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Adsorption of octadecyltrichlorosilane on mesoporous SBA-15

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Abstract

Adsorption of octadecyltrichlorosilane (OTS) on mesoporous SBA-15 has been studied by using Brunauer–Emmett–Teller (BET) surface area analysis, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and thermo-gravimetric analysis (TGA) techniques. BET surface area analysis shows decrease of surface area from 930 to 416 m^2/g after OTS adsorption. SEM pictures show close attachment of SBA-15 particles. EDAX measurements show increase of carbon weight percentage and decrease of oxygen and silicon weight percentage. XPS results closely support EDAX analysis. FTIR spectra shows presence of methyl ($-CH_3$) and methylene ($-CH_2$) bands and oriented OTS monolayer on SBA-15. Thermo-gravimetric analysis shows that the OTS adsorbed on SBA-15 are stable up to a temperature of 230 °C and that the OTS monolayers decompose between 230 and 400 °C.

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Keywords: SBA-15; OTS; Self-assembly; Adsorption; Thermal stability

1. Introduction

Self-assembled organic monolayers, which form spontaneously on solid surfaces, have many applications such as wafer level anti-stiction coating for micro-electromechanical systems (MEMS), passivating layers, chemical sensing, ultra-fine scale lithography, protection of metals against corrosion, in the preparation of new composite and functional materials [1–3]. Different types of organic compounds are used for self-assembled monolayer formation on different surfaces. These include alkanethol monolayers on gold, silver and copper [1], organosilicon on SiO_2, Al_2O_3, TiO_2, Si_3N_4, mica and glass [1]. Recently,

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n-octadecyltrichlorosilane (OTS) self-assembled monolayers have been extensively studied because of its simplicity in the growth technique and possibility of its wide use in MEMS as anti-stiction coating [4]. OTS monolayer growths on variety of substrates [4–6] and on silica nanobeads [7] have been investigated.

Adsorption of OTS on SiO_2 takes place through hydrolysis of the Si–Cl bonds to form Si–OH groups. All Si–Cl bonds become hydrolyzed as no Cl is detected after monolayer formation [8]. The OH groups experience condensation reaction to form Si–O–Si cross-linking bonds between adjacent head groups. The OH groups in OTS also interact with OH groups on silica forming Si–O–Si bonds to the substrate. Formation of OTS monolayer also depends on the presence of thin water layer on silica surface. Presence of too much water causes polymerization of OTS molecules and hence leads to poor quality of monolayers [9]. Since silica is hydrophilic, a thin layer of water exists on its surface, which helps physisorption of OTS molecule. At this stage, OTS molecules are mobile. They move freely and pack themselves closely before condensation reaction takes place, at which point they bond to the silica surface [10].

Though OTS monolayer growth on many substrates [4–6] and silica nanobeads [7] have been studied extensively, to our knowledge, there is no study of OTS monolayer on recently discovered mesoporous [11] materials. Mesoporous materials have very large surface area of the order of 1000 m^2/g, ordered pore structure and extremely narrow pore size distribution [2]. OTS monolayer growth on these mesoporous materials can be interesting because of large surface area and hence large adsorption sites, which may help to grow a large quantity of monolayers. Many different monolayers such as 3-mercaptopropyl groups and 3-aminopropyl groups have been grown on mesoporous silica such as SBA-15 and studied for their selective adsorption property of heavy metal ions [2,12].

In this paper, we study OTS adsorption and its thermal decomposition on SBA-15 mesoporous silica. Brunauer–Emmett–Teller (BET) surface area analysis, energy dispersive X-ray analysis (EDAX), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) techniques have been used for confirmation of OTS adsorption on SBA-15. Thermo-gravimetric analysis (TGA) in air is used to study the thermal degradation of OTS on SBA-15.

2. Experimental

2.1. Preparation of mesoporous SBA-15

Mesoporous SBA-15 was synthesized by a standard method [13,14]. Amphiphilic triblock copolymer, P123 of 4 g was dispersed in 30 g of water and stirred for 4 h and then 120 g of 2 M HCl solution was added and stirred for 2 h. Then, 8.54 g of tetraethylorthosilicate (TEOS) was added to the homogeneous solution under stirring. The resulting gel was aged at 40 °C for 24 h and finally heated to 100 °C for 48 h. After synthesis, the solid was filtered, washed with distilled water and dried in an air oven at 100 °C for 5 h followed by calcination in flowing air at 540 °C to decompose the triblock copolymer.

