



Thermochemistry of formation of ion exchanged zeolite RHO

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ABSTRACT

Zeolites Na,Cs-RHO, Cd,Cs-RHO, and Li,NH₄-RHO were synthesized in an aqueous ion-exchange media and studied by powder X-ray diffraction. Their thermochemistry was investigated by differential scanning calorimetry and high temperature oxide melt solution calorimetry. The formation enthalpy from binary oxide components of hydrated zeolite RHO varies linearly with the average ionic potential (Z/r) of the extra-framework cations and ranges from -34.46 ± 0.52 kJ/mol for Na,Cs-RHO to -16.75 ± 0.57 kJ/mol for Cd,Cs-RHO. The formation enthalpies for dehydrated zeolite RHO range from -25.49 ± 0.64 kJ/mol for Na,Cs-RHO to $+4.12 \pm 0.99$ kJ/mol for Li,NH₄-RHO. These values do not vary linearly with average ionic potential but do show a linear relationship with distortion parameter.

1. Introduction

Zeolite RHO (Si/Al = 3) is composed of truncated cubo-octahedra or secondary building units in a body centered cubic structure with a negatively charged aluminosilicate framework and positive extra-framework cations [1–6]. The charge balancing extra-framework cations are preferentially accommodated by three sites: the single 8-ring (8R), double 8-ring (D8R) and single 6-ring (S6R) [7–12]. Variable amounts of extra-framework cations and H₂O molecules occupy the pores and channels which are very responsive to environmental changes [13]. Cation relocation has been observed in various zeolite RHOs, where cations move from 8R to either 6R or D8R to make the pores more accessible while maintaining the RHO framework [14–16]. Both good uptake of CO₂ and high CO₂/CH₄ selectivity over a wide pressure range can be obtained by selective cations [2,9]. The exceptional flexibility with controllable shape and size of pore openings provides zeolite RHO superior molecular sieving ability and shape/size selectivity as a catalyst, support, or sorbent [1,7,11].

Zeolite RHO exhibits structural distortions and phase transformations induced by the adsorption of water. Structural studies have shown that the hydrated Im $\bar{3}$ m structure can undergo a large distortion and loss of symmetry to form the noncentrosymmetric I $\bar{4}$ 3m form upon dehydration [17–19]. A conformational change of 8R from circular (3.6 Å) to elliptical (2.9 Å) occurs with a contraction of the unit cell, driven by relocation of cations and loss of water molecules [16,20]. The distortion and shape of D8R vary with hydration state [15,18]. Parise et al. proposed a parameter Δ , defined as one half of the difference of

major and minor axes, to describe the distortion or ellipticity, which varies from 0 to ~ 2.49 Å depending on the type and distribution of extra-framework cations [21–23].

However, the thermodynamic properties of zeolite RHO and their dependence on cation content, hydration, and distortion are not known. Our previous calorimetric studies [24–29], of the energetics of a number of zeolites with other framework types have shown the enthalpies of formation from oxide components to be closely correlated with the average ionic potential of guest cations (Z/r , defined as $\sum X_i(Z/r)/\sum X_i$), where X is mole fraction, Z is charge, and r is ionic radius [30]. The present work extends such studies to zeolite RHO, with special attention to the inherent large flexibility of the framework.

2. Experimental methods

2.1. Materials

These RHO samples are part of a suite of materials originating from the Dr. David R. Corbin Zeolite Library at the Center for Environmentally Beneficial Catalysis at the University of Kansas, Lawrence KS. Na,Cs-RHO, the parent material used for cation-exchange was prepared by a modification of the method described by Robson [31]. Cd,Cs-RHO was prepared using standard ion exchange in aqueous 10% Cd(NO₃)₂ at 90 °C. Li,NH₄-RHO was prepared by NH₄⁺ exchange followed by Li⁺ exchange of Na,Cs-RHO. Na,Cs-RHO was first prepared and then exchanged six times (1 h each) in aqueous 10% NH₄NO₃ (10 mL/g) at 90 °C to give NH₄-RHO. The NH₄-RHO was exchanged

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twice (24 h each) in aqueous 0.4 M LiNO₃ (10 mL/g) at 25 °C. Then the sample was exchanged three additional times (24 h each) in aqueous 0.4 M LiNO₃ (10 mL/g) at 90 °C to give Li,NH₄-RHO. Li,H-RHO was obtained by heating Li,NH₄-RHO at 400 °C overnight under vacuum.

