

Water and organic adsorption and structure at alumina and silica surfaces

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Vapor adsorption is an important process influencing the migration and the fate of environmental pollutants. In this study, adsorption of water vapor in addition to several organics onto single crystal α -Al₂O₃ (0001) and fused SiO₂ (amorphous) surfaces was studied with sum frequency generation, a surface-selective vibrational spectroscopy used for probing interfacial phenomena at the molecular level. Water and surface hydrophilic/hydrophobic properties play important roles for the adsorption of organics onto silica and alumina surfaces. The adsorbed organic molecules interact in different ways at the two different oxide surfaces. For example, ethylene glycol molecules weakly physisorb onto the α -Al₂O₃ (0001) surface by forming relatively weak hydrogen bonds with surface water molecules. On the silica surface, the suppression of the polarized silanol OH stretching peak indicates that these molecules form hydrogen bonds with the silanol OH groups. Water (and D₂O) adsorption and surface structure on alumina and silica surfaces will also be discussed.

Amino acid – mineral interaction: Experimental NMR and computational MD investigation of glutamate-intercalated hydrotalcite

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The interaction of biomolecules with minerals at the molecular level is difficult to study and poorly understood, but computational molecular dynamics (MD) modeling combined with NMR spectroscopy and other experimental methods can provide important and novel insight at this level. We describe here such results for the interaction of the amino acid glutamate with the layered double hydroxide (LDH) phase hydrotalcite [(Mg₂Al)(OH)₆A⁺•nH₂O]. Amino acids are anions at normal pHs and interact strongly with the positively charged interlayers and surfaces of LDHs, which are common in many low-temperature geochemical environments.

The results show that glutamate does not crosslink (form covalent bonds) with the hydrotalcite but is associated with it by electrostatic interactions and H-bonding. The pH dependences of the ¹³C NMR chemical shifts and protonation state (total charge) of the glutamate in the hydrotalcite interlayer and on the surface parallel those in bulk aqueous solution. MD modeling of glutamate(1-) and glutamate(2-) intercalated in and adsorbed on hydrotalcite shows good agreement with experimental interlayer spacings and interaction of both the carboxyl and amine groups of the glutamate with the LDH. Deprotonated carboxyl groups dominate the glutamate adsorption and pillaring, and for glutamate(2-), amino groups are additional strong H-bond acceptors from the LDH surface. Glutamate diffusional mobility at the surface is nearly an order of magnitude greater than in the interlayers, but it is six times smaller than in bulk aqueous glutamate solutions.

¹H-¹³C CP-MAS
NMR spectrum
of ¹³C enriched
glutamate-
intercalated LDH.