2.2. Adsorption study

The chemicals used for adsorption study are: *n*-octadecyltrichlorosilane, $CH_3(CH_2)_{17}SiCl_3$ (95%) obtained from Aldrich and toluene (99.5%) obtained from Qualigens. One micromolar OTS solution in toluene was prepared for OTS adsorption study in a nitrogen filled glove box. The amount of toluene taken is 10 ml. SBA-15 powder of 0.2 g quantity was immersed in OTS solution for 24 h with intermediate stirring. After 24 h the SBA-15 powder with OTS adsorbed was recovered after evaporation of toluene in a rotary vacuum evaporator at 80 °C.

2.3. Characterization

2.3.1. Surface area analysis

BET surface area, pore volume and pore diameter of SBA-15 mesoporous material were measured before and after OTS monolayer growth by using Quantachrome Autosorb automated gas sorption system model number NOVA 1200.

2.3.2. Scanning electron microscopy and energy dispersive X-ray analysis

The surface morphology of SBA-15 particles was carried out before and after OTS monolayer growth by using Leica Stereoscan model 440 SEM. The elemental composition of the Si(1 0 0) and SBA-15 powder were also carried out before and after OTS monolayer growth by EDAX analysis coupled with Leica Stereoscan model 440 SEM.

2.3.3. Fourier transform infrared spectroscopy

The FTIR of SBA-15 particles was carried out before and after OTS monolayer growth on Perkin-Elmer 1615 FTIR spectrometer.

2.3.4. X-ray photoelectron spectroscopy

XPS of SBA-15 mesoporous silica was done before and after OTS monolayer growth using VG Micro Tech ESCA 3000 instrument at a pressure below 10^{-9} Torr. The sample was mounted on sample stubs. The wide scan, C 1s, O 1s and Si 2p core level spectra were recorded with a monochromatic Al Kα radiation (photon energy = 1486.6 eV) at pass energy of 50 eV and electron takeoff angle of 60°. The core-level binding energies were aligned taking 'adventitious' of carbon binding energy as 284.6 eV. All peaks were fitted with Gauss–Lorentz peaks using XPSPEAK41 [15] software to obtain peak information. A Shirley's base line was used in the fitting process.

2.3.5. Thermal behavior by thermo-gravimetric analysis

TGA measurements of SBA-15 before and after OTS monolayer growth were performed on Seiko instruments thermal analyzer model no.: TCA/DIA-32 in the temperature range from ambient to 800 °C. The ramp rate used was 10 °C/min.

3. Results and discussion

3.1. General observations

When the SBA-15 particles with OTS monolayer in toluene are kept under illumination (under 200 W electric bulb), the functionalized SBA-15 particles are found to assembly to form a spherical shape of 2–5 mm diameter. However, the bonding was not that strong and when the light was switched off, the particles dispersed. Upon functionalization of SBA-15 mesoporous silica with OTS monolayer, the milky white color of SBA-15 changed to off white color. This could be due to change in the refractive index

3.2. BET surface area analysis

BET surface area analysis before and after OTS adsorption on SBA-15 shows decrease of surface area from 930 to 416 m^2/g, decrease of total volume from 1.25 to 0.9 cm^3/g and decrease of pore size/diameter from 9.2 to 8.65 nm. This result clearly reveals that the surface modification indeed occurred inside the primary mesopores of the SBA-15. Deposition of mercaptopropyltrimethoxysilane self-assembled monolayer on mesoporous silica from supercritical fluids also shows a similar decrease of surface area (approximately half) [16].

3.3. Scanning electron microscopy

The SEM pictures of mesoporous SBA-15 particles before and after surface modification by OTS monolayer are shown in Fig. 1a and b, respectively. The SBA-15 particles are something like spherically shaped with size approximately in the range of 1–2 μm. The particles are clearly visible and are separate. Agglomeration of these particles is not observed. After modification of SBA-15 by OTS monolayers, the particles are found themselves closely attached with each other. The SEM picture in Fig. 1b clearly shows a large number of SBA-15 particles attaching closely with one another. These phenomena observed both in microscopic and macroscopic scale could be due to spine (alkyl chain) like OTS monolayer growth on SBA-15. These spines of one SBA-15 particle may be caught on the spine of another SBA-15. This way the bonding of large number of SBA-15 particles may take place. On the other hand, it could be due to van der Walls and electrostatic interaction of alkyl chains between the OTS monolayers of adjacent SBA-15 particles.