Chemical analyses gave a unit cell composition of Na_{7.1}Cs_{3.8}Al_{11.5}Si_{36.5}O₉₆, Cd_{3.6}Cs_{4.8}Na_{0.4}Al_{12.0}Si_{36.0}O₉₆, Li_{4.98}(NH₄)_{5.65}Cs_{0.08}Na_{0.02}Al_{11.9}Si_{36.1}O₉₆ respectively and they could be rewritten as Na_{0.15}Cs_{0.08}Al_{0.24}Si_{0.76}O₂, Cd_{0.08}Cs_{0.1}Al_{0.25}Si_{0.75}O₂, Li_{0.10}(NH₄)_{0.12}Al_{0.25}Si_{0.75}O₂ on a TO₂ basis. These samples were prepared in earlier studies [1,32]. The dehydrated sample was obtained under vacuum (< 10⁻³ torr) overnight at 400 °C for Na,Cs-RHO and Cd,Cs-RHO while at 250 °C for Li,NH₄-RHO to reduce deammonation.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 Advance diffractometer (Bruker, Madison, WI) operated with Cu Kα radiation (λ = 1.54 Å). The data were collected in the 2θ range of 5–70°, with a step size of 0.02° and dwell time of 3 s per step. Thermogravimetry and differential scanning calorimetry (TG-DSC) were performed using a Netzsch STA 449 instrument. In each measurement, ~15 mg of sample was hand-pressed into a pellet, placed in a Pt crucible, and heated from ambient temperature to 1000 °C (10 °C/min) under argon flow (40 mL/min). The water content of Na,Cs-RHO and Cd,Cs-RHO was obtained from the corresponding weight loss while it was computed by reducing ammonium content from the weight loss according to the stoichiometric composition of Li,NH₄-RHO. Thermal gravimetric mass spectrometry (TG-MS) was performed using Netzsch STA 449 coupled with a Micromeritics Cirrus 2 quadrupole mass spectrometer. About 20 mg of sample was placed in a platinum crucible and subjected to a heating regime in TG from 30 to 1000 °C at 10 °C/min in argon flow (40 mL/min). The mass of the sample is monitored while gases evolved during heating were introduced into the ionization chamber of mass spectrometer. The TG and MS signals were corrected by the reference baselines from runs with empty crucibles under the same experimental conditions. Evolved gases (H₂O, *m/z* = 18, NH₃, *m/z* = 17) were analyzed by mass spectrometry. ATR-FTIR spectra at 100–4000 cm⁻¹ were recorded using a Bruker VERTEX 70 IR spectrometer with correction from an initial background collected before sampling to subtract the contribution from the ambient environment.

2.3. Calorimetry

High temperature oxide melt solution calorimetry experiments were carried out using a Tian-Calvet twin calorimeter described previously [33,34]. Fully hydrated sample pellets (~5 mg) were dropped from ambient temperature into the calorimeter containing the solvent, molten lead borate (2PbO·B₂O₃), in a platinum crucible at 704 °C. All experiments were flushed with air flow (90 mL/min) to purge the evolved water vapor generated by dissolution of samples. The measurement was repeated at least eight times on each sample. Calibration was done against the heat content of α-alumina (Alfa Aesar, 99.997%). This methodology is similar to that used for other zeolites in our laboratory [24–29].

3. Results and discussion

Table 1 summarizes chemical compositions and crystallographic data. The lattice parameters obtained by whole pattern fitting, are listed in Table 1. The refinement was initiated using the starting structural parameters previously reported [1,11] and accurate lattice parameters were achieved after minimizing the residual error of fit.

