Rapidly reversible surface-mediated redox transformation of Mn_2O_3 to Mn_3O_4 triggered by water sorption at room temperature

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Facile variation of manganese oxidation state (Mn^{2+}, Mn^{3+}, Mn^{4+}) lends complexity to their phase behavior and physical and chemical properties. Thermodynamic stability of manganese oxide nanoparticles helps determine the robustness of such oxides and their behavior in soils and larger scale geochemical cycles, as well as in applications in catalysis, renewable energy, and environmental remediation. The position, in temperature - oxygen fugacity space, of oxidation - reduction (redox) equilibria among Mn_3O_4 (hausmannite), Mn_2O_3 (bixbyite) and MnO_2 (pyrolusite) are shifted at the nanoscale due to differences in surface energy. These differences depend on whether such surfaces are wet or dry. To that end, structure and energetics of nanoparticle surfaces are influenced by the surface enthalpy of the nanophase, its oxidation state, and by the extent of surface hydration, thus dry surfaces are structurally and thermodynamically distinct from hydrated surfaces.

The role of water chemisorption on dry nanoparticle Mn_2O_3 was found thermodynamically controlled and rapidly reversible as confirmed by calorimetry, X-ray diffraction, and titration for manganese average oxidation state. Surface reduction of bixbyite (Mn_2O_3) to hausmannite (Mn_3O_4) occurs in nanoparticles arising from differences in surface energies of the two phases (Mn_2O_3 and Mn_3O_4) under conditions where no such reactions are seen or expected on grounds of bulk thermodynamics in coarse-grained materials. Such findings suggests a strong coupling between surface hydration and redox reactions on nanoscale manganese oxide (and likely other metal oxide) surfaces. Such coupling may influence the progress of (bio)geochemical, planetary, environmental, and technological processes.