Heat capacity and thermodynamic functions of partially dehydrated sodium and zinc zeolite A (LTA)

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ABSTRACT

Zeolite A (LTA) is an industrially important zeolite that exhibits sorption-induced framework flexibility, the thermodynamics of which are poorly understood. In this work, we report heat capacity measurements on zinc and sodium zeolite A from 1.8 to 300 K and compare the heat capacity of water in sodium zeolite A with that of water in other zeolites. The heat capacity of zeolitic water varies significantly depending on the hydration level and identity of the host zeolite, and more tightly bound water exhibits strong inflections in its heat capacity curve. This suggests a combination of effects, including differences in water-framework binding strength and hydration-dependent flexibility transitions. We also report fits of the heat capacity data using theoretical functions, and we report values for $C_p$, $\Delta H_m$, $\Delta S_m$, and $\Phi_m$ from 0 to 300 K. These results contribute to a systematic thermodynamic understanding of the effects of cation exchange, guest molecule confinement, and sorbate-dependent flexibility transitions in zeolites.

Keywords: Zeolite, framework flexibility, gate opening, zeolitic water, heat capacity

INTRODUCTION

Zeolite A (also known as Linde-Type A or LTA) is a micro-porous aluminosilicate material that has found wide application in industry for selective sorption (Auerbach et al. 2003; Kim et al. 2016; Yin et al. 2005), molecular sieving (Auerbach et al. 2003; Yin et al. 2005), ion exchange (Auerbach et al. 2003), gas separation (Auerbach et al. 2003; Kim et al. 2016; Yin et al. 2005), and catalysis (Auerbach et al. 2003; Chen 1996; Öhlmann et al. 1991). The many uses of zeolite A, like those of other porous crystalline frameworks (e.g., metal-organic frameworks), are based on interactions between the framework itself and guest molecules introduced into its structure. There is evidence that some porous crystalline frameworks, including zeolite A, exhibit novel behaviors such as framework flexibility and the related phenomenon gate opening (Guo and Navrotsky 2018; Guo et al. 2018). Both phenomena involve structural changes that are induced by guest molecules and alter the material’s sorptive properties. Understanding the thermodynamics of such sorption-based phenomena is necessary to design useful new framework materials.

Zeolite A is composed of a framework of alternating corner-sharing SiO$_4$ and AlO$_4$ tetrahedra, which form a cubic structure of eight α cages (supercages) and eight β cages (sodalite) (Loewenstein 1954). Extra-framework cations (typically Na$^+$) located in the cages of the structure balance the net negative charge caused by the substitution of Al$^{3+}$ for Si$^{4+}$. By exchanging different cations into the structure, it is possible to modify the pore properties, structural properties, and catalytic activity of a zeolite (Armor 1998; Guo et al. 2018; Sun et al. 2016). Transition-metal-exchanged zeolites are of particular interest for properties such as variable oxidation states and multi-coordination capacity, and they exhibit exceptionally high catalytic activity for several useful redox reactions (Armor 1998; Chatterjee et al. 1992). This paper deals with several ion-exchanged versions of zeolite A, which we will refer to using abbreviations of the form M-A, where M is the extra-framework cation (e.g., Na-A and Zn-A).

Thermodynamic studies on porous frameworks both with and without guest molecules provide crucial information about the energetics of confinement. The present work is part of a collaborative investigation of the thermodynamics of strategically chosen synthetic zeolites with controlled variations in structure, cation content, and sorbate content (Guo and Navrotsky 2018; Guo et al. 2018, 2019; Sun et al. 2016; Wu and Navrotsky 2016; Yang and Navrotsky 2000).

THE FLEXIBILITY TRANSITION IN ZEOLITE A

In addition to their industrial importance, the zeolites in this study are of interest for exhibiting a “gate opening” or “flexibility” transition when partially dehydrated, as described by Guo and coworkers (Guo and Navrotsky 2018; Guo et al. 2018). The presence of the transition defines three distinct hydration regimes: (1) a low-hydration phase (which exists from ~0–20% hydration); (2) a transition or “two-phase” region (~20–50% hydration, or roughly 0.2–0.6 mol H$_2$O per Al$_2$SiO$_4$ tetrahedron); and (3) a high-hydration phase (above ~50% hydration). (Note that “100%” or “full” hydration is often defined somewhat arbitrarily as equilibrated with ambient conditions, and we...