

Bromine addition and successive amine substitution of mesoporous ethylenesilica: Reaction, characterizations and arsenate adsorption

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Abstract

Bromination and subsequent ethylenediamine substitution of the C=C double bond in mesoporous ethylenesilica were carried out to explore the characteristics of this periodic mesoporous organosilica. The structures of the products (Br=PMO and EDA–Br=PMO, respectively) were analysed by IR, Br K-edge EXAFS and NMR spectroscopies, as well as X-ray diffraction and nitrogen adsorption. We showed (1) that the formulae of the two products that formed were $[\text{CHBrSiO}_{1.5}]_{0.45}[\text{CHSiO}_{1.5}]_{0.55}$ and $[\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCHSiO}_{1.5}]_{0.05}[\text{CHBrSiO}_{1.5}]_{0.40}[\text{CHSiO}_{1.5}]_{0.55}$, respectively, (2) that the addition of Br_2 at room temperature occurred on the C=C double bonds with disturbing the framework structure, (3) that IR absorption band of C=C bonds that reacted with Br_2 is significantly different from that of inactive C=C bond, (4) that the length of the C–Br bond was considerably longer than in conventional alkyl bromides, and (5) that a large proportion of the $\nu(\text{C–Br})$ band remained at the same position in the IR absorption spectrum after the ethylenediamine (EDA) substitution, while a new $\nu(\text{C–Br})$ absorption also appeared. The mechanisms of these reactions are discussed at both the micro and mesoscopic levels.

Arsenate adsorption on EDA–Br=PMO, in which the EDA is directly bound to the “surface” of the mesopores, was compared with adsorption on EDA–Pr=PMO, which was prepared by the direct synthesis of 3-chloropropyl-functionalized mesoporous ethanesilica followed by the substitution of Cl with EDA. The strength of the adsorption, as measured with the distribution coefficient, was greater for the former adsorbent than the latter. The origin of this difference was attributed to the distance between amino group and the surface. © 2006 Elsevier Inc. All rights reserved.

Keywords: Periodic mesoporous organosilica; Ethylenesilica; Bromination; Amine substitution; Arsenate adsorption

1. Introduction

The functionalization of periodic mesoporous silicas by organic groups has been an important subject in developing new applications of mesoporous materials [1]; they have attracted the interest of chemists because they contain well-developed mesopores with a uniform pore structure. Post-synthetic grafting techniques are widely considered to be simple, easy and versatile and have been widely studied. However, it has been claimed that slow diffusion dur-

ing the grafting process can lead to non-uniform dispersion of the organic groups in the pores, and that pore-blockage is induced in some cases [1,2]. This difficulty can be avoided by the direct co-condensation of tetraalkoxysilane and organosilane with a structure-directing agent [1b,1e,1g,1h,3]. Nevertheless, the disadvantage of introducing partial inactivation of the functional groups has been pointed out as being an intrinsic problem for this co-condensation method [3–5]. Since this effect is believed to occur due to a strong interaction between the functional group and the silicon oxide/hydroxide in the synthetic gel, protection of the functional group by utilizing a stronger interaction with a surfactant molecule has been proposed [1h,6,7],

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though the available combinations of functional groups and templates are quite limited.

Periodic mesoporous organosilica (PMO) is another category of mesostructured material [8–10,14] that contains organic groups within a meso-framework, which act as bridges between silicon atoms. Such materials have been prepared by methods akin to mesoporous silicas, with a high degree of order and uniformity of the pores, by using a silsesquioxane $(R'O)_3SiRSi(OR')_3$ as a precursor. Because of the use of a sole precursor, we ensure a uniform dispersion of the organic groups in the framework structure, a high loading of organic groups, and the avoidance of the pore narrowing/blockage that is often observed in the grafting of mesoporous silicas. Examples of silsesquioxanes that have been successfully incorporated into a framework include bis(triethoxysilyl)ethane [9–13], bis(triethoxysilyl)ethylene [14–16], bis(triethoxysilyl)acetylene [17], bis(triethoxysilyl)benzenes [15,18–22], 2,5-bis(triethoxysilyl)thiophene [17,23] and 1,4-bis(triethoxysilyl)ferrocene [17].

