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Short Communication

Thermochemistry of proton containing borosilicate, aluminosilicate and gallosilicate zeolite beta

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ABSTRACT

The thermochemistry of proton containing borosilicate, aluminosilicate and gallosilicate zeolites with beta topology (B-BEA, Al-BEA and Ga-BEA) is described. Thermogravimetry and differential scanning calorimetry on these materials indicate the substitution of Al by Ga or B in the beta framework reduces the decomposition temperature. Water adsorption calorimetry directly measured the hydration enthalpies of these samples. B-BEA and Ga-BEA have less exothermic hydration enthalpies than Al-BEA. High temperature oxide melt solution calorimetry was performed to derive the formation enthalpies of hydrated samples (8.9–18.8 kJ/mol relative to oxides on TO_2 molar basis). The formation enthalpies of dehydrated phases (33.2–55.1 kJ/mol relative to oxides on TO_2 molar basis) were calculated from the formation enthalpies of hydrated phases and the hydration enthalpy.

1. Introduction

Zeolite beta, first reported by Mobil Oil in 1967 [1], is a tri-directional large-pore zeolite with 12 member rings. In 1988, Treacy and Newsam [2–4] determined its structure to be an intergrowth of two polymorphs, A (tetragonal, $P4_122$, $a = 12.632$ Å and $c = 26.186$ Å) and B (monoclinic, $C2/c$, $a = 17.896$ Å, $b = 17.920$ Å, $c = 14.328$ Å, and $\beta = 114.8°$), in a ratio of 60:40. At the same time, another structure, C (tetragonal, $P4_2/mmc$, $a = 12.769$ Å and $c = 12.977$ Å) was proposed by Newsam et al. [3]. The structure differences among these three polymorphs come from different stacking of the same building layer. Due to its 3D large pore system and high acidity, zeolite beta has drawn considerable attention as a promising catalyst for various chemical reactions, such as hydrocarbon cracking [5,6], disproportionation [7], hydroisomerization of *n*-alkanes [8], alkylation of aromatics [9.10], and methanol conversion [11].

The isomorphous substitution of Al^{3+} or Si^{4+} in zeolite frameworks by different bivalent (Be), trivalent (B, Ga, and Fe) and tetravalent (Ge) elements with different charge/radius ratios is an effective way to vary zeolite acidity and catalytic activity/selectivity [12]. It is also a viable approach to develop novel topologies [13–18]. For examples, the substitution of Al and Si by Ge in zeolite beta has stabilized structure C [17,18]; the incorporation of Ga into several zeolite framework materials, e.g., MAZ [19], NAT [20], ANA [21] etc., has changed the cell parameters, the energetics of the frameworks, and thus the properties of the structures.

Knowledge of thermodynamics of different zeolite structures is essential for understanding the driving force for synthesis, the energy difference and relative stability among different frameworks, and the mechanisms in the assembly of these materials. For instance, the small formation enthalpy difference between high/pure silica zeolites and α-quartz (6.8–14.4 kJ/mol), and silica zeolites and silica glass (0–7 kJ/mol) provides little thermodynamic driving force for inter-conversions among these structures [22,23]. One of the most important interactions in zeolite materials is between the zeolite and water, which directly affects the stability of the zeolite under ambient conditions. Therefore, the energy of dehydration or water adsorption is needed to understand the energetics of zeolite systems and their applications in processes involving H_2O, such as gas separation [24–26] and waste water treatment [27].

In this study, using oxide melt solution calorimetry, we explored the energetics of zeolite beta with B and Ga substitution, and compared them with aluminosilicate analogous. The thermochemical data, together with X-ray diffraction (XRD), nuclear magnetic resonance (NMR), N_2 adsorption and FTIR, address the effect of element substitution on zeolite stability, and provide useful information for possible industrial applications. In our previous work, we studied the energetics of a series of aluminosilicate zeolite beta phases with alkali and alkaline earth cations [28,29]. Thus it is the purpose of this paper to explore the energetics of borosilicate, aluminosilicate and gallosilicate zeolite beta with proton cations, to compare their behavior with that of aluminosilicate zeolite beta phases, and to seek some general trends that enable prediction of the stability of other zeolites in the beta family.

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2. Experimental methods

2.1. Synthesis

B-BEA and Ga-BEA were prepared using a hydrothermal method followed by calcination at 550 °C for 1 day. The details of the procedure are published elsewhere [30,31]. Al-BEA sodium form was obtained from Tricat Zeolites GmbH (Bitterfeld-Wolfen, Germany). Al-BEA proton form was prepared by ion-exchanging sodium with ammonium and then annealing the ammonium form at 550 °C for 1 day. All samples were allowed to rehydrate in a large container with a saturated $Ca(NO_3)_2$ solution for at least 1 day.

2.2. Characterization

The zeolite beta framework was confirmed by powder XRD on a Bruker D8 Advance X-ray diffractiometer with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. All samples were scanned from 10° to 50° 2θ with a step size of 0.02° and a dwell time of 0.5 s/step. Chemical composition of B-BEA was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Galbraith Laboratories, Knoxville, TN). For Al-BEA and Ga-BEA, the chemical composition analysis was carried out on a Cameca SX-100 electron microprobe operating at 15 kV and 10 nA. The total water content of each sample was determined by weighing samples before and after calcination at 1200 °C for more than 6 h. The coordination environments of B, Al and Ga were investigated with solid state NMR spectroscopy on a Bruker Avance 500 WB system (Bruker BioSpin Ltd., Billerica, MA) equipped with an 11.7 Tesla magnet. A 4 mm CPMAS Bruker probe was used for ^{11}B and ^{71}Ga measurement, while a 2.5 mm one was used for ^{27}Al. The hydroxyl groups and acidity of the samples were characterized by FTIR on a Bruker EQUINOX 55 TGA-IR spectrometer (Bruker Optics, Billerica, MA).

