Influence of carbon deposits and subsequent silylation of silica gel on sorption efficiency of explosive nitramines

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HIGHLIGHTS

- Carbon/silica adsorbents and their silylated modifications were prepared.
- Both carbon nanoparticles and grafted silanes modify surface and textural properties.
- Carbosils were used for extraction (SPE) of explosive nitramines from aqueous samples.
- The recovery rate in SPE depends mainly on the surface properties of carbon deposit.

GRAPHICAL ABSTRACT
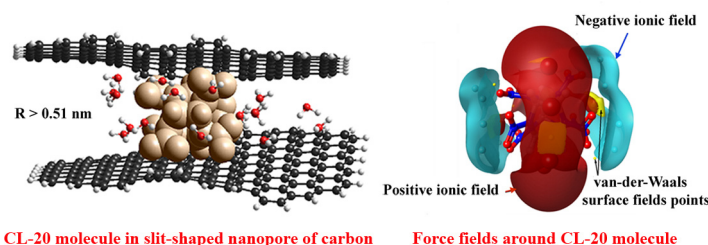
CL-20 molecule in slit-shaped nanopore of carbon

Force fields around CL-20 molecule

ARTICLE INFO

ABSTRACT

A series of carbon/silica (CS) adsorbents was synthesized by carbonization of different amounts of starch bound to silica gel Sipernat 50. To change the adsorption ability of CS in respect to organics with nonpolar fragments, the samples were also silylated by octadecyldimethylchlorosilane. Two sets of CS samples were studied in solid phase extraction (SPE) of three explosive nitramines. The recovery rate of explosives studied in the SPE procedure depends mainly on the amounts of carbon deposits (accessible surface area of carbon phase) in composites. Silylation of the CS samples gives nonlinear changes in the recovery rate which increases for silylated silica gel and CS with small content of carbon deposits and decreases for silylated CS at maximal amounts of carbon deposits.

1. Introduction

Carbon-mineral composites based on silica gels, nanosilicas, or other metal oxide adsorbents with carbon deposits have proved their high potential in many applications [1–16]. Adsorption properties of hybrid carbon-mineral adsorbents depend on the nature and structure of inorganic matrices, features and conditions of pyrolysis of a carbon precursor, amounts and structure of carbon deposits [1–19]. The unique surface properties of the hybrid composites are caused by a mosaic-like surface structure which combines features of nonpolar carbon sheets with polar functionalities at the edges and polar inorganic adsorbents [2,19]. Therefore these hybrids can be used for adsorption, isolation and concentration of trace amounts both of organics, *e.g.* trihalomethanes, nitro- or chlorophenols [20], and heavy metal ions [21] from aqueous solutions, and other applications [1–16].

Previously [22] solid phase extraction (SPE) rates of nitramine hexogen (RDX) from post-blast soil samples were compared for

carbon/silica (carbosils, CS) composites and commercial adsorbents. The results for CS samples were quite promising because unique selectivity was attained for RDX using such complex polar/nonpolar matrix. Therefore the SPE experiments with explosive nitramines CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane or HNIW) and TEX (4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane) were continued in the present work using two sets of CS samples. These CS were based on silica gel Sipernat 50 (Evonik) with carbon deposits prepared by carbonization of starch and with subsequently silylated surface by octadecyldimethylchlorosilane. Silylation of carbosils was aimed to attain better selectivity for explosives. Note that the molecules of CL-20 and TEX have strained cage structures that can affect SPE rates depending on the textural characteristics of adsorbents. Therefore, the aim of this work was to evaluate the influence of the textural and structural characteristics of hybrid CS adsorbents on the SPE performance with respect to CL-20 and TEX in comparison with RDX. The presented data are the first published results concerning SPE of CL-20 and TEX on carbon/silica adsorbents.

2. Materials and methods

2.1. Preparation of carbosils

Silica gel Sipernat 50 (Evonik, Germany, $S_{BET} = 503 \, m^2/g$, average size of particles $d = 50 \, \mu m$) and commercial potato starch were used as precursors to prepare carbosil samples. The first series of carbon/silica samples with various concentration of the carbon phase was prepared using different quantities of starch: 1.6, 2.2, 2.7, 4.0, and 5.4 g per 3 g of dry silica gel. The weighted portions of both components were suspended in 95 ml of water, sonicated, heated to 69 °C (with stirring) and then maintained at this temperature for 1 h. Samples were dried at room temperature and then in a dryer at 40 °C to a constant weight. Dried starch/silica samples were carbonized at 500 °C in a nitrogen flow (100 cm^3/min) in a quartz rotary reactor with heating from 20 °C to 500 °C for 2 h, isothermal treatment at 500 °C for 5 h, and cooling to room temperature. The adsorbents were labeled as Si50 for initial silica and CSi, where i was from 1 to 5, for carbosils.

To modify the adsorption properties of silica gel and CS composites, additional surface functionalities were attached by surface silylation [23,24] with octadecyldimethylchlorosilane (ODDMCS). The silylation reaction was carried out in dry toluene (60 ml) using 9 g of an adsorbent and 7.237 g of silane. Before the reaction, adsorbents were heated at 150 °C in vacuum (10^{-3} atm) for 4 h. After adsorbent cooling to 100 °C, the toluene solution of ODDMCS was added, and the reaction mixture was maintained at 105 °C for 14 h. Modified adsorbents were filtered, washed with toluene and methanol. The silylated samples were named as Si50s and CSis, where $i = 1$–5.