The variations in the organic groups mentioned above are not still large enough to match the applications in mesoporous, further functionalization has been carried out. Direct synthesis with 3-mercaptopropyltrimethoxysilane for benzene-silica and ethane-silica has been employed for the preparation of sulfonic acid-functionalized PMOs [24]. A systematic study of the direct co-condensation of ethane-silica with various $RSi(OR')_3$ type silanes has also been carried out [25]. These direct co-condensation syntheses have clearly demonstrated that the ordered periodic structure is disrupted by the incorporation of silanes as well as the influence found in mesoporous silica. When using a vinylsilane in the direct synthesis of functionalized ethylene-silica, the disruptive effect seems larger than in the synthesis of the equivalent functionalized mesoporous silica [26]. The functionalization that is unique to PMO involves using the conversion of the organic group in PMO. It has been demonstrated that the methylene group in PMO can be converted to the $Si-NH_2-Si$ structure by ammonolysis [27]. In addition, bromination has been carried out in studies of the preparation of mesoporous ethylenesilica [14–16]. These studies show the possibility of designing particular sites for adsorption, catalysis, etc., by making use of various organic reactions. Since the framework of PMO exhibits both organic and inorganic characteristics, the relationship between the structure of the functional groups and the way in which they work should be carefully investigated.

Since the structure of PMOs contains a functional group that is definitely larger than oxygen atom, they may show the structural characteristic between organic polymers and silica. If we compare data in the literature [22,28], a large difference can easily be observed in the conversion of the $C=C$ double bond during the bromination of mesoporous ethylenesilicas, in spite of the similar pore sizes and the surface areas of these ethylenesilicas. This difference can be due to the effective exposure of $C=C$ bond to bro-

mine, suggesting the need for study from the viewpoint of mesostructural and microstructural changes in the framework.

The amino group-functionalization of mesoporous silica has aroused interest in applications of this solid in terms of coordination chemistry, catalysis and oxyanion adsorptions. However, this functional group interacts strongly with the surface, leading to structural disturbances such as lack of uniformity in grafting [27] and disruption of periodic order in direct co-condensation [4]. When PMO is employed as the mesoporous framework, it is possible to partially avoid these problems, since a considerable proportion of the silanol groups/siloxane bonds on the surface are substituted by a hydrophobic group. In this paper, we functionalize $C=C$ double bonds in ethylenesilica with amino groups via the addition of bromine and subsequent substitution by ethylenediamine (EDA). In this functionalization process, the extent of reactions is particularly interesting, because of the intermediate characteristics of PMOs between organic polymer and inorganic solid. For this reason, we analyse the products by using a combination of elemental analysis, ^{13}C NMR, EXAFS and IR spectroscopies, etc. This functionalization is compared in structural analyses and arsenate adsorption with EDA-modified ethanesilica that was prepared by the direct co-condensation of 3-chloropropylsilane and bis(triethoxysilyl)ethane and consecutive substitution of Cl by EDA and with an amino-functionalized mesoporous silica.

2. Experimental section

2.1. Materials

Bis(triethoxysilyl)ethylene (BTESEY, $(C_2H_5O)_3SiCH=CHSi(OC_2H_5)_3$), bis(triethoxysilyl)ethane (BTESE, $(C_2H_5O)_3SiCH_2-CH_2Si(OC_2H_5)_3$) and 3-chloropropyltrimethoxysilane (CPTMS, $ClCH_2CH_2CH_2Si(OCH_3)_3$) were purchased from Gelest, Inc. Brij 56 ($C_{16}H_{33}(OCH_2-CH_2)_nOH$, $n \sim 10$, Aldrich), Brij 76 ($C_{18}H_{37}(OCH_2-CH_2)_nOH$, $n \sim 10$, Aldrich), ethylenediamine (EDA, Tokyo Kasei Kogyo Co., Ltd., reagent grade), bromine (Br_2 , reagent grade, Aldrich) were also commercially available.

2.2. Synthesis of mesoporous ethylenesilica

Brij 76 was dispersed in 0.8 M hydrochloric acid by stirring and the mixture was then heated at 323 K for 12 h. BTESEY was then added to the solution before stirring for 12 h at the same temperature. The mixture was then transferred into a Teflon bottle and heated at 363 K for 24 h. The precipitate was collected by suction filtration and dried at room temperature. The molar ratio of the reactants was 0.11Brij 76:0.56BTESEY:222 H_2O :3.20HCl. The surfactant was extracted by the treatment with acidified ethanol (0.1 N HCl) twice at room temperature. This extracted solid is hereafter referred to as =PMO.

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