

Advances in Fundamental Materials Research

Advances in Hypersorbent Materials for Detection and Protection Applications

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The main purpose of sorbent materials in gas phase applications is to remove and concentrate airborne chemicals of interest to the sorbent phase. There are two main sorbent classes which act either through physisorption or chemisorption of target chemicals, where the former produces reversible binding and the latter irreversible binding. In this work we emphasize the further development of sorbent materials for physisorption applications.

The sorbent materials we will describe exhibit extreme hydrogen-bond (HB) acidic properties to allow the full spectrum of van der Waal forces and in particular extreme Lewis acid-base or HB interactions. The binding or gas partition coefficient to these sorbents for many polar chemicals of interest is in excess of 10^6 allowing them to be referred to as hypersorbents. In addition, the degree and number/density of molecular interactions involved allow infrared (IR) spectroscopic techniques to be used to study reversible binding sites, and to facilitate IR spectroscopic detection of chemical species at trace levels. Alcohol and phenolic HB acidic sorbents with electron withdrawing fluorine atoms acting on the hydroxyl moiety have been previously developed at the U.S. Naval Research Laboratory and by other researchers to augment HB acidity to target complementary HB basicity of a wide range of hazardous target chemicals. Although these interactions have been studied in some detail and a wide range of related HB acidic sorbents have been developed, a significant limitation with them to date has been the propensity for sorbent self-association. This intermolecular bonding between sorbent molecules limits sorbate access to active HB acid sites in the sorbent, decreasing the overall efficacy of the sorbent.

In this current work our aim has been to develop improved HB acidic sorbent structures, activated by fluorine chemistries, which minimize undesired sorbent self-association. By significantly freeing up sorbent HB acid sites we offer the potential for a leap forward in sorbent performance by improved sorptivity for target chemicals at trace levels, sorption kinetics and capacity. These improved hypersorbents are expected to provide physicochemical properties suitable for a wide range of applications including analyte collection, chromatography separation, transducer sensing, and protection applications employing sorbents as filtration media. A series of new HB acidic sorbents have been developed and characterized with techniques such as nuclear magnetic resonance and mass spectrometry to confirm sorbent structures. The sorbent-sorbate interactions have then been tested by coating onto an attenuated total reflection (ATR) crystal used with a Fourier transform infrared (FTIR) spectrometer. Differential IR spectra before and during vapor exposure help elucidate sorbent-vapor interactions. Additional characterization has been performed with quartz crystal microbalance (QCM) gravimetry to quantify sorption kinetics and gas partitions. Finally, inverse gas chromatography (IGC) has been used to develop gas-sorbent solvation equations from a series of empirically measured gas-sorbent partition coefficients. The solvation equations produced help quantify sorbent properties of polarizability, dipolarity, HB basicity, HB acidity, and dispersion/cavity effects and allow gas-sorbent gas partitions to be predicted for a wide range of hazardous chemicals.

This work was sponsored by core NRL research funding with funds administered by ONR.