The XRD patterns of dehydrated and hydrated zeolite RHO are shown in Fig. 1. All the dehydrated forms adopt the noncentrosymmetric structure *I*43m while the hydrated forms of Na,Cs-RHO and Li,NH₄-RHO adopt the centrosymmetric structure *Im*3m except for

hydrated Cd,Cs-RHO. The peaks of zeolite RHO after dehydration have a shift to higher angle. In Na,Cs-RHO, the (110), (211) and (422) peak intensity increases significantly while the (310) peak disappears upon dehydration and the relative intensities change from I₄₁₁: I₄₂₀ ≈ 2:1 in the hydrated state to I₄₁₁: I₄₂₀ ≈ 3:4 in the dehydrated state. This is possibly due to the loss of water coordination, deformation of framework, and relocation of extra-framework cations. The loss of water molecules coordinated to Na⁺ ions at S6R make the (310) and (411) reflections more variable than (110) (211) (420) and (422) upon dehydration [18]. The decreased (420)/(422) intensity ratio might additionally arise from the increased distortion and symmetry change of the framework. In Cd,Cs-RHO, similar phenomena are observed except that the intensity of (411) is still stronger than (420). The smaller increase of diffracted intensity (420) with cation relocation might be due to fewer occupied cation sites by substituting divalent Cd cations for Na⁺. Li,NH₄-RHO exhibits the biggest intensity difference before and after dehydration. A possibly non-uniform distribution of NH₄ groups in the 8R of Li,NH₄-RHO framework may produce doubling of the unit cell [1] but only single peaks are seen after degassing, possibly resulting from more uniformly distributed remaining NH₄ upon dehydration. There is little or no deammonation under the degassing condition as confirmed by FTIR (see Fig. S1 in supporting info). The loss of water and increased framework distortion make both the (211) and (420) peaks more variable than (110) with a full occupancy of all S6R sites by Li. Li,NH₄-RHO shows the largest unit cell shrinkage on dehydration followed by Na,Cs-RHO and Cd,Cs-RHO.

TG-DSC traces are shown in Fig. 2. A broad endothermic peak is observed with a large weight loss at 25–500 °C, which corresponds to dehydration for Na,Cs-RHO and Cd,Cs-RHO but also includes deammonation for Li,NH₄-RHO. In Na,Cs-RHO, dehydration upon heating from 25 to 100 °C is due to the loss of loosely bound water, while a decreasing rate of weight change between 100 and 400 °C represents the loss of coordinated water. The dehydrated (activated) phase of Na,Cs-RHO persists until partially transition to dense phases (possibly sodium aluminum silicate and pollucite) as shown by two small exothermic peaks at 900–1000 °C. These exotherms show that the zeolites are energetically metastable with respect to their dense phases, as has been seen for several other zeolites [26,29]. In Cd,Cs-RHO, a similar dehydration process occurs except that there is one endothermic peak around 400 °C which is possibly associated with a phase transition from the acentric to centric structure and a relocation of Cd²⁺ from the 8R to the 6R site [15]. The dehydrated zeolite persists to 800 °C until it transforms to denser phases (cadmium/cesium aluminum silicate and amorphous phase) with a large exothermic peak. Li,NH₄-RHO shows a broader dehydration process accompanied by deammonation between 25 and 400 °C. The two processes are intertwined and hard to distinguish, even by thermogravimetry accompanied by mass spectrometry (TGA-MS) shown in Fig. S2. A sharp exothermic peak at about 450 °C indicates possible phase change from the centric to acentric structure. The thermal behavior suggests that the dehydrated zeolite RHO phases have good thermal persistence to temperatures near 800 °C.

The water content of each sample was obtained from the weight loss on TG, with correction for ammonia loss in Li,NH₄-RHO. The dehydration enthalpies of zeolite RHO relative to liquid water (ΔH_{dhy,l}) were calculated using integral enthalpy data of water absorption [32] with correction for water vaporization enthalpy. The Li,NH₄-RHO shows the most endothermic dehydration enthalpy (26.1 ± 0.67 kJ/mol of H₂O) with the highest water uptake, while Na,Cs-RHO presents the least endothermic value of 14.47 ± 0.59 kJ/mol of H₂O with the smallest water uptake. The number of water molecules per TO₂ unit and dehydration enthalpy for each sample are plotted versus average ionic potential of the extra-framework cations in Fig. 2D. Both the degree of hydration and dehydration enthalpy increase with increasing ionic potential. Na,Cs-RHO to Li,NH₄-RHO. The dehydration enthalpy in Fig. S3 shows a generally monotonic increase with water content.

The formation enthalpies from binary oxides were calculated by

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