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Porous organic–inorganic hybrids for removal of amines via donor–acceptor interaction

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Abstract

Highly porous organic–inorganic hybrids have been prepared from 3-(2,4-dinitrophenylamino)propyltriethoxysilane (DNPTES) and tetraethylorthosilicate (TEOS) by sol-gel method. The hybrids were characterized by FT-IR spectroscopy, UV–vis spectroscopy and elemental analysis, and their pore characteristics were studied by nitrogen sorption porosimetry. The applicability of the hybrids as adsorbent of amines was investigated, and it was demonstrated that aniline and ethylenediamine could be removed from their hexane solutions.

Keywords: Microporous hybrid; Sol–gel; Amine removal

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1. Introduction

Volatile organic compounds (VOCs) such as low-molecular-weight amines and sulfides are known to affect human health, environment, and the quality of industrial products [1]. Aniline, for example, could affect blood of living animals, and often needs to be removed from a liquid or gas stream. The elimination of amine impurities has also been important in chemical plants [2], power plants [3], microelectronic device industries [4–7], and petroleum refineries [8]. Various approaches have been reported to remove the amine contaminants. Examples include chemical [9] and biological treatment [10,11]. These methods, however, consist of several steps involving chemical or biological reactions, thus are time-consuming and expensive. Some physical separations of amines were employed such as solvent extraction [12,13], ion exchange-, coordination-, and adsorption-chromatography [14]. Recently, an efficient and selective method of amine removal from gas oils was developed utilizing charge–transfer interaction between an electron-accepting adsorbent and electron-donating amines [8]. An organic cross-linked polymer was used as a support for the acceptor groups. However, we expected that the use of highly porous metal oxide support instead of the organic polymer could offer the advantages of higher surface area, chemical stability, and mechanical strength [15].

Porous metal oxide materials are readily prepared by sol–gel processing under near ambient conditions (≤60 °C and 1 bar) [16]. Surface area, pore size, and surface chemistry of the metal oxides can be easily controlled by varying reaction conditions and/or type of precursors. Various organic components may be incorporated into the gel network through chemical bonds by co-polymerizing inorganic and organic precursors together during sol–gel processing [17,18]. One of the main purposes of incorporating organic groups into gel network is to introduce desired surface chemistry to the porous solid so as to promote the interaction between the solid surface and small organic molecules. Examples of possible interaction forces are van der Waals force, electrostatic force, donor–acceptor interaction, and chemisorption.

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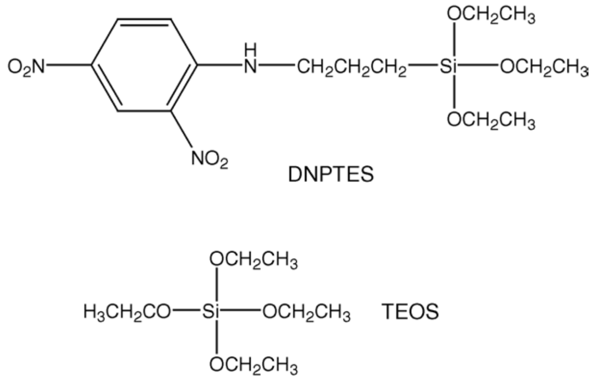

Fig. 1. Chemical structures of DNPTES and TEOS.

In this work, 3-(2,4-dinitrophenylamino)propyltriethoxysilane (DNPTES) was chosen as organic precursor since it has simultaneously a dinitrophenyl group and ethoxysilane groups (Fig. 1), so that the electron-accepting dinitrophenyl moiety can be covalently incorporated into silica network via sol–gel process. It is well known that aromatic nitro compounds form charge-transfer complexes with amines that can donate their lone-pair electrons [19,20]. DNPTES/TEOS-derived porous hybrids were synthesized and characterized, and their applicability in amine removal was investigated. As far as we know this work is the first example of amine removal using highly porous organic–inorganic hybrids via donor–acceptor interaction.