2.2. Textural and structural characteristics

To analyze the textural characteristics of samples degassed for several hours, low-temperature (77.4 K) nitrogen adsorption–desorption isotherms were recorded using a Micromeritics ASAP 2405N adsorption analyzer. The specific surface area (S_{BET}) was calculated according to the standard BET method [25]. The total pore volume V_p was evaluated from the nitrogen adsorption at $p/p_0 \approx 0.99$, where p and p_0 denote the equilibrium and saturation pressure of nitrogen at 77.4 K, respectively [26]. The nitrogen desorption data were used to compute the pore size distributions (PSDs, differential $f_V(R) \sim dV_p/dR$ and $f_S(R) \sim dS/dR$) using a self-consistent regularization (SCR) procedure under non-negativity condition ($f_V(R) \geq 0$ at any pore radius

R) at a fixed regularization parameter $\alpha = 0.01$ with a complex pore model with slit-shaped (S) (for carbons) and cylindrical (C) (for silica) pores and voids (V) between spherical nonporous nanoparticles (for carbons) packed in random aggregates (for CS samples). Void-cylindrical pore model (CV/SCR) was used for silica gels initial and silylated [2,19]. The differential PSDs with respect to pore volume $f_V(R) \sim dV/dR$, $\int f_V(R) dR \sim V_p$ were re-calculated to incremental PSD (IPSD) at $\Phi_V(R_i) = (f_V(R_{i+1}) + f_V(R_i))(R_{i+1} - R_i)/2$ at $\sum \Phi_V(R_i) = V_p$. The differential $f_S(R)$ functions were used to estimate the deviation of the pore shape from the model as follows

$$\Delta w = \left(\frac{S_{BET}}{\int_{R_{min}}^{R_{max}} f_S(R) \, dR} \right) - 1, \tag{1}$$

where R_{max} and R_{min} are the maximal and minimal pore radii, respectively [19]. The $f_V(R)$ and $f_S(R)$ functions were also used to calculate contributions of micropores (V_{micro} and S_{micro} at $0.35 \, nm < R < 1 \, nm$), mesopores (V_{meso} and S_{meso} at $1 \, nm < R < 25 \, nm$), and macropores (V_{macro} and S_{macro} at $25 \, nm < R < 100 \, nm$). The average values of the pore radii were determined with respect to both pore volume and specific surface area, respectively, as the ratio of the first and zero moments of the distribution functions

$$\langle R_V \rangle = \frac{\int_{R_{min}}^{R_{max}} R f_V(R) \, dR}{\int_{R_{min}}^{R_{max}} f_V(R) \, dR}, \tag{2}$$

$$\langle R_S \rangle = \frac{\int_{R_{min}}^{R_{max}} R f_S(R) \, dR}{\int_{R_{min}}^{R_{max}} f_S(R) \, dR} \tag{3}$$

Additionally, the PSD were calculated using nonlocal density functional theory (NLDFT) method [27] using equilibrium models with cylindrical pores in silica (for silica gel) and slit-shaped/cylindrical pores in carbons (for CS).

The adsorption of *p*-nitrophenol (PNP) as described by Kamegawa and Yoshida [28] was applied to determine the specific surface area of carbon deposits *per se* on CS samples. PNP is not practically adsorbed on silica gel (hydrophilic surface) but adsorbed on carbonaceous fragments (hydrophobic surface). For different kinds of carbons the quantity of adsorbed PNP per a surface unit can be similar if very narrow micropores are absent.

The initial PNP solution at relative concentration 0.40 (relatively to the saturated solution) was prepared by dissolving of 3.673 g PNP (Sigma) in 0.5 L of 0.01 M HCl. A series of 20 solutions at relative concentrations of 0.02–0.40 was prepared. A calibration curve (absorbance *vs.* relative PNP concentration) was prepared using a spectroscopic method with a ThermoSpectronic HEλIOSγ UV–vis apparatus (Thermo Scientific) at $\lambda = 400 \, nm$. The standard PNP solutions were prepared in 25 ml volumetric flasks by dilution of 12.5 μl portions of the PNP solutions in 0.0001 M NaOH. The adsorption was measured for samples prepared in closed vials by mixing of 100 mg CS portions with 1 ml of standard solutions at 20 °C for 24 h using a laboratory shaker, and then the vials were centrifuged. The average equilibrium concentration of PNP was obtained from three replicated measurements.

2.3. Thermogravimetry

The content of carbon deposit (C_{dep}) in CSi and attached silanes (C_{sil}) in CSis was determined by thermogravimetry (TG) with differential thermal analysis (DTA). The samples were heated in air from 293 K to 1273 K using a Derivatograph C (Paulik, Paulik and Erdey, MOM) at a heating rate of 10 K/min. The C_{dep} and C_{sil} values were estimated from the mass loss of dry samples (pretreated at 473 K).