Chabazite: Energetics of hydration, enthalpy of formation, and effect of cations on stability

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ABSTRACT

The stability of synthetic cation-exchanged zeolites having the chabazite framework (CHA) and their cation-water interaction were studied using high-temperature reaction calorimetry. Four cations (K, Na, Li, and Ca) were exchanged into CHA. The enthalpies of formation were determined for all samples, and the partial molar enthalpy of hydration was measured by varying the water content of one Ca-CHA.

The enthalpy of formation depends strongly on the exchanged cation, becoming more exothermic in the order Ca, Li, Na, K. The integral hydration enthalpy does not depend strongly on the nature of the cation, but becomes slightly less exothermic with increasing aluminum content. For the one Ca-CHA studied in detail, the average enthalpy of hydration is –34.6 ± 1.2 kJ/mol relative to liquid water. A quadratic fit to the transposed temperature drop data gives \( \Delta h_{H_2O} = -52.97 (±4.74) + 2.94 (±0.68) n \) (kJ/mol), where \( \Delta h_{H_2O} \) is the partial molar enthalpy of hydration and \( n \) is the number of water molecules per 24 oxygen formula.

Although these observations are mostly qualitative and both kinetic and thermodynamic factors are probably involved, it is obvious that the cations play an important role in zeolite stability.

Many studies have shown that there are two major types of water in the zeolite cage: one has strong interaction and may be associated with the hydration of the extra-framework cations, and the other has little interaction with the zeolite and may simply fill the voids. For example, leonhardtite (CaAl2Si4O12·3.5H2O) shows significant differences in the enthalpy of hydration associated with H2O molecules in different positions (Kiseleva et al. 1996a). Although the loss of one mole of H2O in the initial stage of dehydration has a near zero enthalpy of interaction (6.4 ± 9.2 kJ/mol, relative to liquid water), removal of the water molecules from the Ca coordination sphere requires 40.2 ± 2 kJ/mol. Carey and Bish (1996, 1997) studied the clinoptilolite-H2O equilibrium and measured the partial molar enthalpies of hydration. The hydration enthalpies became less exothermic in the sequence Ca, Na, K at low water content, but converged to similar values at saturation.

Water having weak interaction with the framework was also observed in cordierite, Mg2AlSiO18·nH2O. Cordierite absorbs water on a well-defined crystallographic site without hydration of any cations. Its enthalpy of hydration (relative to liquid H2O) is zero over a range of water contents (Carey and Navrotsky 1992). This implies that the molecular environment of H2O in cordierite is energetically similar to that of H2O in liquid water.

INTRODUCTION

Zeolites \( [(\text{Li,Na,K})(\text{Mg,Ca,}\text{Sr,Ba})(\text{Al}(\alpha+2\delta)\text{Si}n-(\alpha+2\delta)\text{O}2n)·m\text{H}2\text{O})] \) are hydrated framework aluminosilicates that incorporate molecular H2O in structural pores. The interaction of water with cations and with the framework in a zeolite cage is important in a variety of applications, including pollution abatement, catalysis, cation exchange, and gas separation. Thermodynamic data are essential to evaluate zeolite stability and characterize the hydration process. Zeolite minerals occur in several near-surface geologic settings. Thermodynamic data help determine their paragenesis.

Extra-framework cations and the Al/Si ratio affect stability and hydration of zeolites. Barrer and Langley (1958) and Barrer and Baynham (1956) found that the thermal stability (temperature at which the zeolite decomposes on heating at a constant rate) of chabazite increased in the order Li, Na, K, Rb, Cs, and water retentivity increased in the order Rb, K, Na, Li. Cartlidge and Meier (1984) observed that Na-exchanged natural chabazite showed solid-state transformation to a sodalite structure at 600 °C in a dry nitrogen atmosphere, whereas K-exchanged natural chabazite did not transform. According to their Rietveld refinement, Na and K occupied different positions and coordination states with H2O molecules and framework O atoms.

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American Mineralogist, Volume 84, pages 1870–1882, 1999

0003-004X/99/1112–1870$05.00

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