Computer modeling of apparently straight bond angles: The intriguing case of all-silica ferrierite

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ABSTRACT

The relationships between synthetic zeolites and their natural counterparts that have been unveiled by theoretical studies have contributed to improving the properties and applications of zeolite-based materials in strategic areas such as industrial catalysis, environmental protection, and solar energy harvesting. To pinpoint the role of modeling in zeolite science, we discuss an example of computationally driven problem solving: can tetrahedral frameworks sustain straight (i.e., 180°) Si-O-Si bond angles? The true crystal symmetry of zeolite ferrierite (FER), especially in its all-silica form, had been intensely debated for 30 years before being solved in the Pnma space group. Yet there are indications that an Immm structure with energetically unfavorable linear Si-O-Si linkages could be formed at high temperature. To gather insight, we perform density functional theory (DFT) optimizations and frequency calculations of all-silica ferrierite in both the Pnma and Immm space groups. Our results indicate that Pnma is more stable than Immm, in line with experiments. While the Pnma structure is a true minimum in the energy profile of ferrierite, the Immm structure has four imaginary frequency vibrations, three of which are localized on the 180° Si-O-Si angles. This suggests that ferrierites with Immm symmetry may be classified as metastable phases. Such a designation is also supported by first-principles molecular dynamics on Immm FER, showing that the average value of 180° actually results from Si-O-Si angle inversion. An implication of this study with interesting geological and technological consequences is the association of straight Si-O-Si angles experimentally detected in open-framework or low-density silicates to an angle-inversion process occurring at the femtosecond scale. Such flexibility of the apparently flat Si-O-Si linkages might play an important role in sorption phenomena, which are ubiquitous in geological processes and industrial applications alike.

Keywords: Zeolites, high temperature, framework flexibility, open framework silicates, molecular dynamics, density functional theory; Microporous Materials: Crystal-Chemistry, Properties, and Utilizations

INTRODUCTION

Zeolites are porous silicates important in mineralogical research as well as industrial and technological applications (Čejka et al. 2010; Gottardi and Galli 2012). Adsorption of geochemical fluids, solar energy transfer, and catalytic cracking all occur within zeolite nanospaces (Tabacchi 2018). These processes require multi-technique approaches to be understood, exploited, and improved (VanSpeybroeck et al. 2015; Evans et al. 2017; Paul et al. 2018; Li and Pidko 2019). Computational techniques, such as geometric models (Sartbaeva et al. 2008; Wells and Sartbaeva 2012; Fletcher et al. 2015; Wells et al. 2015), force field methods (Demontis et al. 1991, 2017; Desbiens et al. 2005; Cailliez et al. 2008; Coudert et al. 2009; Demontis and Suffritti 2009; Wang et al. 2014), and quantum chemistry calculations (Fois et al. 1993; Campana et al. 1997; Ugliengo et al. 2005; Coudert et al. 2006; Giustetto et al. 2011; Dovesi et al. 2018), are effective tools to examine these processes.

Besides predicting crystal structures and elastic behavior of geochemical systems (Kubicki 2016), simulations may guide experiments by providing atomistic insight often difficult to access in a laboratory (Marx and Hutter 2009; Tabacchi et al. 2014b; VanSpeybroeck et al. 2015; Gaigeot and Sulpizi 2016). Theoretical techniques are particularly valuable at the temperature and pressure conditions typical of Earth’s mantle or extra-terrestrial environments (Cruciani 2006; Liang et al. 2007), where experimental observation is often unfeasible (Gatta et al. 2018; Kong et al. 2018). Zeolites are attractive materials for technology owing to their high resistance to thermal and mechanical stress (see Lotti et al. 2016; Santoro et al. 2016; Comboni et al. 2018; Kim et al. 2018; Marqueño et al. 2018; Seryotkin and Bakakin 2018; Confalonieri et al. 2019; Gigli et al. 2019; Seryotkin 2019 for recent experimental studies and Arletti et al. 2003; Cruciani 2006; Gatta 2008; Gatta and Lee 2014; Vezzalini et al. 2014; Gatta et al. 2018 for reviews). Modeling, often combined with experiments, has enabled researchers to analyze the deformation mechanisms of zeolites under high-temperature and high-pressure conditions (Ballone et al. 2002; Ferro et al. 2002; White et al. 2004; Fois et al. 2008d; Jordá et al. 2013; Kreml et al. 2013; Torres et