

Adsorption of methanol on mesoporous SBA-15

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Abstract

The adsorption of methanol on mesoporous SBA-15 has been studied by using Brunauer–Emmett–Teller (BET) surface area analysis, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). The BET surface area analysis shows decreases of the surface area from 387 to 383 m²/g, pore volume from 0.88 to 0.81 cm³/g and pore diameter from 9.07 to 8.4 nm after methanol adsorption. The appearance of strong IR bands at 2862 and 2964 cm⁻¹ due to methyl (–CH₃) symmetric and asymmetric stretching demonstrate the presence of methanol and evidence of successful methanol adsorption. XPS results show increase of carbon and oxygen content on the surface of SBA-15. Thermogravimetric analysis shows that the methanol adsorbed on SBA-15 is stable up to a temperature of 265 °C and that the methanol adlayers decompose between 265 and 588 °C.

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1. Introduction

The interaction of organic molecules with inorganic surfaces has attracted a great deal of attention in the past few years due to its relevance in number of technological applications [1]. The main applications include nano-technology, molecular electronics, nano-catalysis, non-linear optics, bio/chemical sensors; micro-electro-mechanical systems, passivating layers, ultra-fine scale lithography, corrosion resistant layers, and preparation of new composite and functional materials [1–4]. Organic solvents are widely used in semiconductor technology. Adsorption of organic solvents like methanol on various inorganic materials is important and has been studied. Adsorption of methanol on pure silicon substrate has been studied [1,5] in order to grow high quality ultra-thin silicon oxide films which is challenging and important in microelectronics. Methanol adsorption on fuel cell catalyst has been studied for direct methanol fuel cell applications [6]. Methanol adsorption on mica has been studied by using atomic force microscope and the results confirm bilayer structure [7]. Methanol adsorption on SiO₂ powder

has also been studied [8–16]. Though methanol adsorption has been studied on various materials, to our knowledge, there is no study of methanol adsorption on recently discovered mesoporous [17] SBA-15 materials. Mesoporous materials have very large surface area ordered pore structure and extremely narrow pore size distribution [18]. Methanol adsorption on these mesoporous materials can be interesting because of large surface area and hence large adsorption sites, which may help to adsorb more quantity of methanol.

In this paper, we study methanol adsorption and its thermal decomposition on SBA-15 mesoporous silica. BET surface area analysis, SEM, FTIR and XPS techniques have been used for confirmation of methanol adsorption on SBA-15. Thermogravimetric analysis in air is used to study the thermal degradation of methanol adlayer on SBA-15.

2. Experimental section

2.1. Preparation of mesoporous SBA-15

Mesoporous SBA-15 was synthesized by a standard method [19,20]. Amphiphilic triblock copolymer, P123 of 4 g was

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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

Methanol (99.8%) obtained from Euclid was used for the adsorption study. SBA-15 powder of 0.3 g quantity was immersed in 10 ml methanol solvent for 24 h with intermediate stirring. After 24 h the SBA-15 powder with methanol adsorbed was recovered after evaporation of methanol under a 250 watt light bulb. The evaporation temperature was more than the boiling point of methanol so that only chemisorbed methanol will remain on SBA-15 and physisorbed methanol will evaporate.

2.3. Characterization

2.3.1. Surface area analysis

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

2.3.2. Scanning electron microscopy (SEM)

The surface morphology of SBA-15 particles was carried out before and after methanol adsorption by using Leica Stereoscan model 440 SEM.

2.3.3. Fourier transform infrared spectroscopy (FTIR)

The FTIR of SBA-15 particles was carried out before and after methanol adsorption on a Perkin Elmer 1615 FTIR spectrometer equipped with DTGS detector and Ge-coated KBr

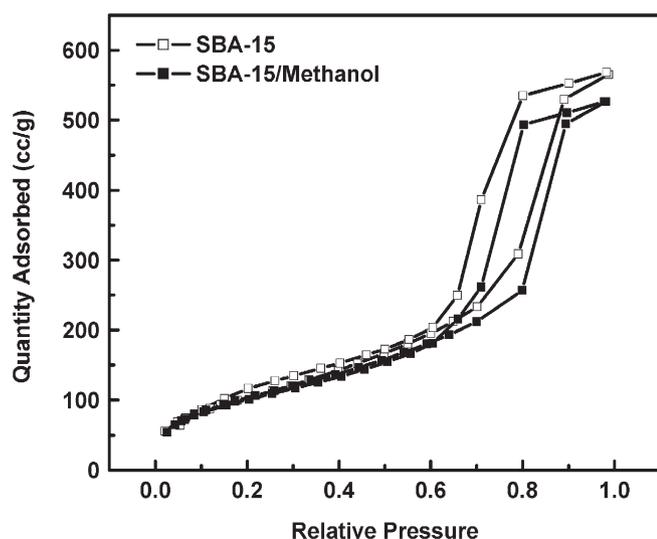


Fig. 1. Nitrogen adsorption/desorption isotherms of SBA-15 before and after methanol adsorption.

