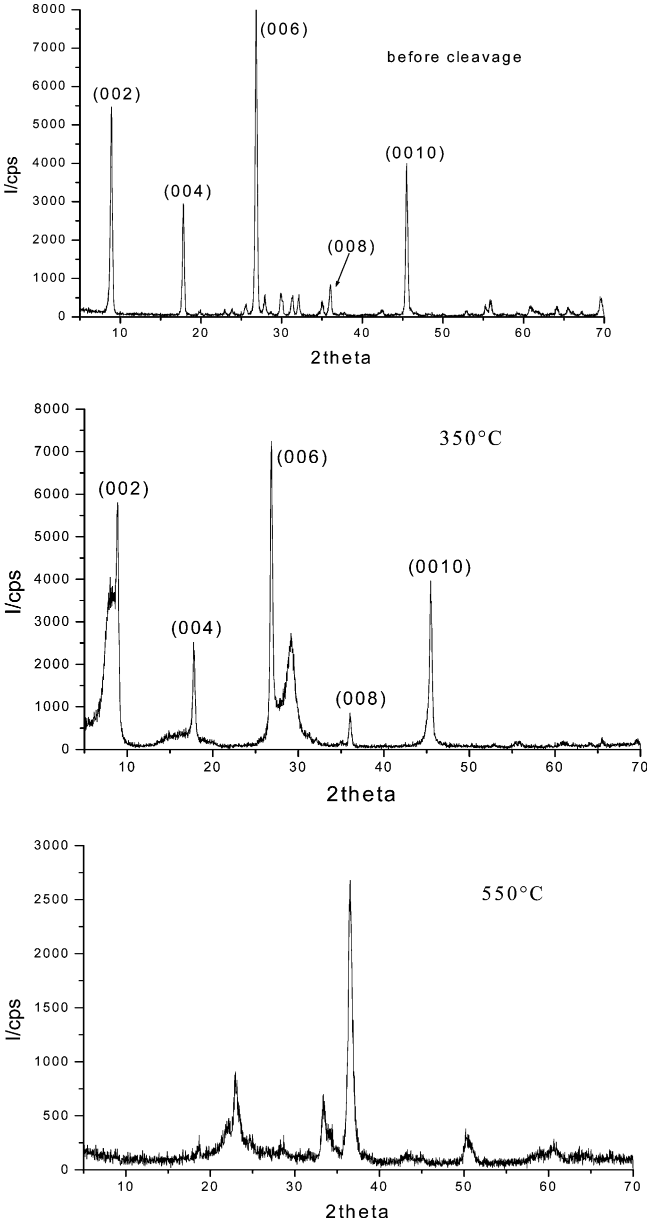

Fig. 3 XRD patterns of untreated muscovite and muscovite cleaved at 350 and 550 °C

was destroyed and new chemical phases were produced at higher temperatures.

The IR spectrum of muscovite cleaved at 350 °C was very similar to that of untreated muscovite (Fig. 2) and the peak positions agree with the literature values [15]. This indicates that the silicate structure was not damaged. The IR spectrum of muscovite cleaved at 550 °C was quite different and indicated some structural changes.

At cleavage temperatures below 400 °C, the diffraction peaks of muscovite showed no changes in the position (Fig. 3). During the cleavage process, Li^+ ions exchange K^+ ions and increase the basal spacing in the presence of water. When the cleavage temperature was >400 °C, the characteristic reflections of muscovite disappeared and new reflections were observed. It was not possible to identify the newly formed compounds.