2. Experimental

The hybrids were synthesized by copolymerizing DNPTES and TEOS using a two-step acid–base catalyzed sol–gel process, which involves hydrolysis and condensation reactions [17]. To a solution of DNPTES and TEOS in ethanol was added a deionized (DI) water and an aqueous HCl solution. The molar ratio of DNPTES/TEOS:ethanol:H_2O:HCl was 2:7.7:2.2:0.0014. The resulting mixture was stirred for 90 min at 60 °C. After additional DI water and ethanol were added, an aqueous ammonium hydroxide solution was added to adjust pH to 8.0. The volume of the additional ethanol was the same as that of the sol obtained in the first step, and the Si/H_2O molar ratio of the final sol was approximately 1:5. The sol obtained was allowed to age in a sealed vial at room temperature until gelation. The hybrid powders were prepared by heating the gel in an oven for 24 h at 100 °C to remove all residual solvent, and by subsequent grinding of the resultant monolith using a mortar. In order to remove unreacted and low-molecular-weight species, each hybrid was put into a large amount of a mixture of methanol and dimethyl sulfoxide and stirred for 5 days at 150 °C. After filtration, the powders were washed with methanol and dried for 3 days in vacuo at 150 °C. Four hybrids, Hy2.5, Hy5.0, Hy7.5, and Hy10, having different content of dinitrophenyl group, were prepared (Table 1). For comparison, silica powders without dinitrophenyl group, Hy0, were prepared from TEOS under the same conditions. The hybrids were characterized by Fourier Transform Infrared (FT-IR) spectroscopy (Nicolet 5DXB, Madison), elemental analysis (EA 1108 CHNS-O, Fisons Instrument), and nitrogen sorption porosimetry at 77 K (Micromeritics ASAP 2000M, Norcross). Transparent hybrid films were also prepared by a dip-coating method. Hydrolyzed glass plates were immersed into the hybrid sols for 1 min and withdrawn using a dip-coater at a withdrawal rate of 14 cm min^{-1}, followed by drying at 100 °C for 24 h in an oven. The change in optical absorption of the films was investigated by UV–vis spectroscopy (8453-A, Hewlett-Packard).

3. Results and discussion

The hybrids showed similar gelation times (Table 1), indicating that the condensation rates of their sols were similar. Generally the higher concentration of bulky organic groups a sol has, the more viscous it becomes. The increased viscosity would lead to less diffusivity of the reacting molecules, and thus slower condensation rate. However, in our study, the dinitrophenylamino groups might have a certain catalytic effect on the condensation, resulting in the similar condensation rates in all runs.

Optical transparency has been used as a criterion for the formation of a homogeneous molecular hybrid composed of organic and inorganic constituents [21,22]. The dried solids before grinding were transparent, implying that homogeneous organic–inorganic hybrids without detectable phase segregation were obtained. FT-IR spectra of the hybrids

Table 1
Gelation time and the results of nitrogen sorption porosimetry of the DNPTES/TEOS-derived hybrids

Code	DNPTES/TEOS in feed (molar ratio)	DNP/SiO_2 in hybrid (molar ratio)[a]	Gelation time (h)	Surface area (m^2/g)	Pore volume (cm^3/g)	Porosity (%)	Pore size (Å)
Hy0	0/100	0/100	17	1036	0.82	65.5	38.4
Hy2.5	2.5/97.5	2.4/97.6	15	887	0.62	59.0	38.0
Hy5.0	5.0/95.0	4.4/95.6	18	674	0.40	48.1	37.9
Hy7.5	7.5/92.5	6.5/93.5	16	448	0.27	38.5	37.7
Hy10	10/90	8.2/91.8	17	308	0.23	34.8	37.8

[a] Molar ratio of dinitrophenyl (DNP) groups to SiO_2 for the hybrids determined by elemental analysis.

