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Thermodynamics of manganese oxides: Effects of particle size and hydration on oxidation-reduction equilibria among hausmannite, bixbyite, and pyrolusite

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ABSTRACT

The surface enthalpies of manganese oxide phases, hausmannite (Mn_3O_4), bixbyite (Mn_2O_3), and pyrolusite (MnO_2), were determined using high-temperature oxide melt solution calorimetry in conjunction with water adsorption calorimetry. The energy for the hydrous surface of Mn_3O_4 is 0.96 ± 0.08 J/m^2, of Mn_2O_3 is 1.29 ± 0.10 J/m^2, and of MnO_2 is 1.64 ± 0.10 J/m^2. The energy for the anhydrous surface of Mn_3O_4 is 1.62 ± 0.08 J/m^2, of Mn_2O_3 is 1.77 ± 0.10 J/m^2, and of MnO_2 is 2.05 ± 0.10 J/m^2. Supporting preliminary findings (Navrotsky et al. 2010), the spinel phase (hausmannite) has a lower surface energy than bixbyite, whereas the latter has a smaller surface energy than pyrolusite. Oxidation-reduction phase equilibria at the nanoscale are shifted to favor the phases of lower surface energy—Mn_3O_4 relative to Mn_2O_3 and Mn_2O_3 relative to MnO_2. We also report rapidly reversible structural and phase changes associated with water adsorption/desorption for the nanophase manganese oxide assemblages.

Keywords: Manganese oxides, nanomaterials, calorimetry, surface energy, surface hydration, phase equilibria