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Thermodynamics of ion-exchanged and natural clinoptilolite

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ABSTRACT

Natural clinoptilolite (Cpt: $Na_{0.085}K_{0.037}Ca_{0.010}Mg_{0.020}Al_{0.182}Si_{0.818}O_2 \cdot 0.528H_2O$) from Castle Creek, Idaho, and its cation-exchanged variants (Na-Cpt, NaK-Cpt, K-Cpt, and Ca-Cpt) were studied by high-temperature calorimetry. The hydration enthalpy for all the clinoptilolites is about –30 kJ/mol H_2O (liquid water reference state) at 25 °C. The energetic stabilization effect of hydration on each clinoptilolite can be largely correlated to its hydration capacity. The higher the average ionic potential of the extra-framework cations, the larger the hydration capacity of the clinoptilolite. This trend may be attributed to the small size as well as the efficient water-cation packing of high field strength cations in the zeolite structure. The hydration properties of these clinoptilolites are compared with those previously reported in the literature. The dehydration conditions as well as the measurement direction (dehydration of the initially hydrated sample or rehydration of the dehydrated zeolites) are important factors to control to obtain consistent thermodynamic properties for hydration.

The standard enthalpy for formation of the clinoptilolites from the constituent elements at 25 °C based on two framework O atoms was obtained from the calorimetric data: –1117.57 ± 0.95 kJ/mol Cpt, –1130.05 ± 1.00 kJ/mol Na-Cpt, –1109.49 ± 1.04 kJ/mol NaK-Cpt, –1094.21 ± 1.12 kJ/mol K-Cpt, and –1153.78 ± 1.07 kJ/mol Ca-Cpt. Their molar entropy was determined by a summation method based on the thermodynamic properties of the component oxides. Thus the standard free energy based on two framework O atoms was derived: –1034.01 ± 1.05 kJ/mol Cpt, –1044.19 ± 1.10 kJ/mol Na-Cpt, –1027.26 ± 1.13 kJ/mol NaK-Cpt, –1014.89 ± 1.21 kJ/mol K-Cpt, and –1064.95 ± 1.16 kJ/mol Ca-Cpt.