Characterization and thermal behavior of kaolin

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Abstract The decomposition behavior of kaolin samples has been carried out by simultaneous TG–DTA experiments. New layer-structure formation during the calcination process was found, and metakaolin compound was detected between 600 and 900 °C. The thermal stability of kaolin samples was then identified by TG–DTA, and the results are confirmed by characterization of X-ray powder diffraction (XRD), N_2 adsorption (Brunauer-Emmet-Teller model, BET), and scanning electron microscopy (SEM).

Keywords Kaolin · Thermal analysis · Calcination · Layer structure

Introduction

Kaolin $[Al_2Si_2O_5(OH)_4]$ is a common phyllosilicate mineral, which belongs to a large general group known as the clays. Its structure is composed of silicate sheets (Si_2O_5) bonded to aluminum oxide/hydroxide $[Al_2(OH)_4]$ layers. It is a conventional raw material for ceramics, porcelain, paper, coatings, rubber, plastics, fire-proof materials, chemicals, pesticides, medicines, textiles, petroleum, and building materials [1]. In particular, it is an important material of a catalyst support or catalyst for hydrogenation due to its specific characteristics such as high versatility, wide range of preparation variables, use in catalytic amounts, ease of set-up and work-up, mild experimental conditions, gain in yield and/or selectivity, and low cost [2]. Thermal stability, morphology and physical properties such as crystallinity, porosity, and surface area are very important factors for kaolin application. Therefore, research on these properties is necessary.

Kök and Smykats-Kloss studied the decomposition behaviour of dolomite samples by simultaneous TG–DTA [3]. Ip et al. [4] used thermogravimetric (TG) and differential scanning calorimetry (DSC) to characterize the clay components removed from weathered and unweathered sandstone, and identified two types of kaolin clays, namely, kaolin and its polymorph, dickite. Cekerevac and Laloui [5] studied the thermal effects on the mechanical behavior of saturated clays such as kaolin. Magaraphan et al. [6] studied the preparation, structure, properties, and thermal behavior of rigid-rod polyimide/montmorillonite nanocomposites. Castelein et al. [7] focused on the influence of heating rate on the thermal behavior and mullite formation from a kaolin raw material. Liu et al. synthesized NaY zeolites with coal-based clay as raw material using an activating treatment, hydroxide sodium fusion, and subsequent in situ crystallization hydrothermal synthetic methods. The in situ synthesis may provide a commercial route for the utilization of coal-based clay [8]. The thermal behavior of the different kinds of clay, sepiolite, dolomite, bentonite, etc., has been widely studied [9–12]. Hence, many studies had been conducted to study the thermal behavior of clay. Nevertheless, very few investigations are currently available on the thermal behavior of kaolin.

In this study, the thermal behavior of kaolin was focused on. Samples calcined at different temperatures were studied by X-ray diffraction (XRD) and simultaneous TG–DTA experiments. Scanning electron microscopy (SEM),

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specific surface area determination, and energy-dispersive X-ray spectrometry were used to complement XRD and TG–DTA results. Significant variations in the properties of calcined kaolin were observed.

Experimental

Materials and preparations

In this article, kaolin's study was provided by Shijiazhuang Minerals Co., Ltd. (China). Samples were crushed and sieved to obtain particle sizes between 74 and 149 μm. The fresh kaolin was dried at 100 °C for approximately 2 min in a vacuum drying oven (FZG-4A, Yiheng Instruments, China), and then its components were analyzed on an energy dispersive X-ray spectrometer (EDX, EDX-700HS, Shimadzu, Japan). The material is mainly compos of SiO_2 and Al_2O_3 (Table 1).

Calcination of natural kaolin was performed in a muffle furnace from room temperature to 400, 700, and 1050 °C at a heating rate of 5 K min^{-1}, and then kept at the final temperature for 2 h in an air environment. The calcined samples were labeled according to the calcination temperature, namely, M-400, M-700, and M-1050. The fresh material was labeled as FM. All samples were kept in desiccators before use.

Sample characterization

XRD patterns were recorded on a diffractometer, using Ni-filtered CuKα-radiation. Room temperature diffractograms were recorded at a scanning speed of 0.002° 2θ s^{-1} from 5° to 50°. BET specific surface areas were determined by nitrogen adsorption at the temperature of liquid nitrogen on a Gemini 2380 (Mac Inc., USA). SEM was done using a field emission scanning electron microscope JSM-6700F (Jeol Datum Ltd., Japan). The compositions of the samples were analyzed using an EDX (EDX-700HS Shimadzu, Japan).

