

Porous Organic-inorganic Hybrids for Removal of Amines

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Received July 1, 2005

Porous organic-inorganic hybrids have been prepared from tetraethylorthosilicate (TEOS) and organosilane precursors by sol-gel method. Two organosilanes, 3-(2,4-dinitrophenylamino)propyltriethoxysilane (DNPTES) and *N*-[[[(2-nitrophenyl)methoxy]carbonyl]-3-triethoxysilylpropylamine (NPTES) were used to incorporate electron-accepting (di)nitrophenyl groups into the hybrids. The hybrids were characterized by FT-IR spectroscopy and elemental analysis, and their pore characteristics were studied by nitrogen sorption porosimetry. Surface area of the hybrids ranged from 563 to 770 m²/g, pore volume, 0.23-0.30 cm³/g, and porosity, 35-41%. It was demonstrated by UV-vis spectroscopy that aniline, ethylenediamine, and 1-aminonaphthalene could be removed from their hexane solutions in the presence of the hybrid powders. The removal of amines is attributable to donor-acceptor interaction between the electron-donating amines and electron-accepting (di)nitrophenyl moiety.

Key Words : Porous hybrid, Sol-gel, Amine removal, Donor-acceptor interaction

Introduction

Volatile organic compounds such as low-molecular-weight amines are often required to be removed from a liquid or gas stream because of their malodor and their effects on human health, the environment, and the quality of industrial products.¹⁻⁶ Various approaches have been reported to eliminate the amine contaminants, including chemical,⁷ biological^{8,9} and physical treatment.¹⁰⁻¹² Recently, an efficient method of amine removal from gas oils was developed utilizing an organic cross-linked polymer support functionalized with an electron-accepting organic moiety.⁶ Amines, a class of electron-donors, were adsorbed on the organic functional groups via charge-transfer (donor-acceptor) interaction. In the present study, we employed porous silicon oxide materials instead of the organic polymer support, because it was expected that porous silicon oxides could offer various advantages such as high surface area, chemical stability, and mechanical strength.¹³

Porous silicon oxide materials are readily prepared by sol-gel processing under near ambient conditions from silicon alkoxides.¹⁴ Functional organic groups can be incorporated into the gel network through chemical bonds by co-condensation of silicon alkoxides and functionalized organosilane precursors during the sol-gel process.^{15,16} In this work 3-(2,4-dinitrophenylamino)propyltriethoxysilane (DNPTES) and *N*-[[[(2-nitrophenyl)methoxy]carbonyl]-3-triethoxysilylpropylamine (NPTES) (Figure 1) were employed as functionalized precursors since they have the electron-accepting (di)nitrophenyl moiety, which can be covalently immobilized in silica network *via* sol-gel reaction of their triethoxysilyl group. It is well known that aromatic nitro compounds form charge-transfer complexes with amines that can donate their lone-pair electrons.^{17,18} DNPTES/

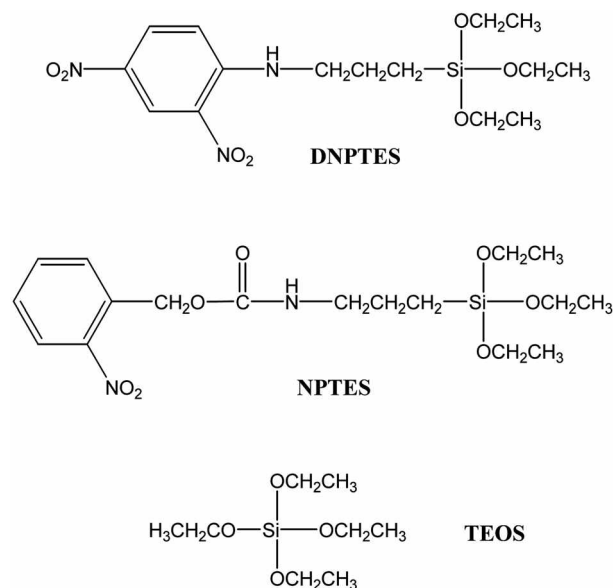


Figure 1. Chemical structures of DNPTES, NPTES and TEOS.

tetraethoxyorthosilicate (TEOS) and NPTES/TEOS-derived porous hybrids were synthesized and characterized, and their applicability in amine removal was investigated.

