

Molecular Structure and Binding Sites of Cobalt(II) Surface Complexes on Kaolinite from X-ray Absorption Spectroscopy

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Abstract: X-ray absorption spectroscopy (XAS) was used to determine the local molecular environment of Co(II) surface complexes sorbed on three different kaolinites at ambient temperature and pressure in contact with an aqueous solution. Interatomic distances and types and numbers of backscattering atoms have been derived from analysis of the extended X-ray absorption fine structure (EXAFS). These data show that, at the lowest amounts of Co uptake on kaolinite ($0.20\text{--}0.32\ \mu\text{mol m}^{-2}$), Co is surrounded by ≈ 6 O atoms at $2.04\text{--}2.08\ \text{\AA}$ and a small number of Al or Si atoms ($N = 0.6\text{--}1.5$) at two distinct distances, $2.67\text{--}2.72\ \text{\AA}$ and $3.38\text{--}3.43\ \text{\AA}$. These results indicate that Co bonds to the kaolinite surface as octahedrally coordinated, bidentate inner-sphere mononuclear complexes at low surface coverages, confirming indirect evidence from solution studies that a fraction of sorbed Co forms strongly bound complexes on kaolinite. In addition to inner-sphere complexes identified by EXAFS spectroscopy, solution studies provide evidence for the presence of weakly bound, outer-sphere Co complexes that cannot be detected directly by EXAFS. One orientation for inner-sphere complexes indicated by XAS is bidentate bonding of Co to oxygen atoms at two Al-O-Si edge sites or an Al-O-Si and Al-OH (inner hydroxyl) edge site, i.e., corner-sharing between Co octahedra and Al and Si polyhedra. At slightly higher surface sorption densities ($0.51\text{--}0.57\ \mu\text{mol m}^{-2}$), the presence of a small number of second-neighbor Co atoms (average $N_{\text{Co}} < 1$) at $3.10\text{--}3.13\ \text{\AA}$ indicates the formation of oxy- or hydroxy-bridged, multinuclear surface complexes in addition to mononuclear complexes. At these surface coverages, Co-Co and Co-Al/Si distances derived from EXAFS are consistent with edge-sharing between Co and Al octahedra on either edges or (001) faces of the aluminol sheet in kaolinite. Multinuclear complexes form on kaolinite at low surface sorption densities equivalent to $< 5\%$ coverage by a monolayer of oxygen-ligated Co octahedra over the N_2 -BET surface area. These spectroscopic results have several implications for macroscopic modeling of metal ion uptake on kaolinite: 1) Primary binding sites on the kaolinite surface at low uptake are edge, non-bridging Al-OH inner hydroxyl sites and edge Al-O-Si bridging oxygen sites, not Si-OH sites typically assumed in sorption models; 2) specific adsorption of Co is via bidentate, inner-sphere complexation; and 3) at slightly higher uptake but still a small fraction of monolayer coverage, formation of Co multinuclear complexes, primarily edge-sharing with Al-OH octahedra, begins to dominate sorption.

Key Words: Cobalt • EXAFS • Kaolinite • Sorption • Surface complex

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