TG–DTA curves of the air-dried sample were recorded using a Diamond TG/DTA (Perkin Elmer Co., Ltd., USA). Approximately 20 mg of sample was placed in a platinum crucible in the microbalance and was heated from ambient temperature to 1200 °C. Analysis was performed under 60 mL min^{-1} supplied airflow and at a heating rate of 10 K min^{-1}.

Table 1 Chemical composition of kaolin (% mass/mass)

Composition	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	TiO_2
Content/%	53.57	43.54	1.08	1.52	0.078	0.085	0.094	0.073

Results and discussion

Thermal and structural characteristics

The XRD patterns of FM, M-400, M-700, M-1050 are shown in Fig. 1. The TG–DTA curves of the kaolin samples at 20–1200 °C are illustrated in Fig. 2. The first endothermic mass loss at 20–200 °C is due to moisture loss. The major endothermic mass loss of the kaolin sample was observed at 450–600 °C. The minimum weight loss occurs above 500 °C. This can be attributed to endothermic dehydroxylation (or alternatively, dehydration) to produce disordered metakaolin ($Al_2Si_2O_7$). Dehydroxylation continued up to 900 °C [13, 14]. This may be attributed to the gradual oxolation of the metakaolin. Extensive research has led to a general consensus that metakaolin is not a simple mixture of amorphous silica (SiO_2) and alumina (Al_2O_3), but rather a complex amorphous structure that retains some longer-range order (not strictly crystalline) due to the stacking of its hexagonal layers [15]. The structure loses its crystallographic order between 500 and 750 °C, which is observed by the lack of Bragg scattering from materials heated above these temperatures. The exothermic peak above 1000 °C can be ascribed to the formation of the crystalline phase [16–18]. These TG–DTA results further support the XRD data on the effect of thermal treatment on kaolin.

$$2\ Al_2Si_2O_5(OH)_4 \rightarrow\ 2\ Al_2Si_2O_7\ +\ 4\ H_2O$$
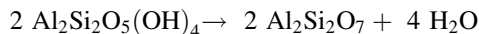
Further heating to 925–950 °C converts metakaolin to a defect, aluminum-silicon spinel ($Si_3Al_4O_{12}$), which is also referred to as a gamma-alumina type structure.
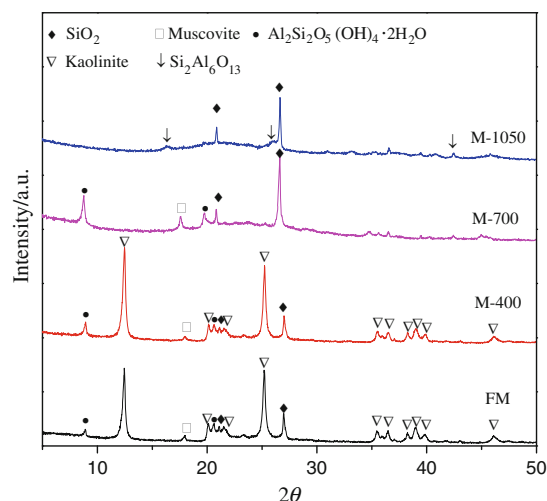

Fig. 1 X-ray diffraction patterns of fresh kaolin and its thermal treated samples at different calcination temperatures
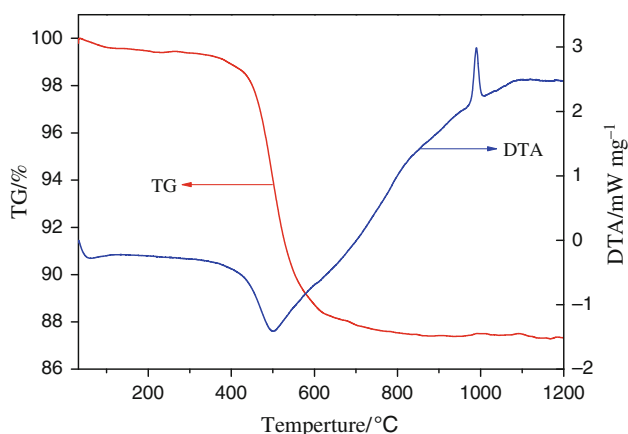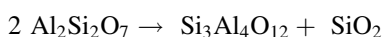
Fig. 2 TG–DTA data for fresh kaolin
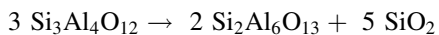
$$2\ Al_2Si_2O_7 \rightarrow\ Si_3Al_4O_{12} +\ SiO_2$$