Experimental Section

Materials and Instruments. 2-Nitrobenzyl alcohol, 3-(triethoxysilyl)propylisocyanate, lithium metal, TEOS, aniline, ethylenediamine, 1-aminonaphthalene, and naphthalene were purchased from Aldrich Chemical Co., and used without purification. DNPTES was purchased from Gelest Co. ¹H and ¹³C NMR spectra were taken on a Varian Gemini 300-MHz spectrometer in deuteriochloroform using tetra-

Table 1. Results of elemental analysis and nitrogen sorption porosimetry of the hybrids

Code	DNPTES/TEOS in feed (mol ratio)	NPTEs/TEOS in feed (mol ratio)	(Di)nitrophenyl/SiO ₂ in hybrid (mol ratio) ^a	Surface area (m ² /g) ^b	Pore volume (cm ³ /g)	Porosity (%)
Hy0	–	–	–	1,200	0.51	54
DHy2.5	2.5/97.5	–	2.4/97.6	770	0.30	41
DHy5.0	5.0/95.0	–	4.4/95.6	563	0.23	35
NHy2.5	–	2.5/97.5	2.4/97.6	657	0.28	39
NHy5.0	–	5.0/95.0	4.3/95.7	643	0.26	38

^aMolar ratio of (di)nitrophenyl group to SiO₂ for the hybrids determined by elemental analysis. ^bLangmuir surface area determined by nitrogen sorption porosimetry.

methylsilane as an internal standard. IR spectra were recorded on a Genesis FTIR spectrophotometer (Mattson Instrument). Elemental analysis was done with an EA 1108 CHNS-O (Fisons Instrument). Nitrogen sorption porosimetry was carried out at 77 K with a Micromeritics ASAP-2010. Porosity was calculated by dividing pore volume of a sample by the sum of pore volume and reciprocal of density of the sample. UV-vis spectroscopy was conducted using a Hewlett-Packard 8453-A.

Preparation of NPTEs. To a solution of 2-nitrobenzyl alcohol (3.07 g, 0.020 mol) in diethyl ether (50 mL) was added lithium metal (0.19 g, 0.025 mol), and the mixture was refluxed for 4 h. 3-(Triethoxysilyl)propylisocyanate (4.95 g, 0.020 mol) was added dropwise to the mixture and the resultant mixture was refluxed for 70 min. After filtration to remove the metal, the solvent was stripped off and NPTEs was obtained as a light-brown liquid (7.93 g, 99%). IR (neat): ν (cm⁻¹) 1337, 1518, 1695, 2964. ¹H NMR (CDCl₃, 300 MHz): δ 0.63 [t, 2H, CH₂CH₂CH₂-Si], 1.17 [t, 9H, 3 OCH₂CH₃], 1.59-1.69 [m, 2H, CH₂CH₂CH₂-Si], 3.20 [t, 2H, CH₂CH₂CH₂-Si], 3.80 [q, 6H, 3 OCH₂CH₃], 5.23 [s, 1H, NH], 5.48 [s, 2H, Ar-CH₂O], 7.43-7.63, 8.06-8.08 [m, 4H, Ar]. ¹³C NMR (CDCl₃, 75 MHz): δ 7.54 [CH₂CH₂CH₂-Si], 18.13 [OCH₂CH₃], 23.12 [CH₂CH₂CH₂-Si], 43.12 [CH₂CH₂CH₂-Si], 58.31 [OCH₂CH₃], 62.82 [Ar-CH₂O], 124.68, 128.29, 128.51, 133.42, 133.58, 147.22 [Ar], 155.84 [C=O]. Elemental analysis: calculated for C₁₇H₂₈N₂O₇Si, C 50.98, H 7.05, N 7.00, O 27.96, Si 7.01; found, C 50.80, H 7.21, N 6.82, O 28.36.