3.4. Energy dispersive X-ray analysis

The presence of silicon, oxygen and carbon in SBA-15 before and after OTS monolayer growth was examined with EDAX measurements. The EDAX spectrum was used to obtain qualitative information about OTS adsorption. The EDAX spectrum shows

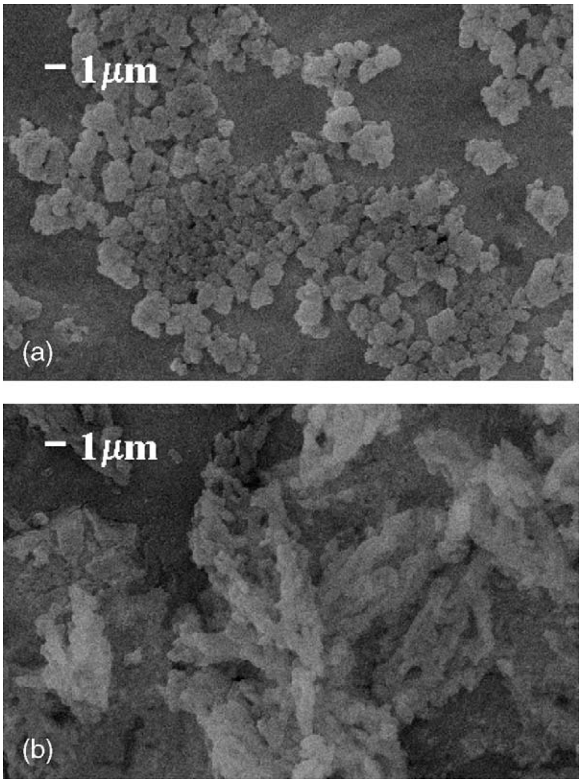

Fig. 1. SEM monograph of mesoporous SBA-15: (a) before OTS monolayer growth and (b) after OTS monolayer growth.

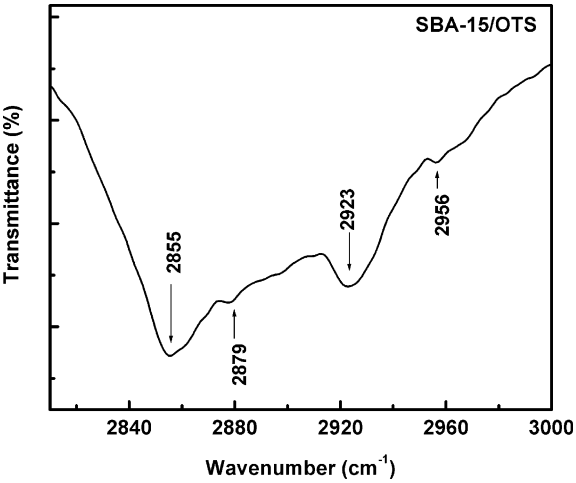

Fig. 2. FTIR spectra in the C–H stretching region of SBA-15 with OTS adsorption showing $–CH_2$ and $–CH_3$ stretching bands.

53.1 wt% oxygen and 46.9 wt% silicon, which closely matches with the calculated weight percent age of 53.3 wt% oxygen and 46.7 wt% of silicon in SiO_2. Carbon peak was not detected in SBA-15. After OTS adsorption for 24 h on SBA-15 the EDAX spectrum shows 7 wt% carbon, 51.5 wt% oxygen and 41.5 wt% silicon. OTS molecule predominantly consists of carbon; therefore, presence of carbon peak indicates OTS adsorption.

3.5. Fourier transform infrared spectroscopy

The FTIR spectra in the C–H stretching region of SBA-15 after OTS adsorption are shown in Fig. 2. Methylene ($–CH_2$) and methyl ($–CH_3$) asymmetric and symmetric C–H bands are observed. These observations clearly suggest OTS adsorption. Highly ordered, densely packed OTS monolayer with close to perpendicular chain axis orientation has a methylene ($–CH_2$) asymmetric and symmetric stretching at 2920 and 2850 cm^{-1}, respectively, and methyl ($–CH_3$) asymmetric and symmetric stretching at 2968 and 2879 cm^{-1}, respectively [17,18]. CH_2 asymmetric and symmetric stretching observed for OTS on SBA-15 are 2923 and 2855 cm^{-1}, respectively. CH_3 asymmetric and symmetric stretching observed are at 2956 and 2879 cm^{-1}, respectively. The results are closely in agreement with reported data [17,18]. The intensity ratio of $\nu_a(–CH_3)$ to $\nu_a(–CH_2)$ vibrations indicate the orientation of alkyl chain relative to the surface [19].

