



Research paper

Effects of microstructure of clay minerals, montmorillonite, kaolinite and halloysite, on their benzene adsorption behaviors

Liangliang Deng^{a,b}, Peng Yuan^{a,*}, Dong Liu^a, Faïza Annabi-Bergaya^c, Junming Zhou^{a,b}, Fanrong Chen^a, Zongwen Liu^d^a CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c CNRS, UMR7374, Interface Confinement Matériaux et Nanostructures, 45071 Orléans, France^d School of Chemical and Biomolecular Engineering, University of Sydney, NSW 2006, Australia

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ABSTRACT

Montmorillonite (Mt), kaolinite (Kaol) and halloysite (Hal) are commonly investigated porous clay minerals, but their performance for the adsorption of volatile organic compounds (VOC) was rarely studied. In this work, the dynamic adsorption of benzene, as a model VOC, on Mt, Kaol and Hal was investigated. The effect of the microstructures of the above-mentioned clay minerals on benzene adsorption were explored by comparing the benzene adsorption of the different derivatives of these clay minerals, which were obtained by adjusting the interlayer space and the porosity of the clay minerals through heating treatment. Calcium-based montmorillonite (Ca²⁺-Mt) heated at 120 °C exhibited higher benzene adsorption capacity (141.2 mg/g) than sodium-based montmorillonite (Na⁺-Mt) heated at 120 °C (87.1 mg/g), because the interlayer distance of Ca²⁺-Mt was sufficiently large to accommodate the adsorption of benzene. However, for calcined Ca²⁺-Mt and Na⁺-Mt, the collapse of their interlayer space resulted in that the interlayer micropores no longer existed and reduced benzene adsorption. Kaol exhibited the lowest benzene adsorption capacity (56.7 mg/g) among the studied clay minerals because its interlayer space was not available for adsorption and because its specific surface area (SSA) was relatively small. As a polymorph of Kaol but with a tubular morphology, Hal showed a higher benzene adsorption capacity than Kaol owing to its larger SSA. In particular, heating at 120 °C resulted in the increase of the benzene adsorption of Hal, which was ascribed to the exposure of the adsorption sites initially occupied by water molecules. These results demonstrate that the benzene adsorption capacity of the above-mentioned clay minerals was not only highly related to their SSA but also strongly affected by their porosity features.

1. Introduction

The emission of volatile organic compounds (VOC), the most common air pollutants from petrochemical, chemical, pharmaceutical and printing industries, has become one of the most serious environmental problems because VOC are toxic, hazardous and even carcinogenic. VOC are the main sources of the photochemical reaction, and they can trigger the formation of secondary organic aerosols that are harmful to human health (Doyle et al., 2004; Ng et al., 2007; Pöschl, 2005). Hence, the treatment of VOC has caused extensive attention. Many technologies, such as adsorption (Dimotakis et al., 1995; Yu et al., 2015a), membrane separation (Belaïssaoui et al., 2016), oxidation (Cordi and Falconer, 1997; Kamal et al., 2016) and biological treat-

ments (Doble, 2006) have been proposed for VOC control, among which adsorption is the most applicable technology because of its inexpensive operation cost, low energy and flexibility of adsorption systems (Yu et al., 2015b).

Activated carbon and synthetic zeolites are two types of commonly used adsorbents. Activated carbon is regarded as the most versatile adsorbent owing to its low cost and excellent adsorption capacity. However, its practicability is restricted by drawbacks such as fire risk, pore clogging and difficulties in regeneration (Zhao et al., 1998). Compared to activated carbon, synthetic mesoporous zeolites, such as SBA-15 (Dou et al., 2011) and ZSM-5 (Serrano et al., 2007), have the advantages of controllable pore sizes and good chemical stability in the adsorption of VOC. However, the synthesis process is complex and time-

* Corresponding author at: CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, China.

E-mail address: yuanpeng@gig.ac.cn (P. Yuan).

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Table 1
Chemical compositions of Mt, Kaol and Hal.

Sample	Chemical compositions (mass%)										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	L.O.I.*
Mt	57.41	15.66	4.93	4.98	2.98	0.11	0.12	0.03	0.31	–	13.33
Kaol	46.66	38.20	0.39	0.10	–	0.04	0.37	–	0.36	0.03	13.60
Hal	41.05	34.97	0.30	0.16	0.23	0.25	0.06	0.03	0.22	–	22.76

L.O.I.* denotes loss on ignition.

consuming (Cundy and Cox, 2003). In addition, the source materials, such as tetraethyl orthosilicate and cetyltrimethyl ammonium bromide are relatively expensive. These shortcomings would be very detrimental for the widespread application of synthetic zeolites. Therefore, many efforts were made to find low cost adsorbents with good adsorption performance and desirable thermal stability. Raw clay minerals have been proposed as alternative adsorbents due to their bidimensional structure and the ample active groups on the surface, such as silanol (Si-OH) and/or aluminol (Al-OH) groups, which were thought as the potential adsorption sites (Hernandez et al., 2004). The feasibility of clay minerals as VOC adsorbents might also be due to their excellent heat resistance and recyclability via thermal desorption. In addition, the wide distribution and abundant reserves of clay minerals make them be the promising environmental adsorbents that can be used in industrial processes.