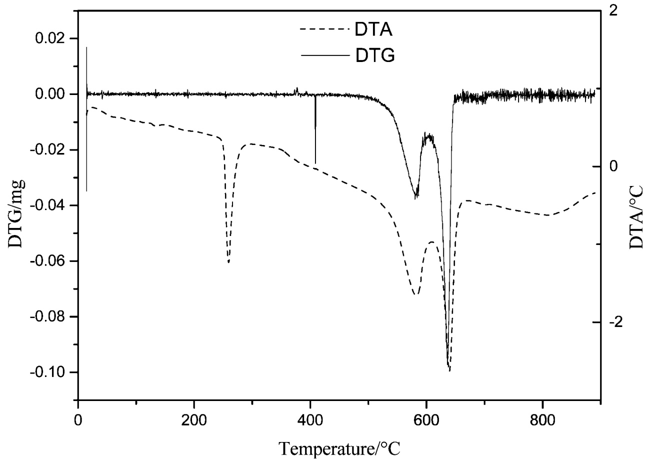

Fig. 4 DTG–DTA curves of muscovite and $LiNO_3$ (mass ratio 1:6)

The maximum of the specific surface area of cleaved muscovite was 200 m^2/g for a $LiNO_3$/muscovite mass ratio 32:1 at 400 °C, 12 h, which was smaller than that by Caseri's method [9]. In their experiments, the maximum specific surface area was 295 m^2/g ($LiNO_3$/muscovite mass ratio 285:1, 180 °C, 46 h). We used a muscovite sample with 170 m^2/g specific surface area for a second cleavage procedure ($LiNO_3$/muscovite mass ratio 17:1, 350 °C, 12 h) and reached a specific surface area of 309 m^2/g. In contrast to Caseri's method, we obtained muscovite with high specific surface area using a smaller amount of $LiNO_3$ and in a shorter time. The limitation in our cleavage experiment is that $LiNO_3$ and muscovite do not mix completely during the cleavage procedure.

Other molten alkali metal salts were also used for cleaving muscovite: LiCl, Li_2CO_3, NaCl, Na_2CO_3 and $NaNO_3$. Except for $NaNO_3$, these salts reacted with the muscovite and destroyed the structure. When 22 g of $NaNO_3$ was reacted with 1 g muscovite at 350 °C for 12 h, the specific surface area reached only 29.8 m^2/g.

From the ICP analysis, the formula of muscovite before and after cleavage at 350 °C was $(K_{0.85}Na_{0.15})(Al_{1.73}Fe_{0.12}Mg_{0.12})[Si_{3.08}Al_{0.92}]O_{10}(OH)_2$ and $(K_{0.52}Na_{0.10}Li_{0.32})$ $(Al_{1.75}Fe_{0.11}Mg_{0.12})[Si_{3.09}Al_{0.91}]O_{10}(OH)_2$. The amount of Li^+ was equal to the displaced amount of K^+ ions. For muscovite cleaved at 550 °C, the K^+ content decreased to almost zero and the Li^+ content increased far beyond the initial content of K^+ ions. This shows that muscovite has actually reacted with lithium nitrate producing new lithium compounds.

Figure 4 shows DTG–DTA curves of the mixture of muscovite and $LiNO_3$. The DTA curve exhibited a sharp endothermic peak at 259 °C without weight loss due to the melting of $LiNO_3$. The DTG curve showed a sharp peak at ca. 408 °C, which indicated the decomposition of KNO_3 because Li^+ ions replaced the interlayer K^+ ions and KNO_3 was produced. The two DTG peaks at 582 and 639 °C corresponded to the two endothermic peaks of the DTA curve. The endothermic peak at 582 °C represents the chemical reaction between muscovite and $LiNO_3$, and the peak at 639 °C of the DTA curve is ascribed to the decomposition of $LiNO_3$.

The ICP data and DTG–DTA analysis show that the Li^+ ions replace the interlayer K^+ ions during the cleavage reaction. The main reason for the cleavage reaction is the distinctly higher hydration enthalpy and the absence of the specific interaction of the Li^+ ions compared to the K^+ ions. It may also be possible that in molten $LiNO_3$, Li^+ NO_3^- ion pairs penetrate between the layers, promoting the cleavage when the sample is dispersed in water.

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