Confined water in tunnel nanopores of sepiolite: Insights from molecular simulations

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ABSTRACT

Sepiolite is a type of magnesium-rich fibrous clay mineral. The unique fibrous structure endows it with various applications in many fields. Revealing the behavior of confined water in sepiolite nanopores is crucial to understand the macroscopic properties of sepiolite. Aiming to ascertain the distribution and dynamics of the confined water, molecular simulations using grand canonical Monte Carlo and molecular dynamics methods have been performed. We obtain the water adsorption isotherm, density distribution profiles, and dynamic information of the confined waters in sepiolite tunnels. We find that zeolitic water is very hard to be desorbed from sepiolite under ambient conditions. Based on the distribution profile and trajectories of the water, we reveal the accurate distribution sites and propose a new distribution model of the confined water including one bound water site and four zeolitic water sites, which are determined by sepiolite lattice. The zeolitic water at different sites can exchange freely and frequently, and thus these sites may be energetically similar. This model provides more fundamental understanding of the hydration of sepiolite, and highlights the water behaviors in the tunnel pores of microporous minerals, which are thought being controlled by the crystallographic structure. The much lower mobility of zeolitic water in sepiolite than that in montmorillonite implies that materials with nano-sized tunnel pores could have more efficient fixation on foreign molecules or ions in environmental applications than those layered materials with slit pores.

Keywords: Sepiolite, zeolitic water, adsorption isotherm, molecular dynamics, grand canonical Monte Carlo

INTRODUCTION

Sepiolite is a typical fibrous Mg clay mineral, containing a 2:1 layer structure like other phyllosilicates. However, sepiolite only has continuous planes of basal oxygen atoms and lacks continuous octahedral sites, which differs from other layer silicates and leads to tunnels. This structure could be described as ribbons of 2:1 phyllosilicate structures and each ribbon is connected with the next one by inverted SiO₆ tetrahedra (Galan 1996). Due to its unique structure, sepiolite is comprehensively applied in many fields, such as special absorbent, cigarette filter, carrier of agricultural chemicals and catalysts, and so on (Anderson et al. 1993; Celis et al. 2000; Dogan et al. 2007; Giustetto et al. 2011a, 2011b; Gupta and Suhas 2009; Kara et al. 2003; Ozcan and Ozcan 2005; Samper-Madrigal et al. 2015; Sanchez et al. 2011; Shimizu et al. 2004). Sepiolite is proved to have the ability to adsorb heavy metal ions (e.g., Cu²⁺, Zn²⁺, Co³⁺) (Brigatti et al. 1996; Celis et al. 2000; Kara et al. 2003; Sheikhhosseini et al. 2014; Shimizu et al. 2004; Vico 2003) and organic matter (Darder et al. 2007; Dogan et al. 2007; Hubbard et al. 2003; Ruiz-Hitzky 2001; Rytvo et al. 2002; Shariatmadari et al. 1999). Delgado et al. successfully used sepiolite to remove CO₂ from CO₂/CH₄ gas mixture (Delgado et al. 2007).

The ideal formula of sepiolite is Mg₈Si₄O₁₄(OH)₂(OH₂)₂·nH₂O, which rarely has heterovalent cation substitutions and layer charge. OH is the hydroxyl of octahedral sheet, and OH₂ is the bound water coordinated with octahedral magnesium at the edge of the tunnel. H₂O is zeolitic water in the tunnel. The amount of zeolitic water could change with environmental relative humidity (RH), and therefore n is variable. The structure of sepiolite is hard to be determined by single-crystal diffraction methods due to its fine-grained and poor crystallinity. A widely accepted structure of sepiolite is a three zeolitic water sites model deduced by Brauner and Preisinger (1956) from X-ray diffraction experiments.

With the applications of sepiolite increasing, more microscopic information at the atomic scale is needed. Especially a better characterization of the water confined in sepiolite is important to understand the behavior of the other foreign ions and molecules adsorbed into the tunnel. Therefore, the behavior of water in sepiolite is not only important to mineralogists, but also to the applications (Shimizu et al. 2004). The hydration and dehydration of sepiolite have been studied experimentally for decades (Bukas et al. 2013; Caturia et al. 1999; Frost and Ding 2003; He et al. 1996; Rautureau and Mifsud 1977; Tsampodimou et al. 2015). However, the details of intracrystalline water in sepiolite are still under debate, especially the water distribution sites in the tunnel pores. Brauner and Preisinger deduced three zeolitic water sites with topology (Brauner and Preisinger 1956; Preisinger 1959). Post et al. (2007) introduced the synchrotron-based powder X-ray diffraction method to investigate the dehydration of sepiolite, and they proposed a model of four zeolitic water sites, which is different from the previous topology results, and a folding structure with water loss (Post et al. 2007).

Compared with experiments, computational simulation methods could obtain more precise microscopic information than direct measurements and observation (Benli et al. 2012; Ockwig et al. 2009). Ockwig et al. studied the hydrogen bonding patterns in sepiolite and palygorskite using computational...