SAND2011-4389C

Trends in Binding Phenomena of Small Organic Molecules and CW Simulants to Selected Materials

Dr. Margaret E. Welk, Dr. Jeff Greathouse
Sandia National Laboratories

We have employed a series of simulations and practical experiments to understand the interactions of C1-3 alcohols and thiols as well as CWA simulants DMMP and 2-CEES with alumina, iron oxide, activated carbon and magnesium-aluminum hydrotalcite clay. Classical molecular dynamics simulations were used to investigate the interaction of methyl, ethyl, and n-n-propyl alcohols and thiols with the hydroxylated basal surfaces of aluminum hydroxide and iron oxyhydroxide, as well as a model graphite surface. Adsorption enthalpies obtained from simulations at infinite adsorbate dilution show that adsorption is greatly favored on the hydroxylated surfaces compared to the graphite surface, with the ethyl molecules adsorbing most favorably. In general, alcohols adsorb more strongly than thiols on the hydroxylated surfaces, while the reverse is true on the graphite surface. Monolayer surface densities decreased with increasing molecule size. The hydroxylated surfaces were found to be amphoteric with respect to both alcohol and thiol adsorption, and primary adsorption sites facilitate hydrogen bonding between the adsorbate and several surface hydroxyl groups. Alcohols and thiols adsorb at much larger distances to the graphite surface, resulting in the smaller adsorption enthalpies.

Pulsed chemisorption analysis was used to create adsorption isotherms and determine heats of desorption for comparison to simulation results. A Micromeritics Autochem II 2920 combined with a surface area analyzer was used in pulse chemisorption and temperature programmed desorption mode over five different ramp rates to obtain heats of desorption of the alcohols, DMMP and 2-CEES on alumina, activated carbon, and magnesium/aluminum hydrotalcite clay. In good agreement with simulation, ethanol interacted more strongly with the alumina than either methanol or propanol. The interactions between all the C1-C3 alcohols and alumina were stronger than the interactions between the alcohols and activated carbon owing to the presence of hydrogen bonding sites on the alumina surface. DMMP was found to adsorb slightly more strongly to activated carbon than any of the C1-C3 alcohols.