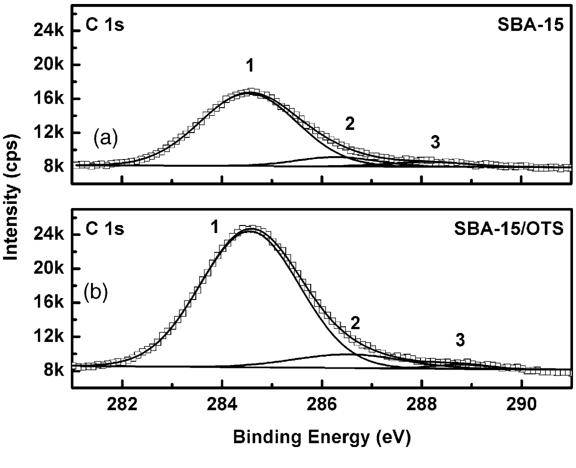

Fig. 3. X-ray photoelectron spectra showing C 1s binding energy range: (a) SBA-15 before OTS adsorption and (b) SBA-15 after OTS adsorption.

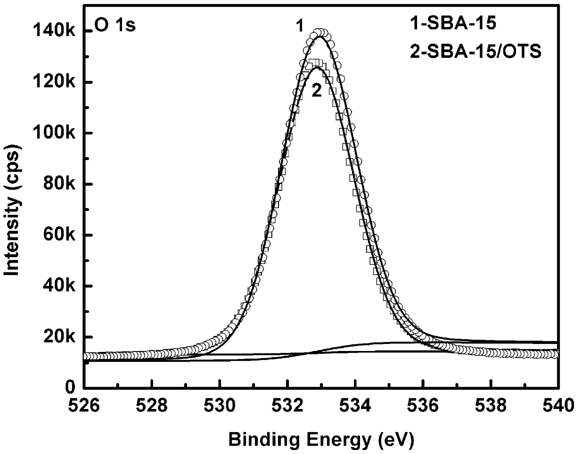

Fig. 4. X-ray photoelectron spectra showing O 1s binding energy range: (curve 1) SBA-15 before OTS adsorption and (curve 2) SBA-15 after OTS adsorption.

This ratio is ≈1, closely in agreement with reported data [19]. Therefore, the OTS adsorption on SBA-15 forms monolayers with 72–80° oriented alkyl chains relative to the surface [19].

3.6. X-ray photoelectron spectroscopy

Figs. 3–5 show X-ray photoelectron spectra in the C 1s, O 1s and Si 2p binding energy range, respectively. The spectra are fitted with Gauss–Lorentz peaks using XPSPEAK software to obtain peak information. A Shirley's base line was used in the fitting process. For C 1s binding energy spectra, three peaks are required to get a good fit to experimental data. The peak binding energies obtained are approximately 284.6, 286.4 and 288.5 eV. Peak 1 is important to us because it belong to OTS adsorption [20]. Relatively small peaks, 2 and 3, may be due to impurities in the system or may be due to "ghost" peaks. After OTS adsorption the integrated area of peak 1 increases by about 1.9 times as compared to bare SBA-15 'adventitious' carbon peak. This large increase could be due to large adsorption of OTS due to very large surface area of SBA-15. It can also be due to combined adsorption of OTS and toluene solvent. The toluene adsorption also gives C 1s binding energy spectra close to 284.7–285.1 eV [21]. After OTS adsorption O 1s peak integrated area is found to decrease as shown in Fig. 4. The decrease of O 1s integrated area is attributed to screening of electrons from the oxide layer below the OTS layer. More decrease of integrated area of O 1s, therefore, corresponds to better quality (densely packed) OTS monolayer [20]. The Si 2p peak integrated area also decreases after OTS adsorption. The decrease is due to screening of Si 2p electrons from the SiO_2 due to the presence of OTS monolayer. More screening of electrons, therefore, implies more decrease of integrated area of Si 2p [20]. Full width at half middle (FWHM) of C 1s, O 1s and Si 2p peaks slightly increase after OTS adsorption. This could be due to aggregation of SBA-15 particles (Fig. 1) after OTS adsorption.

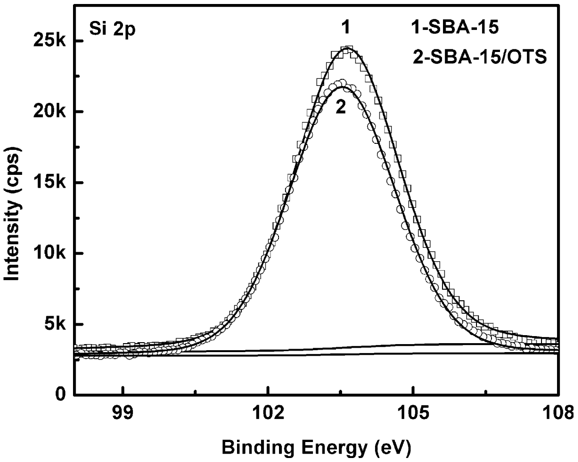

Fig. 5. X-ray photoelectron spectra showing Si 2p binding energy range: (curve 1) SBA-15 before OTS adsorption and (curve 2) SBA-15 after OTS adsorption.