Montmorillonite, kaolinite and halloysite are three commonly studied clay minerals. Montmorillonite is a 2:1 dioctahedral clay mineral with a layer composed of an alumina octahedral sheet sandwiched between two opposing silica tetrahedral sheets and with more or less hydrated exchangeable cations occurring in the interlayer space. Kaolinite is a 1:1 dioctahedral clay mineral. Each layer contains a silica tetrahedral sheet and an alumina octahedral sheet, which are bound tightly by sharing a common plane of oxygen atoms, and the repeating layers of the mineral along the *c* axis are hydrogen bonded together (Miranda-Trevino and Coles, 2003). Halloysite was first described by Berthier (1826) as a dioctahedral 1:1 clay mineral of the kaolin group. As a hydrated polymorph of kaolinite, halloysite shows some similarities in structure and chemical composition to kaolinite, but the unit layers in halloysite are separated by a monolayer of water molecules (Yuan et al., 2015a). The hydrated form of halloysite is referred to as “halloysite (10 Å)” in which one layer of water molecules is presented in the interlayer space, and where the “10 Å” designation indicates *d*₀₀₁-value in the multilayer walls. The dehydrated form of halloysite is referred to as “halloysite (7 Å)”, and it may be obtained through the loss of the interlayer water molecules under mild heating and/or in a vacuum environment (Joussein et al., 2005). The dominant morphology of halloysite is tubular, resulting from the wrapping of halloysite layers that is driven by a mismatch between the oxygen-sharing tetrahedral SiO₄ sheet and the adjacent octahedral AlO₆ sheet in the 1:1 layer under favorable crystallization conditions (Singh and Mackinnon, 1996). Generally, the length of the tubular halloysite is 0.02–30 μm, and the external and internal diameters are respectively 30–190 nm and 10–100 nm (Yuan et al., 2008, 2013). These sizes vary in different halloysite deposits (Pasbakhsh et al., 2013). The tubular halloysite has a porous structure, including the cylindrical lumen in the mesopore size range (2–50 nm) and even macropores (> 50 nm) derived from the inner cavity of the tubular halloysite particles (Tan et al., 2013). In spite of the numerous studies on the structure and surface properties of the above-mentioned clay minerals, the mechanism on how the structural characteristics and surface properties of the minerals affect their performance for VOC adsorption has rarely been studied.

In this study, benzene was used as a model organic pollutant to evaluate the VOC dynamic adsorption performance of the above-mentioned clay minerals via the breakthrough curve method. Benzene

was selected because it is a commonly used solvent in industrial processes, and it is ranked on top of the list of VOC pollutants. Benzene is toxic and hazardous, and it can enter into the human body through breathing and contacting with the skin, resulting in injury to the nervous system.

The main objectives of this study are to investigate i) the benzene adsorption performance of montmorillonite, kaolinite and halloysite and ii) the relevant adsorption mechanism, such as the effects of the structure and surface properties of these minerals on benzene adsorption. Therefore, different derivatives of the above-mentioned minerals were used for benzene adsorption, and they were heated to adjust the hydration state or the interlayer distance of the initial clay minerals. X-ray diffraction (XRD), N₂ adsorption-desorption and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy methods were adopted to characterize the structural features and surface properties of the clay minerals.

2. Materials and methods

2.1. Materials

Montmorillonite (Mt) was sourced from the Inner Mongolia province of China. Kaolinite (Kaol) was collected from the Guangdong province of China, and halloysite (Hal) from the Shanxi province of China was also used for comparison. A purification method of hand-picking followed by repeated sedimentation was carried out to remove impurities. The chemical compositions of the purified Mt, Kaol and Hal were listed in Table 1.

According to the chemical compositions data (Table 1), the Mt was assigned to calcium-based montmorillonite (denoted as Ca²⁺-Mt). Sodium-based montmorillonite (denoted as Na⁺-Mt) was prepared by dispersing Ca²⁺-Mt in deionized water and by treating it with 0.5 M sodium chloride solution under vigorous stirring at 80 °C for 24 h. The solid phase was then separated from the solution and treated with fresh salt solution, followed by two repetitions of the cation-exchange procedure to enable a complete exchange. The product was repeatedly washed with distilled water and then dried at 60 °C before it was ground to a powder.

Ca²⁺-Mt and Na⁺-Mt were heated at 120 °C and 600 °C in a programmed temperature-controlled muffle oven for 3 h and denoted as Ca²⁺-Mt_x and Na⁺-Mt_x, where *x* represented the heating temperature in degrees Celsius. Kaol was heated at 120 °C and denoted as Kaol_{120 °C}. The dehydrated Hal was obtained by thermal treatment at 120 °C of the hydrated form of Hal and denoted as Hal_{120 °C}. To prevent the dehydration of the hydrated form of Hal, the hydrated Hal was placed in a water vapor-saturated desiccator at room temperature and denoted as Hal_{RT}. Meanwhile, the heated samples were placed in a desiccator, which was loaded with allochroic silica gel, and vacuumization was performed to maintain a dry environment, thus preventing the re-adsorption of water. All samples were ground by hand for 1 min in an agate mortar.

2.2. Benzene adsorption tests

The benzene adsorption performance of the obtained samples was

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