Preparation of Hybrids. The hybrids were synthesized from DNPTES (or NPTEs) and TEOS through a two-step sol-gel process involving hydrolysis and subsequent condensation.¹⁵ The DNPTES/TEOS-derived hybrids were prepared as follows. To a solution of DNPTES and TEOS in ethanol were added a deionized (DI) water and an aqueous HCl solution. The molar ratio of DNPTES/TEOS : ethanol : H₂O : HCl was 2 : 7.7 : 2.2 : 0.0014. After the resulting mixture was stirred for 90 min at 60 °C, additional DI water and ethanol were added, followed by adding an aqueous ammonium hydroxide to adjust pH of the solution to 8.0. The volume of the ethanol added was the same as that of the sol obtained in the first step, and the Si/H₂O molar ratio of the final sol was approximately 1 : 5. The sol obtained was stored in a sealed vial at room temperature until gelation. The hybrid powders were obtained by drying the gel in an

oven for 24 h at 100 °C, 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. The NPTEs/TEOS hybrids were prepared in a similar fashion. Four hybrids, DHy2.5, DHy5.0, NHy2.5, and NHy5.0, having different content of (di)nitrophenyl group, were prepared (Table 1). For comparison, silica powders without (di)nitrophenyl group, Hy0, were prepared from TEOS under the same conditions.

DHy2.5. IR (KBr): ν (cm⁻¹) 792, 959, 1083, 1230, 1344, 1526, 1624, 2905-2986, 3379. Elemental analysis: found, C 4.21, H 1.01, N 1.54, O 48.29.

DHy5.0. IR (KBr): ν (cm⁻¹) 792, 959, 1083, 1230, 1344, 1526, 1624, 2905-2986, 3379. Elemental analysis: found, C 7.32, H 1.09, N 2.73, O 50.12.

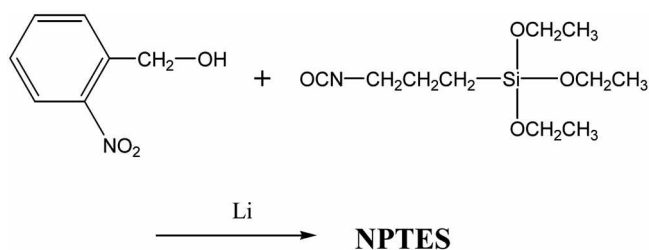
NHy2.5. IR (KBr): ν (cm⁻¹) 789, 942, 1083, 1208, 1345, 1524, 1628, 2846-2957, 3446. Elemental analysis: found, C 5.21, H 1.02, N 1.03, O 49.58.

NHy5.0. IR (KBr): ν (cm⁻¹) 789, 942, 1083, 1208, 1345, 1524, 1628, 2846-2957, 3446. Elemental analysis: found, C 9.15, H 1.11, N 1.82, O 48.94.

Removal of Amines. One hundred milligrams of hybrid powders were added to a 5.6-mL aniline solution (in hexane), and the mixture was stirred for 1 min. A transparent solution was taken after centrifugation of the mixture for 1 min, and its optical absorbance was measured by UV-vis spectroscopy. The absorbance values before and after adding the hybrids were compared to estimate the amount of aniline removed from its solution. For the other amines and naphthalene, removal experiments were carried out using the same method.

