



The thermochemical activity of dolomite occurred in dolomite–palygorskite



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ABSTRACT

Dolomite–palygorskite (DP) composed of dolomite and palygorskite is a kind of special palygorskite. In this work, the phase, microstructure, and morphology of DP were characterized before and after calcination using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). Additionally, the process of thermal decomposition of DPC was determined by thermal gravity (TG) and differential thermal gravity (DTG) analysis and was compared with that of common dolomite. The results showed that the decomposition temperature of dolomite occurred in DPC started at 500 °C and ended at 780 °C, with a maximum peak at 745 °C. The decomposition temperature of dolomite in DPC was found to be 50 °C lower than that of common dolomite. Two reasons may explain this phenomenon. One involved the nano-effect of DPC caused by the nanoscale of dolomite in DPC and the special embedded structure between dolomite and palygorskite. The other was contributed to the reaction of carbonate with silicate enhancing the decomposition of dolomite in DPC.

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1. Introduction

The intergrowth of dolomite and palygorskite has been documented in the geology and mineralogy of palygorskite clay. Both dolomite and palygorskite are authigenic minerals because they form in similar environments (Chen et al., 2004a; Xie et al., 2013). The unique layer-chained structure and nano-rod appearance of palygorskite make it an excellent adsorbent, thixotropic agent, and thickening agent, among others (Chen et al., 2004b; Galan and Singer, 2011). However, when palygorskite occurred together with dolomite, it did not have the same adsorptive property. Therefore, dolomite negatively influenced the properties of palygorskite. In addition, when dolomite and palygorskite occur together, they form an embedded structure, which makes it difficult to separate the two minerals. Thus, palygorskite clay containing dolomite (50–85 wt.%) was generally used as a weak plugging compound or discarded as solid waste during mining.

Up to now, only a few studies evaluated the processing and application of DPC involving its origin and environmental characteristics (Botha and Hughes, 1992; Birsoy, 2002; Neaman and Singer, 2004). Therefore, it is necessary to study the application of DPC; however, it is critical to investigate its mineralogy before utilizing it. In recent years, dolomite has attracted much attention as an environmental

material because of its following four specific properties or applications. (1) The characterization of the structural evolution of its physicochemical properties and its resistance to water after thermal treatment (Marouf et al., 2009; Trindade et al., 2009; Ghosh and Tripathi, 2012; Sasaki et al., 2013a,b). Marouf et al. revealed the effects of various calcination temperatures on the zeta potential of dolomite. Trindade et al. investigated the transformation of dolomite compared with clay-rich calcite. Ghosh et al. studied the sintering behavior and the water resistance of thermally treated dolomite. Sasaki et al. revealed the relationship between phase change, pore structure, adsorption, and calcination temperature. (2) The application of dolomite and activated dolomite as adsorbents of heavy metals and dyes (Pehlivan et al., 2009; Boucif et al., 2010; Albadarin et al., 2012). Albadarin et al. identified the kinetics and dynamics of dolomite as an adsorbent of Cr(VI). Pehlivan et al. studied the ability of dolomite to adsorb Cu²⁺ and Pb²⁺. Boucif et al. (2010) investigated the adsorptive behavior of thermally treated dolomite in adsorbing azo dyes. (3) The use of thermally treated dolomite as an esterification catalyst (Ngamcharussrivichai et al., 2007; Miao et al., 2010; Yoosuk et al., 2011; Ilgen, 2012). Ngamcharussrivichai et al. described the catalytic reactivity of modified dolomite in the esterification of palm kernel oil. Ilgen et al. studied the kinetics of the catalytic activity of dolomite in the transesterification of canola oil and methanol. Yoosuk et al. investigated the use of the hydration–dehydration technique in improving the properties and activity of calcined natural dolomite in heterogeneous biodiesel production. Miao et al. utilized porous dolomite pellets for the catalytic

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decomposition of acetic acid. (4) The application of dolomite as a catalyst in the catalytic pyrolysis of organic waste (Yu et al., 2009; Andrés et al., 2011; González et al., 2011; Sarioğlan, 2012; Sun et al., 2012; Wang et al., 2012). Andrés et al. investigated the catalytic behavior of dolomite in the catalysis of sewage sludge in air–steam gasification. González et al. studied the role of dolomite in the catalytic cracking of biomass tar in two-stage gasifiers. Yu et al. studied the effects of dolomite in the catalytic cracking of biomass tar. Wang et al. studied the role of NiO supported on dolomite in producing hydrogen-rich gases by steam gasification of municipal solid waste. Sarioğlan and Sunn investigated the role of dolomite as catalyst or catalyst carrier in the reforming of tar. The results of these studies indicated that thermal activation changed the structure and properties of dolomite, which played a crucial role in improving the performance of dolomite and enabling its application.

Based on the application study of dolomite and the presence of the special DP resulted from the intergrowth of nano-structural dolomite and one-dimensional palygorskite, the thermal stability of dolomite occurred in dolomite–palygorskite was investigated and compared with common dolomite. In particular, the aim of the present work was to investigate the phase composition, the microstructure, and thermochemical activity of nanoscale dolomite to provide a theoretic base for the application of DPC in new fields as mentioned above.

2. Experimental

Dolomite–palygorskite clay was obtained from the Huaguoshan mine located in Mingguang City, Anhui Province, China. Five samples were labeled as “H-5-1,” “H-5-2,” “H-5-3,” “H-5-4,” and “H-5-5.” High-grade palygorskite (>90 wt.%) was obtained from the Guanshan mine that was located in Mingguang City, Anhui Province, China. Amorphous silicon oxide was prepared according to previously published methods (Chen et al., 2004a,c). After a 4 h reaction between palygorskite and hydrochloric acid (10 v%) mixed as a ratio of 1:4, the residue was centrifuged, washed, dried and ground. Rod-like nanocalcite, which was synthesized from calcium hydroxide and EDTA, was provided by Southwest University of Science and Technology. The common dolomite was collected in Chaohu City, China.