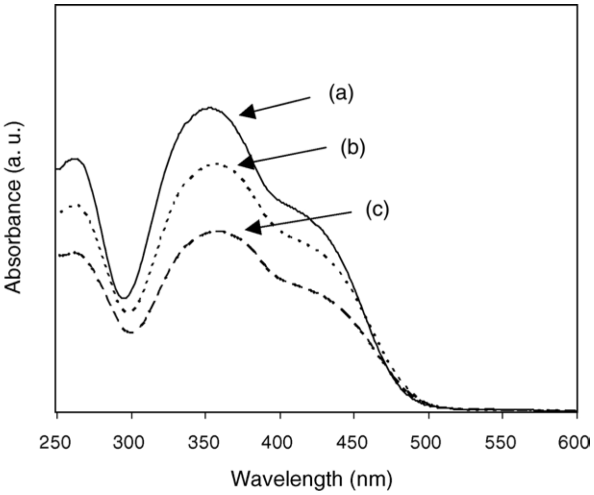

Fig. 2. Optical absorption curves of Hy10 films (a) before exposure to amine, and after exposure to (b) aniline and (c) ethylenediamine.

showed characteristic Si–O–Si framework vibrations at 792, 959, 1083 cm^{-1} and other absorption bands at 1230 cm^{-1} (Si–C), 1344 and 1526 cm^{-1} (nitro), 1624 cm^{-1} (benzene), 2905–2986 cm^{-1} (C–H), and 3379 cm^{-1} (N–H), indicating the dinitrophenyl moiety was incorporated into the silicon oxide network. Elemental analysis for Hy5.0 gave 1.82% (N), 7.79% (C), 2.33% (H), suggesting that ca. 4.4 mol% of the dye functionality was incorporated into the silica structure. In a similar manner the amount of the dinitrophenyl group introduced into Hy2.5, Hy7.5, and Hy10 was estimated to be 2.4, 6.5, and 8.2 mol%, respectively (Table 1). In UV–vis spectroscopy, all the hybrid films showed two absorption bands at 352 and 440 nm which are characteristic of NO$_2$ groups (Fig. 2a).

The hybrids were characterized by nitrogen sorption porosimetry and the isotherm of Hy10 is shown in Fig. 3. Surface area, pore volume, porosity, and pore size of the hybrids are presented in Table 1. As the mol% of DNPTES increased, surface area, pore volume, and porosity decreased (Table 1). This is partly attributable to reduced connectivity of the gel network by the incorporation of DNPTES having three ethoxy groups. Another possible explanation is that the highly polar organic moiety of DNPTES might lead to higher capillary force. The less connectivity and/or increased capillary force would result in more collapse of the gel network, leading to less porous structure. However, the mean pore size remained almost unchanged.

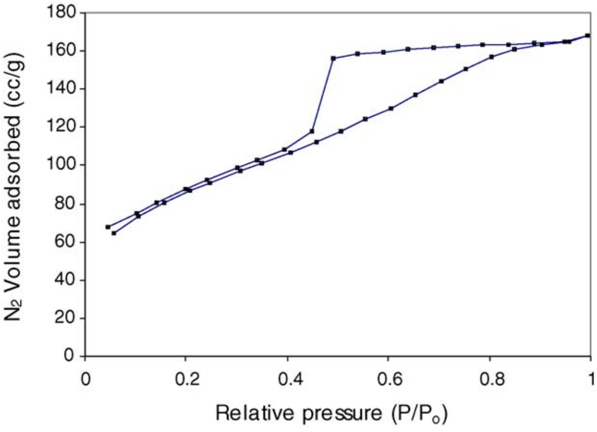

Fig. 3. A nitrogen sorption isotherm of Hy10.

A donor–acceptor complex usually shows a UV–vis spectrum different from spectra for its original free donor or acceptor form, due to an electronic state change resulting from the charge transfer interaction [23]. The hybrid films were exposed to aniline or ethylenediamine, and blown with air to remove free residual amine on the surface. Optical absorption of the films was measured by UV–vis spectroscopy (Fig. 2). The hybrid films showed λ_{max} of 357 and 358 nm (3.48 eV) when exposed to aniline and ethylenediamine, respectively, while it was 352 nm (3.54 eV) before exposure. The λ_{max} shift (red shift) is attributable to the donor–acceptor interaction between the amines and the dinitrophenyl groups in hybrid. Bandgap decreased, but the extent of decrease was very small, corresponding to 0.06 eV.