2.3. Calorimetry

Thermal stability of these materials was investigated via TG-DSC measurements on a Netzsch STA 449 instrument (Netzsch Instruments, Burlington, MA). The differential heats of water adsorption on zeolites at room temperature were measured on an apparatus combining a Micromeritics ASAP 2020 surface area analyzer (Micromeritics Corp., GA, USA) and a Seraram DSC 111 Calvet microcalorimeter (Seraram Instrumentation, Caluire, France). This methodology has been described previously [32] and is now standard in the Peter A. Rock Thermochemistry Laboratory. Before the water adsorption experiment, hydrated zeolite pellets were dehydrated by heating and evacuation at 600 °C for 5 h. This process did not result in complete dehydration of the samples, but annealing at high temperature led to degradation of the zeolite. The remaining water content was determined by weight loss experiments.

Table 1
Chemical compositions of synthesized zeolites.

Sample	Molar formula on TO_2 basis	n_1[a]	n_2[b]	Si/T (T = B, Al or Ga)
B-BEA	$H_{0.0714}Na_{0.0072}B_{0.0787}Si_{0.9213}O_2$	0.73	0.10	11.7
Al-BEA	$H_{0.0654}Na_{0.0019}Al_{0.0672}Si_{0.9328}O_2$	0.74	0.16	13.9
Ga-BEA	$H_{0.0337}Na_{0.0233}Ga_{0.0549}$-$Si_{0.9430}O_2{\cdot}0.003Ga_2O_3$[c]	0.76	0.14	17.1

[a] n_1 refers to the moles of water that one mole hydrated H-BEA contains.
[b] n_2 refers to the moles of water that one mole partially dehydrated H-BEA contains.
[c] The amount of Ga_2O_3 is calculated by combining the microprobe and NMR data.

The enthalpies of hydrated samples were determined by high temperature oxide melt solution calorimetry in a Tian–Calvet twin calorimeter described in detail by Navrotsky [22,33,34]. Sample pellets (about 5 mg each) were dropped from room temperature into the $2PbO–B_2O_3$ molten solvent at 700 °C. A flow of oxygen gas at 40 ml/min was used to flush the headspace in the calorimeter to remove the evolved water vapor. This methodology has been used extensively for other zeolites [22,29,31,35].

3. Results and discussion

Comparison of the powder XRD patterns of all samples in this study (Supplementary Fig. 1) with those in the literature [4] reveals that they are highly crystalline and no reflections other than

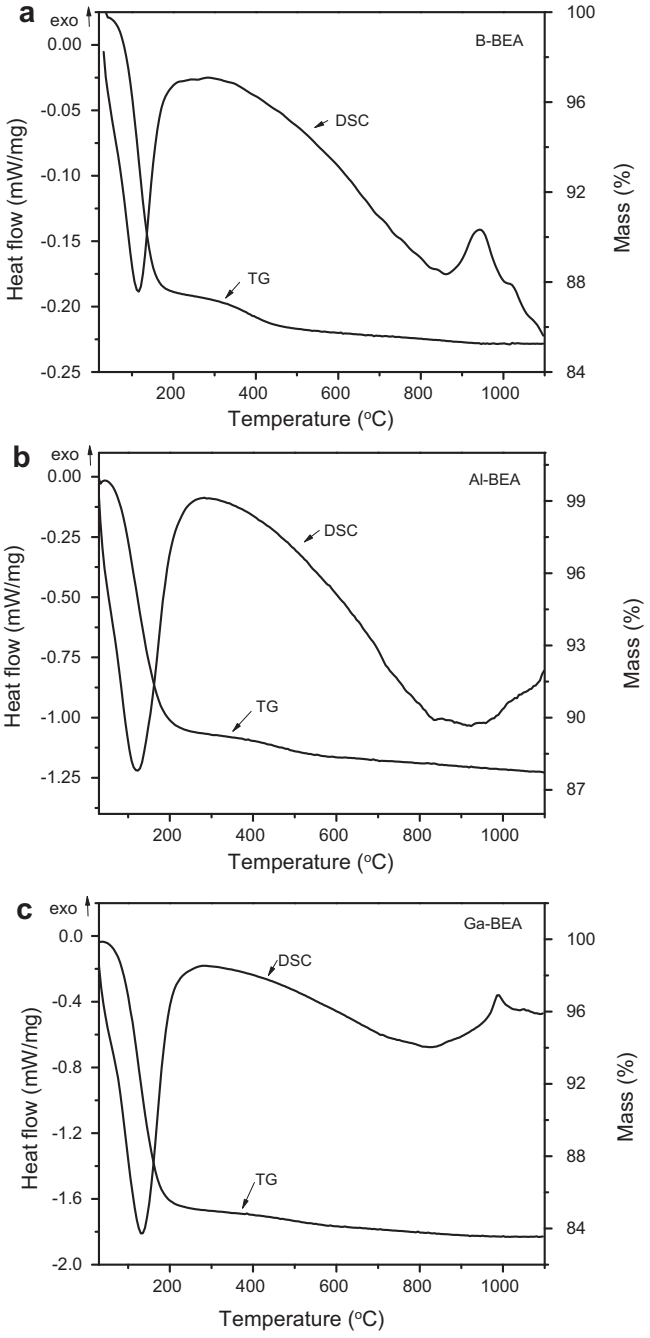

Fig. 1. TG-DSC traces of B-BEA, Al-BEA, and Ga-BEA.