The loss of ignition of the samples was determined by calcination at 900 °C for 3 h, and the chemical compositions of samples were measured with an X-Ray Fluorescence Spectrometer (Shimadzu 1800, Japan). The weight of acid-insoluble substance was determined by dissolution of the samples in hydrochloric acid (5 v%) for 3 h. All samples were characterized by X-Ray diffraction (XRD) using Cu K α radiation in a range of 3–70° at a scan speed of 4 min⁻¹ using an X-Ray Diffractometer (Dandong Haoyuan-DX-2700, China). The thermal gravity (TG) and differential thermal gravity (DTG) analyses of the samples were carried out in a Thermo Gravimetry/Differential Thermal Analyzer (7300, SEIKO Instrument Inc., Japan). The appearance and microstructure of the dolomite–palygorskite clay were measured before and after calcination using a JEM 2010 transmission electron microscope (JEOL Ltd., Japan) and a JSM-6490LV scanning electron microscope (JEOL Ltd., Japan).

3. Results

3.1. Composition of dolomite–palygorskite clays

The chemical composition and the loss of ignition of the five dolomite–palygorskite clay samples are summarized in Table 1. The main components of the dolomite–palygorskite clay were followed: CaO with 21.98–25.25 wt.%; MgO with 23.08–25.27 wt.%; SiO₂ with 2.43–8.46 wt.%; Al₂O₃ with 0.52–0.94 wt.%; Fe₂O₃ with 0.13–0.56 wt.%; and F with 0.61–0.88 wt.%. The percent by mass of K₂O, SrO, MnO₂, TiO₂, SO₃, and P₂O₅ each was lower than 0.25 wt.%, the loss of ignition was 42.16–45.50%, and the percent by mass of acid-insoluble substance was 4.09–11.85 wt.%.

As shown in Fig. 1(c), the mineral phase of common dolomite was mainly composed of dolomite (JCPDS 36-0426) and a small quantity of quartz (JCPDS 65-0466). Here the reflection of dolomite was observed at 2 θ = (22.0°(d = 4.030), 24.1°(d = 3.696), and 31.0°(d = 2.883)), and quartz was observed at 2 θ = (26.7°(d = 3.341)). The XRD pattern of DPC was approximately the same as that of common dolomite. Although palygorskite were not found in the XRD pattern, the presence of palygorskite (JCPDS 31-0783) was confirmed by the TEM image and the XRD pattern of the acid-insoluble substance as shown in Fig. 1(a). Here the reflection of palygorskite was observed at 2 θ = (8.6°(d = 10.297), 13.8°(d = 6.375), and 16.4°(d = 5.406)). This phenomenon should be ascribed to the considerably strong reflection intensity of dolomite, which concealed the reflections of palygorskite. The amount of dolomite was estimated to be 88–95 wt.% based on the amount of acid-insoluble substance (4.09–11.85 wt.%). As presented in Fig. 1(a), palygorskite and quartz were identified as the main mineral phase of the acid-insoluble substance, indicating that the dolomite was completely dissolved after acid washing. The amount of palygorskite was estimated to be 5–10 wt.% based on the results of the XRD and the amount of acid-insoluble substance present.

3.2. Microstructure of dolomite–palygorskite clay

The palygorskite crystal was ubiquitously observed in the FE-SEM images (Fig. 2(a)), although palygorskite could not be identified from the XRD results (Fig. 1(c)). The following microstructural characteristics of dolomite–palygorskite clay were shown by SEM images: (1) Dolomite–palygorskite clay had a loose and porous structural nature; (2) The embedded and inter-textural structure of dolomite–palygorskite indicated that dolomite and palygorskite were authigenic minerals in the depositional environment; (3) The sub-idiomorphic dolomite crystal, the surface of which had a symmetric step with a rhombohedral shape, had cavities; (4) The palygorskite crystal penetrated the cavities of the dolomite crystal, which indicated that the growth of part of the palygorskite occurred later than that of dolomite. This phenomenon also implied that the crystallization of palygorskite occurred in the magnesium-rich cavities of the dolomite crystal, which likely resulted in the corrosion of dolomite as the palygorskite grew. The TEM image of an ultrathin slice of dolomite–palygorskite clay (70 nm thickness) also displayed the inter-textural structure between dolomite and palygorskite, which lead to the formation of interspaces between the two minerals that varied in size from nanoscale to microscale.

Table 1

The composition of dolomite–palygorskite clay.

Samples	SiO ₂ /wt.%	Al ₂ O ₃ /wt.%	CaO /wt.%	SO ₃ /wt.%	MgO /wt.%	Fe ₂ O ₃ /wt.%	MnO ₂ /wt.%	F /wt.%	Loss of ignition /wt.%	Acid-insoluble /wt.%
H-5-1	2.42	0.54	25.25	0.08	25.27	0.13	0.01	0.61	45.50	4.095
H-5-2	8.46	0.53	22.30	0.10	24.45	0.23	0.02	0.85	42.89	10.36
H-5-3	8.21	0.72	21.98	0.14	25.21	0.43	0.02	0.88	42.16	11.085
H-5-4	6.34	0.94	24.65	0.10	23.08	0.56	0.13	0.81	43.11	10.09
H-5-5	5.88	0.68	24.73	0.09	23.53	0.53	0.14	0.58	43.57	8.905

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