Energetics of ethanol and carbon dioxide adsorption on anatase, rutile, and γ-alumina nanoparticles

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ABSTRACT

Nanoparticles are widely present in the natural environment. Their surface reactivity, redox ability, and adsorption properties are related to geochemical processes. To explore the thermodynamics of interaction between nano oxides and small gas molecules, we applied gas adsorption calorimetry to investigate the energetics of ethanol and carbon dioxide adsorbed on surfaces of nanoscale anatase, rutile, and γ -alumina particles. The measured zero-coverage adsorption enthalpies per mole of gas adsorbed are -97.7, -107.3, and -84.8 kJ/mol for C₂H₅OH on anatase, rutile, and γ -Al₂O₃, respectively. The corresponding values for CO₂ adsorption are -59.4, -47.4, and -47.1 kJ/mol. The results indicate the ethanol adsorption is generally more exothermic than carbon dioxide and water adsorption. The isotherm and differential enthalpies show type II isotherms and step-wise patterns for ethanol adsorption in all three oxides. However, CO₂ adsorption shows simple continuous isotherms and energetics that suggest dominant physical adsorption occurred. The repeated adsorption cycle shows that ethanol adsorption on these nanoparticles is partially reversible at room temperature. This thermodynamic evidence indicates that ethanol and similar organics may protect mineral oxide surfaces from reaction with aqueous solutions, which may affect crystal growth, dissolution, and biomineralization.

Keywords: Thermodynamics, gas adsorption, nanoparticle, rutile, anatase, gamma-alumina