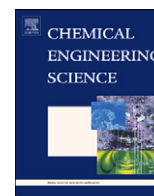




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Functionalized organosilicate materials for irritant gas removal

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ABSTRACT

Organosilicate materials functionalized through post-synthesis grafting have been evaluated for their potential to remove irritant gases. Organosilicate scaffolds were synthesized through a technique combining surfactant-templating and phase separation to produce a macro-textured scaffold with a combination of micro- and mesopores. This structure facilitates diffusion through the sorbent material providing enhanced access to the available surface area. Post-synthesis grafting was used to incorporate amine and isocyanate groups on the surfaces of the pore walls in an attempt to modify the binding and reactive character of the materials. These modified materials were compared to the unmodified organosilicate scaffold. The removal of irritant gases including ammonia, sulfur dioxide, cyanogen chloride, and octane was evaluated for the materials variants. Results have been compared to the removal of the gases by carbons as well as other materials reported in recent literature.

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1. Introduction

Traditional air purification materials often rely on porous carbons such as activated carbon or activated charcoal (Carey, 1998). Through modification of these types of carbon materials, functional moieties can be combined with high surface area and adsorptive properties to provide air purification materials with improved characteristics or novel function (Bashkova and Bandosz, 2009; Seredych et al., 2010). Ongoing efforts seek to improve the performance of carbon materials in air purification applications as well as to provide alternatives to these materials (Bae et al., 2010; Glover et al., 2011; Mu et al., 2010; Mulfort et al., 2010; Yazaydin et al., 2009). Here, we seek to demonstrate the potential of porous organosilicate materials to provide the type of functionality desired in new adsorptive and reactive sorbents for air purification applications.

Periodic mesoporous organosilicas (PMOs) (Asefa et al., 1999; Inagaki et al., 1999; Melde et al., 1999; Yohsina-Ishii et al., 1999)

Abbreviations: PMOs, Periodic mesoporous organosilicas; TIC, Toxic Industrial Chemical; TIM, Toxic Industrial Material; APS, 3-aminopropyltrimethoxysilane; ICS, 3-isocyanatopropyltriethoxysilane; BTE, 1,2-bis(trimethoxysilyl)ethane; TEDA, triethylenediamine; CK, cyanogen chloride; E50, ethane-bridged organosilica sorbent; E50-A, E50 functionalized with APS; E50-I, E50 functionalized with ICS

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combine organic and inorganic components mixed at the molecular scale with the ordered porosity of surfactant-templated mesoporous silicates (Hatton et al., 2005; Hoffmann et al., 2006a). During synthesis polysilsesquioxane precursors are condensed around surfactant micelles, which act as a template for the structure and organization of the pores (Burleigh et al., 2001; Goto and Inagaki, 2002; Kresge et al., 1992). The silica component of these materials provides the structural rigidity required to employ surfactant templating methods while the organic groups provide characteristics normally associated with organic polymers. The mesoporous nature of PMOs can limit their applicability when flow of targets through the materials is desired as in, for example, chromatography or filtration applications. One approach to address this problem is to incorporate hierarchical structure into the sorbents including both macro- (> 50 nm) and meso-scale (2–50 nm) morphology (Brandhuber et al., 2006; Johnson et al., 2010a; Johnson et al., 2010b; Melde et al., 2010; Nakanishi, 1997; Nakanishi et al., 2004). The macropores provide improved flow through the sorbents and enhanced access to the mesopore volume which is advantageous to diffusion dependent applications.

Porous organosilicates have been utilized in a wide range of applications from catalysis to sensing (Hoffmann et al., 2006b; Melde et al., 2008; Weitkamp et al., 2001). They have also been applied to the capture and/or detection of gases (Jansat et al., 2007; Palaniappan et al., 2006a; Palaniappan et al., 2008a; Palaniappan et al., 2008b; Palaniappan et al., 2006b; Yulianto et al., 2009). Selectivity in the materials has been altered through

the introduction of active groups providing discrimination of hydrocarbons and alcohols (Palaniappan et al., 2006b) and coordinated metals have been used for detection of nitric oxide (Palaniappan et al., 2008a; Palaniappan et al., 2008b) and carbon monoxide (Jansat et al., 2007). Alteration of the bridging groups in organosilicates has also been shown to impact the binding characteristics of the sorbents for gases. (Johnson et al., 2011; Yuliarto et al., 2009).

We have previously reported on our efforts directed at optimizing the characteristics of organosilicate materials for capture of nitroenergetic (Johnson et al., 2008; Johnson et al., 2010a), hydrocarbon (Johnson et al., 2011), and organophosphate targets (Johnson et al., 2010b). Those efforts focused on the development of a scaffold with high binding capacity and selectivity for the targets through alteration of the bridging groups comprising the pore walls. Here, we have taken a different approach in that a simple scaffold was utilized and alterations to the characteristics of that scaffold were achieved through post-synthesis modification. While organic functionalities can be incorporated in high amounts by one-step co-condensation of silanes during synthesis, this can significantly affect the final pore structure of a product (Hoffmann et al., 2006b). Post-synthesis grafting also increases the likelihood that pendant functional groups are located on the surface. This study details the impact of post-synthesis grafting on the interaction of the organosilicate scaffold with the irritant gases ammonia, octane, sulfur dioxide, and cyanogen chloride. These targets were selected as a result of the 2009 document released by the Toxic Industrial Chemical/Toxic Industrial Material (TIC/TIM) Task Force (Force, 2009), which focuses on inhalation hazards in an operational environment and provides a list of compounds prioritized based on toxic hazard and the likelihood of an encounter.