Results and Discussion

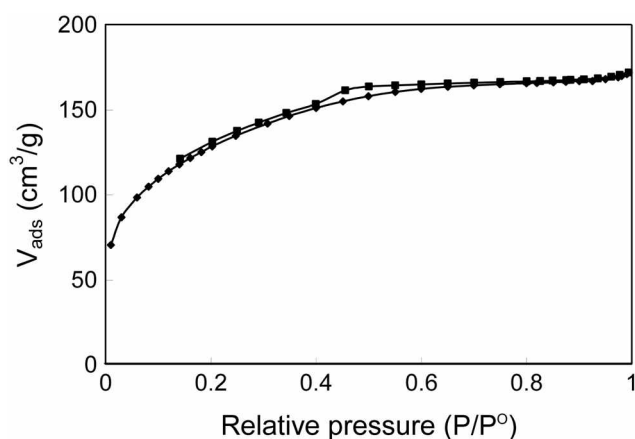
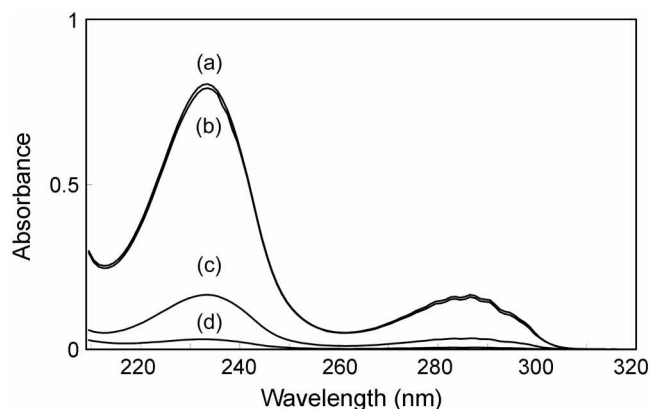
NPTEs was synthesized (Scheme 1) and fully characterized by FT-IR, ¹H and ¹³C NMR, and elemental analysis. DNPTES and NPTEs, along with TEOS, were used to prepare organic-inorganic hybrids through a sol-gel process (Table 1). After gelation, transparent monoliths were obtained without observable phase segregation. FT-IR spectra of the hybrids showed characteristic Si-O-Si framework vibration at 1083 cm⁻¹, Si-C absorption at 1230 cm⁻¹ (DHy)


Scheme 1. Synthesis of NPDES.

and 1208 cm^{-1} (NHy), nitro stretching at 1526 cm^{-1} (DHy) and 1524 cm^{-1} (NHy), and aromatic C=C stretching at 1624 cm^{-1} (DHy) and 1628 cm^{-1} (NHy), indicating the (di)nitrophenyl moiety was incorporated into the silicon oxide network. Elemental analysis for DHy5.0 gave 2.73% (N), 7.32% (C), 1.09% (H), suggesting that molar ratio of dinitrophenyl : SiO_2 is approximately 4.4 : 95.6 (Table 1). In a similar manner the content of the (di)nitrophenyl groups in DHy2.5, NHy2.5, and NHy5.0 was estimated to be 2.4, 2.4, and 4.3 mol%, respectively.

The hybrids were characterized by nitrogen sorption porosimetry and the results are presented in Figure 2 and Table 1. The incorporation of the organic groups into silica network resulted in significant reduction in surface area, pore volume, and porosity. This might be attributable to reduced degree of connectivity of the gel network by incorporation of the triethoxysilanes (DNPDES and NPDES) and correspondingly more collapse of the hybrid gel network.^{19,20} Another possible explanation is that increased capillary force due to the organic moiety would have resulted in more collapse of the network during drying. As the mol% of the organosilanes in feed increased from 2.5 to 5.0%, surface area, pore volume, and porosity decreased slightly. The difference between pore characteristics of DHy and NHy hybrids is not significant.

The applicability of the hybrid powders as adsorbent of amines was investigated using aniline, ethylenediamine, and 1-aminonaphthalene. The aromatic amines are known to behave as a lone-pair (*n*)- or π -donor depending on the type of acceptor structure, and ethylenediamine, as a *n*-donor.¹⁷


Figure 2. A nitrogen sorption isotherm of DHy5.0.

Figure 3. Decrease in optical absorbance of an aniline solution: a) original solution; after adding 100 mg of b) Hy0, c) DHy2.5, and d) DHy5.0.