Upon calcination to around 1050 °C, the spinel phase ($Si_3Al_4O_{12}$) nucleates and transforms to mullite [$3Al_2O_3 \cdot 2SiO_2$], and highly crystalline cristobalite (SiO_2).

$$3\ Si_3Al_4O_{12} \rightarrow\ 2\ Si_2Al_6O_{13} +\ 5\ SiO_2$$

[19]

Morphology

The morphologies of the kaolin materials were studied by SEM. The SEM pictures of FM, M-400, M-700, and

**Table 2** BET analysis of nature kaolin and its calcined sample at different temperatures

	FM	M-400	M-700	M-1050
BET surface area/m^2 g	11.6	10.7	11.3	7.00
Pore volume/cm^3 g	0.0564	0.622	0.0704	0.0874
Pore size/Å	194.6	233.3	248.6	501.7

M-1050 are shown in Fig. 3. Kaolin has a layered structure [20]. Layer stripping occurred at increased calcination temperatures. This indicates that a higher calcination temperature promotes lamellar layer formation and an increase in specific surface area. However, the clay structure collapsed at 1050 °C [19].

BET surface area and porosity

The BET surface area and porosity of all the samples are summarized in Table 2. The surface area of the samples decreased with increased calcination temperature, whereas pore volume and pore size increased on the contrary. Kakali et al. [21] in their study, pointed out that well-ordered kaolin transformed in a less-reactive metakaolin with thermal treatment. Loose structure brings larger pore volume and pore size. Compared with other samples, the sample that calcined at 1050 °C showed different properties. This suggests the formation of the crystalline phase.

Fig. 3 SEM images of kaolin calcined at different temperatures for 2 h

FM

M-400

M-700

M-1050
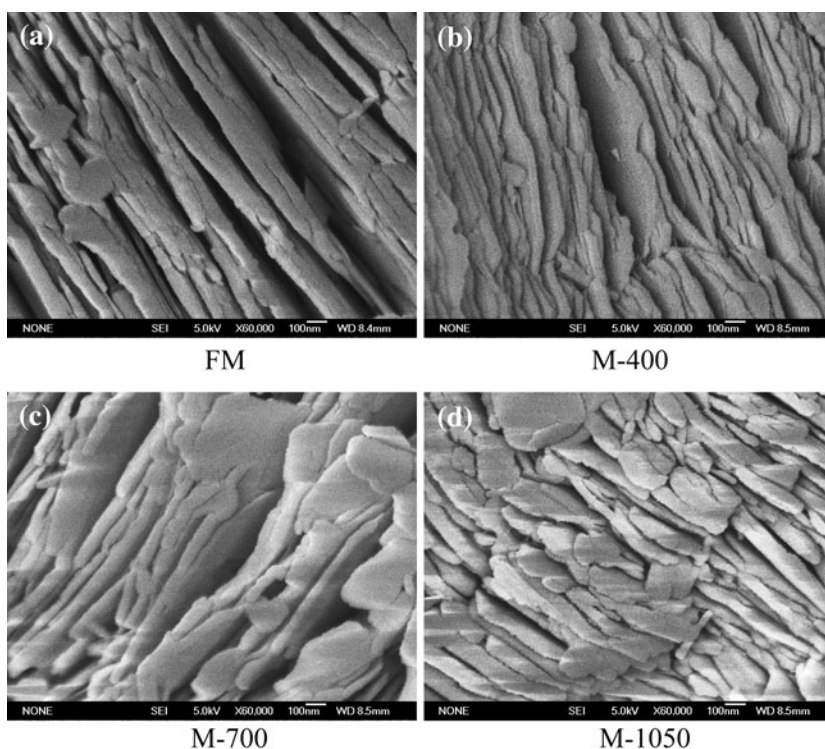
Conclusions

TG–DTA and XRD analyses demonstrate dehydroxylation of kaolin during calcination. Metakaolin was formed during 600–900 °C. The surface area of the samples decreased with increased calcination temperature. Pore volume and pore size also increased with temperature. The SEM result shows that stripping has occurred, and the lamellar structure was formed at the calcination temperature. Well-ordered kaolin transformed in a less-reactive metakaolin concurrently achieved increased thermal stability.

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