3.7. Thermo-gravimetric analysis

Thermo-gravimetric analysis of SBA-15 powder before and after OTS adsorption is shown in Fig. 6. The thermal analysis was carried out in the temperature range from 30 to 800 °C, in air at a heating rate of 10 °C/min. The TGA pattern of SBA-15 shows a total weight loss of 15% over the temperature range from ambient to 600 °C. The understanding of this weight loss requires knowledge of thermally adsorbed species on the surface of SBA-15. The surface of SBA-15 like any SiO_2 surface consists of a small portion of free silanols; a large amount of hydrogen bonded silanols and adsorbed

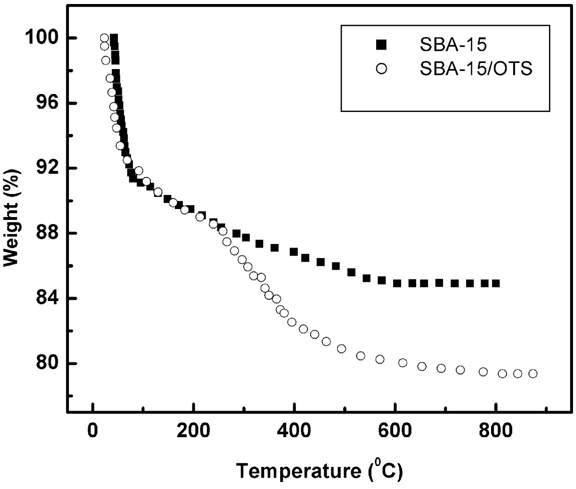

Fig. 6. Thermo-gravimetric analysis of SBA-15, before and after OTS adsorption.

water molecules [22,23]. The initial weight loss of about 10% up to a temperature of 150 °C can be associated with breakup of hydrogen bonded network and removal of adsorbed water from silica. The second stage of weight loss from 150 to 600 °C can be associated with desorption of the adsorbed water as well as water generated by the condensation of part of free silanols [24].

A multi-step weight loss is observed in case of OTS adsorbed on SBA-15. The weight loss occurred in two distinct regions, from ambient to 150 and 230–400 °C. The total weight loss observed is 20.6% in the entire temperature range from ambient to 800 °C. The weight loss in the first step is about 10%, approximately same as the weight loss in case of bare SBA-15. In the temperature range, 70–100 °C, the weight loss in SBA-15 with OTS monolayer is less than the weight loss in case of bare SBA-15. This could be due to water layer on SBA-15, which has been used for the OTS monolayer growth. The weight loss in the second step that is from 230 to 400 °C is 6%. Decomposition of OTS monolayer in air has been reported in this temperature range [25,26]. Therefore, we associate this weight loss to decomposition of OTS monolayer. Our calculations, however, show that maximum 2% loss can be attributed to decomposition of OTS monolayer. The 4% extra weight loss cannot be attributed to OTS decomposition. Adsorption of toluene on SBA-15 may not explain 4% extra weight loss because toluene does not decompose at this temperature. Only reason that may explain 4% extra weight loss could be filling of pores of SBA-15 with toluene solvent and closing of these pore with OTS monolayer. When the OTS monolayer decomposes, the toluene inside the pore evaporates and causes the weight loss. If this explanation is factual then these mesoporous materials will have many applications for storage and controlled release of chemicals and medicines.

4. Conclusions

All our measurements clearly show OTS adsorption on mesoporous SBA-15. Significant decrease of surface area, pore volume and size after OTS adsorption reveals the surface modification inside the primary mesopores of SBA-15. Close assembly of SBA-15 particles both in macroscopic and microscopic scale is an interesting evidence of spine like growth of OTS monolayers. EDAX and XPS results show increase of carbon content on the surface of SBA-15 and screening of oxygen and silicon signals. FTIR results clearly show –CH_2 and –CH_3 stretching bands. Thermo-gravimetric analysis shows that the OTS adsorbed on SBA-15 are stable up to a temperature of 230 °C and that the OTS monolayers decompose between 230 and 400 °C.

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