Effects of crystal chemistry on adsorption, occurrence, and mobility of water in palygorskite tunnels

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ABSTRACT

Palygorskite is a fibrous magnesium-rich clay mineral with a typical tunnel structure, and its adsorption properties make it an ideal adsorbent for broad applications. Thus, revealing the confinement effects on tunnel species can help in understanding its adsorption properties. Grand canonical Monte Carlo and molecular dynamics simulations were performed to analyze the effects of the crystal chemistry of palygorskite on the adsorption, occurrence, and mobility of tunnel water. Water adsorption isotherm, distribution models, and mobility were achieved from these simulations. Zeolitic water emerges into the tunnels even at a low relative humidity (RH) (such as 5%) and completely fills the tunnels as the RH increases to 10%. In neutral palygorskite, the influence of the octahedral type on water adsorption is not obvious, but the influence of tunnel cations is obvious. The occupation of Na+ ions in tunnels can reduce the maximum water amount and affect the spatial distribution of zeolitic water. The water distribution in tunnels can be described by a two-zeolitic water-site model for neutral palygorskite and a one-zeolitic water-site model for charged one. The zeolitic water confined in the tunnel presents very low mobility, and the appearance of Na+ ions in the charged palygorskite further reduces the mobility of zeolitic water. Compared with other clay minerals, the much lower water mobility of palygorskite implies that it may have a more efficient fixation on foreign molecules or ions in environmental applications.

Keywords: Palygorskite, water, adsorption, molecular dynamics simulations, Grand canonical Monte Carlo, confining effects, mobility

INTRODUCTION

Palygorskite is a fibrous magnesium-rich clay mineral with fine particles and poor crystallinity. Similar to sepiolite, the tetrahedral sheet of palygorskite is continuous, and the octahedral sheet is discontinuous. The O atoms on the top of every two tetrahedral six-membered rings (three in sepiolite) are twisted, which is shown as a discontinuous octahedral sheet in a two-dimensional view and ribbon patterns in a three-dimensional (3D) view. The tunnels extend along the c-axis, resulting in the fibrous structures of palygorskite and sepiolite. Palygorskite has a smaller pore width than sepiolite. The fibrous structure endows palygorskite with excellent properties, such as large specific surface area, abundant micropores, and high adsorption capacity. Hence, palygorskite has seen wide applications, such as in the pharmaceutical and fertilizer production industries (Galan 1996; VanScoyoc et al. 1979). Because of its strong hydrophilicity and excellent environmental friendliness, palygorskite has been used as a desiccant and adsorbent (Singer et al. 2011) and in oil-water separation for improving the separation efficiency and recovery rate (Li et al. 2015). Moreover, palygorskite can be modified by different treatments. The performance of modified palygorskite can be obviously improved in adsorbing organic matter and heavy metal ions, and more applications of palygorskite have been developed by modification (Alvarez et al. 2011; Xi et al. 2010). Thus, modified palygorskites attract significant attention for adsorbing polar organics and as catalyst carriers (Jones and Galán 1988).

Palygorskite has been mined and applied for centuries, but its first crystal structure had not been published until 1940 by X-ray diffraction (XRD), with a monoclinic crystal system and a C2/m space group (Bradley 1940). However, Drits and Sokolova (1971) found that palygorskite could also be an orthorhombic crystal system. Later, its monoclinic and orthorhombic structural models were both confirmed by Rietveld refinement (Artioli and Galli 1994; Chiari et al. 2003; Giustetto and Chiari 2004). In fact, natural palygorskite ores are commonly a mixture of orthorhombic and monoclinic systems. Although palygorskite ore with a pure monoclinic system is found, palygorskite with a pure orthorhombic system has never been reported (Chisholm 1992). Galan and Carretero (1999) reviewed the reported chemical analysis and proposed that the octahedral sheets of palygorskite are a combination of dioctahedra and trioctahedra, and the common ratio of Mg2+/(Al3++Fe3+) is close to 1.0. Thus, there are different crystal chemical features of palygorskite.

There are three types of water in palygorskite, namely, hydroxyl, bound water, and zeolitic water, which are hardly affected by the variation in crystal chemistry (Singer et al. 2011). The occurrence of water determines the dehydration of palygorskite. Post and Heaney (2008) distinguished two zeolitic water sites. As the zeolitic water can move in the tunnel and appear at different sites, the loss of zeolitic water is a continuous process. Many reported thermogravimetric and differential