Preliminary testing of the hybrid powders as adsorbent of amines was conducted using aniline and ethylenediamine (EDA). Aniline is known to behave as a lone-pair (n)- or π-donor depending on the type of acceptor structure and EDA acts as a n-donor [19]. The concentration change of the amines was readily measured by UV–vis absorption spectroscopy.

Hy5.0 powders were added to a 5.6 mL aniline solution in hexane with a concentration of 3.81×10^{-4} mol L, and the mixture was stirred for 1 min. A transparent solution was taken after centrifugation for 1 min, and its absorbance was measured (Fig. 4). As more hybrid powders were added, the absorbance of aniline decreased (Fig. 4c–e). When 10, 50 and 100 mg of the Hy5.0 powders were added to the aniline solutions, 30, 69, and 84% of the initial aniline was removed, respectively. In contrast, the addition of Hy0 powders having

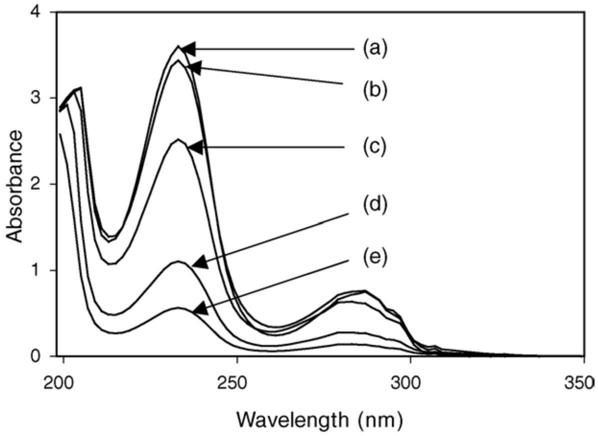

Fig. 4. Decrease in optical absorbance of an aniline solution: (a) original solution; (b) after adding 100 mg of Hy0 powders; after adding Hy5.0 powders of (c) 10 mg, (d) 50 mg, and (e) 100 mg.

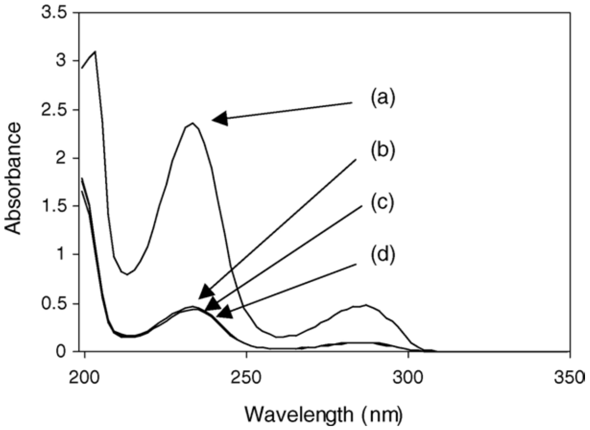

Fig. 5. Decrease in optical absorbance of an aniline solution in the presence of 100 mg of Hy5.0 powders: (a) original solution; (b) 1 min, (c) 3 min, and (d) 5 min after adding the hybrid.

no dinitrophenyl functionality caused no significant change in absorbance (Fig. 4b). These results indicate that aniline was removed from the solution, via donor–acceptor interaction between aniline molecules and the dinitrophenyl moieties linked to the silica network [19,20]. EDA could also be effectively eliminated from its solution under the same conditions: 97% of EDA was removed by adding 100 mg of Hy5.0 powders.

As shown in Fig. 5, the concentration of aniline decreased to a certain point in one minute after adding the hybrid powders, and no appreciable decrease in concentration upon prolonged stirring was observed. It was considered that the mixture reached an equilibrium state within one minute after adding the powders. The formation of organic charge-transfer complexes is known to involve equilibrium [19].

In summary, highly porous DNPTES/TEOS-derived hybrids have been prepared by sol–gel method and their applicability as adsorbent of amines was demonstrated. The hybrids would be promising for application in amine removal because of its ease of preparation and high surface area.

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