2. Experimental

2.1. Reagents

3-Aminopropyltrimethoxysilane (APS), 3-isocyanatopropyltriethoxysilane (ICS), and 1,2-bis(trimethoxysilyl)ethane (BTE) were obtained from Gelest, Inc. (Tullytown, PA). Pluronic®P123 was generously donated by BASF. Dichloromethane ($\geq 99.5\%$), magnesium turnings (98%), and mesitylene (1,3,5-trimethylbenzene or TMB) were purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were used as received. Water was deionized to 18.2 M Ω cm using a Millipore Milli Q UV-Plus water purification system.

2.2. Materials synthesis and grafting

Our preparation method for the materials using Pluronic®P123 in acidic media has been described elsewhere (Melde et al., 2010; Nakanishi et al., 2004). Briefly, 1.9 g P123 and 0.5 g TMB were dissolved in 6.07 g, 0.1 M HNO₃ with stirring at $\sim 60^\circ\text{C}$. The solution was allowed to cool to room temperature and silane precursor (2.12 g BTE) was added drop-wise. The reaction mixture was stirred until homogeneous and then transferred to a culture tube, which was sealed tightly and heated at 60°C overnight. The tube was unsealed and heated at 60°C for 2 d, and then 80°C for 2 d. The product in the form of a white monolith was refluxed three times in 1 M hydrochloric acid in ethanol for at least 12 h to extract the surfactant, a process that resulted in crushing the monolith to a powder. The powder was collected by suction filtration, rinsed with ethanol and water, and dried at 110°C . Functional groups were incorporated on the surface of the organosilicate material (E50) through post-synthetic grafting. Sorbent material was dried at 110°C and added to a solution of

either the APS (E50-A) or the ICS (E50-I) precursor in 200 mL toluene to achieve a final concentration of 0.6 mol precursor per gram sorbent. The mixture was refluxed for 18 h. Grafted material was collected by vacuum filtration, washed with toluene, and dried at 110°C .

BPL activated carbon (12×30 mesh) impregnated with 5% (nominal) zinc oxide by weight was provided by Calgon Carbon Corporation. Triethylenediamine (TEDA; DABCO, Aldrich Chemical Company) was added to the carbon (3%, nominal) in a large vial. The vial was placed on a rotating mixer and equilibrated for 2 days at room temperature, allowing the TEDA to sublime into the pores of BPL carbon. The resulting material was pulverized to a powder before breakthrough testing to reduce bulk mass transfer effects and used as a reference for gauging the performance of the novel organosilicate materials.

2.3. Materials characterization

Nitrogen sorption analysis was completed using a Micromeritics ASAP 2010 or a Quantachrom Autosorb Automated Gas Sorption System at 77 K on samples degassed to 1 μm Hg at 120°C (24 h). Standard methods were applied to the calculation of characteristics: surface area was determined by the use of the Brunauer–Emmett–Teller (BET) method; average pore sizes are reported; total pore volume was calculated by the single point method at relative pressure (P/P_0) 0.97. Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku high-resolution powder diffractometer with 18 kW CuK α radiation derived from a high-power Rigaku rotating anode X-ray generator. Powder samples were mounted on SEM stubs using conducting carbon tape for imaging by scanning electron microscopy (SEM). Sputter coating with gold was accomplished under argon using a Cressington 108 auto sputter coater for the duration of 60 s. SEMs of the samples were collected using a LEO 1455 SEM (Carl Zeiss SMT, Inc., Peabody, MA).

2.4. Breakthrough experiments

Organosilicate materials were evaluated as powders in a micro-breakthrough apparatus that has been described elsewhere (Peterson et al., 2009). Sorbent volume was fixed at 55 mm³ with masses ranging from 5 to 50 mg. Experiments were conducted at 20°C at 0% (-40°C T_{dp}) or 80% relative humidity with the sorbents pre-equilibrated to those conditions. Target flow rate was fixed at 20 mL/min. Materials with ammonia, cyanogen chloride, octane, and sulfur dioxide were evaluated. Ammonia (NH₃, 1000 mg/m³) is used to probe the materials for efficacy against basic/base-forming gases. Cyanogen chloride (CNCl, 4000 mg/m³) and sulfur dioxide (SO₂, 1000 mg/m³) represent acidic/acid-forming gases; the former typically requires a hydrolysis mechanism (Peterson et al., 2010) with the latter requiring an oxidation mechanism for permanent removal. Finally, octane (4000 mg/m³) probes the materials for physical sorption capacity and retention.

Briefly, materials were packed at a constant volume of approximately 55 mm³ into a fritted glass tube. The tube was submerged in a temperature-controlled water bath set to 20°C . In ammonia, cyanogen chloride (CK), and sulfur dioxide tests, a ballast containing a known mass of gas was charged with air to create a pressurized, concentrated reservoir. In the case of octane, a saturator cell was employed, with an air stream sweeping across liquid octane, creating a saturated vapor. The resulting stream was mixed with either dry or humid air to achieve the required challenge concentration and relative humidity. The mixed stream was pushed through the packed bed, and the effluent was monitored using a photoionization detector (PID) equipped with a 10.6 eV lamp for ammonia, a flame ionization detector (FID) for cyanogen chloride and octane, and a flame photometric detector

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