After the powders were added to an amine solution in hexane, the mixture was stirred for 1 min, and the concentration change of the amine was measured by UV-Vis absorption spectroscopy. No appreciable further decrease in amine concentration upon prolonged stirring was observed. A similar test was conducted with naphthalene for comparison.

As shown in Figure 3, the optical absorbance of the aniline solution decreased when DHy2.5 and DHy5.0 powders were added. Compared with DHy2.5, DHy5.0 has more acceptor groups (Table 1), resulting in larger decrease in aniline concentration (Figure 3). In contrast, the addition of Hy0 powders without (di)nitrophenyl functionality caused no appreciable change in absorbance of the aniline solution. Similar results were obtained in the experiments using NHy2.5 and NHy5.0. These results indicated that aniline was removed from its solution, *via* donor-acceptor interaction between aniline molecules and (di)nitrophenyl groups in the hybrids.

DHy5.0 and NHy5.0 have almost the same mol% of (di)nitrophenyl groups (Table 1), but DHy5.0 removed larger amount of aniline than NHy5.0 (Table 2). The same tendency was observed in removal of the other compounds. This is attributable to stronger electron-accepting property of the dinitrophenyl groups in DHy5.0 than that of the nitrophenyl groups in NHy5.0. The values of surface area, pore volume, and porosity for NHy5.0 are higher than those for DHy5.0, but the efficiency of amine removal seemed not to be greatly influenced by the pore characteristics.

Table 2. Percentage of amine removed from its hexane solution by adding 100 mg of DHy5.0 or NHy5.0 hybrid powders

Amine	Absorbance of original solution (λ_{max} , nm)	DHy5.0 (Removed, %)	NHy5.0 (Removed, %)
Aniline	0.80 (234)	96	82
Ethylenediamine	1.18 (213)	97	92
1-Aminonaphthalene	0.71 (313)	66	55
Naphthalene	1.05 (275)	8	4

The aliphatic amine, ethylenediamine, could also be effectively eliminated from its solution having an absorbance of 1.18 at 213 nm: 97 and 92% of ethylenediamine was removed by adding 100 mg of DHy5.0 and NHy5.0 powders, respectively (Table 2). By adding DHy5.0 powders the concentration of 1-aminonaphthalene decreased by 66%, while that of naphthalene, by only 6%; the same tendency was observed in the experiments using NHy5.0. This suggested that 1-aminonaphthalene might form a charge-transfer complex with (di)nitrophenyl moiety more effectively than naphthalene, while polycyclic aromatic hydrocarbons such as naphthalene are also known to behave as π -donors and participate in charge-transfer interactions with nitroaromatic acceptors.²¹

It is considered that two factors affect the efficiency of amine removal: accessibility of amine molecules to the (di)nitrophenyl groups and strength of donor-acceptor interaction. Generally smaller molecules should have higher accessibility, so aniline, smaller than 1-aminonaphthalene, was removed more efficiently. The accessibility, however, is not likely a dominant factor because larger amount of 1-aminonaphthalene was removed compared to naphthalene despite its bigger molecular size. It was concluded that the donor-acceptor interaction is a main factor in the amine removal by this hybrid system, based on the following facts: first, DHy hybrids having stronger (dinitrophenyl) acceptor groups showed higher removal efficiency than NHy hybrids, and second, 1-aminonaphthalene having stronger donor property than naphthalene was eliminated more effectively.

Conclusion

Highly porous DNPTEs/TEOS and NPTEs/TEOS-derived hybrids have been prepared by a sol-gel method. Various amine compounds could be successfully removed from their solutions by adding the hybrid powders. It was demonstrated that the donor-acceptor interaction was a dominant factor in the removal of the organic compounds. The hybrids would be advantageous for application in amine removal because of its ease of preparation and high surface area.²²

Acknowledgement. This work was supported by Yonsei University Research Fund of 2003.

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