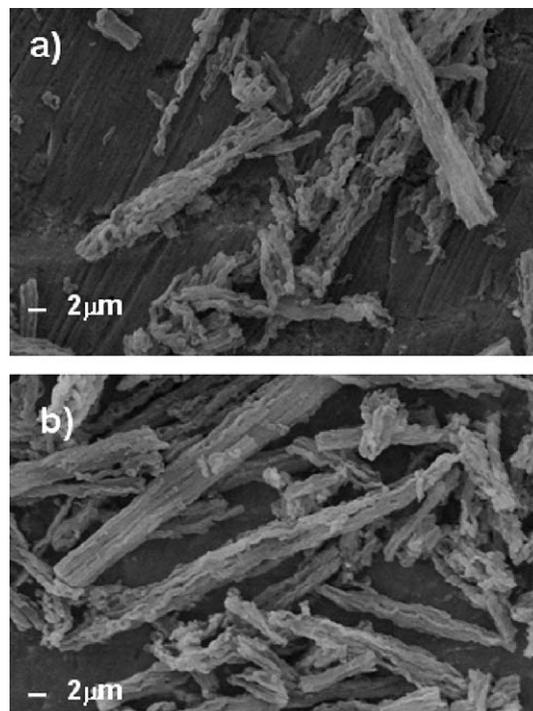


Fig. 2. SEM monograph of mesoporous SBA-15 a) before and b) after methanol adsorption.

beam splitter. The spectrum was recorded at a resolution of 4 cm^{-1} over 256 scans at ambient temperature.

2.3.4. X-ray photoelectron spectroscopy (XPS)

XPS of SBA-15 mesoporous silica was done before and after methanol adsorption 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-K α 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 bare SBA-15 (SiO₂) binding energy as 103.5 eV. All peaks were fitted with Gauss-Lorentz peaks using XPSPEAK41 [21] software to obtain peak information. A Shirley's base line was used in the fitting process.

2.3.5. Thermal behavior by thermogravimetric analysis (TGA)

TGA measurements of SBA-15 before and after methanol adsorption were performed on Diamond TG/DTA instrument in the temperature range from ambient to 1000 °C. The ramp rate used was 10 °C/min.

3. Results and discussion

3.1. BET surface area analysis

The nitrogen adsorption isotherms of SBA-15 before and after methanol adsorption are shown in Fig. 1. The material exhibits type IV isotherm with apparent hysteresis loop, indicative of defined mesoporous in the frameworks. The adsorbed amount at the saturated pressure decreases after methanol adsorption. This shows that the lower porosity may be obtained by the incorporation of methanol in the mesoporous network. The surface

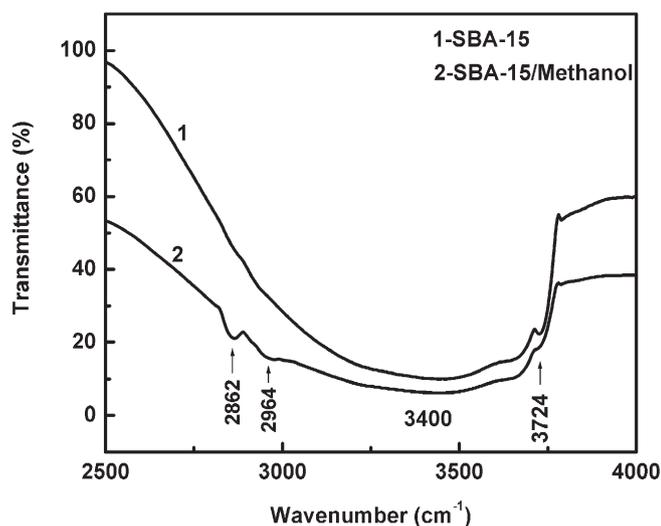


Fig. 3. FTIR spectra in the C–H stretching region of SBA-15 before and after methanol adsorption showing —CH_3 stretching bands.

area decreases from 387 to 383 m²/g (~1%), pore volume from 0.88 to 0.81 cm³/g (~8%) and pore diameter from 9.07 to 8.4 nm (~7%) after methanol adsorption. The decrease of pore volume corresponds to ~0.06 g of methanol adsorption per one gram of SBA-15 (~6%). This result clearly reveals that, the surface modification indeed occurred inside the primary mesopores of the SBA-15.

3.2. Scanning electron microscopy

The SEM pictures of mesoporous SBA-15 particles before and after methanol adsorption are shown in Fig. 2a) and b) respectively. The SBA-15 material is observed to contain lengthy hair like material arranged in a bundle of diameter of ~2 μm and length of 30–50 μm. After adsorption of methanol a similar morphology is observed. There is no significant change in the micrographs due to methanol adsorption.

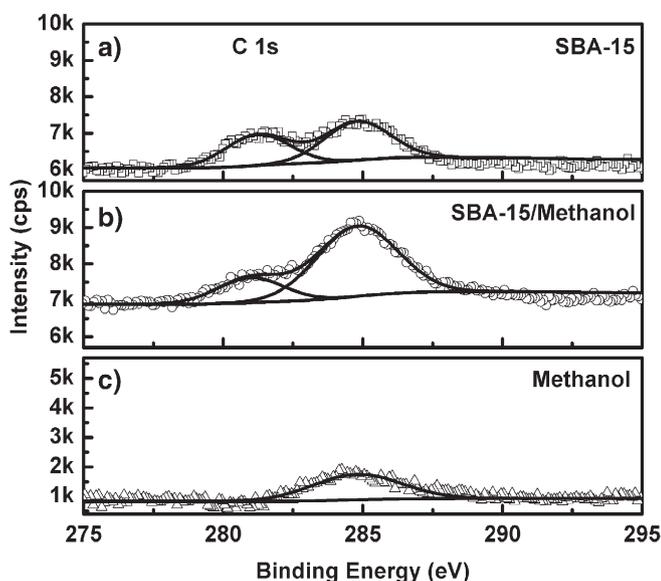


Fig. 4. X-ray photoelectron spectra showing C 1s binding energy range of: a) SBA-15 before methanol adsorption, b) SBA-15 after methanol adsorption and c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption spectra, adsorption time=1 day.

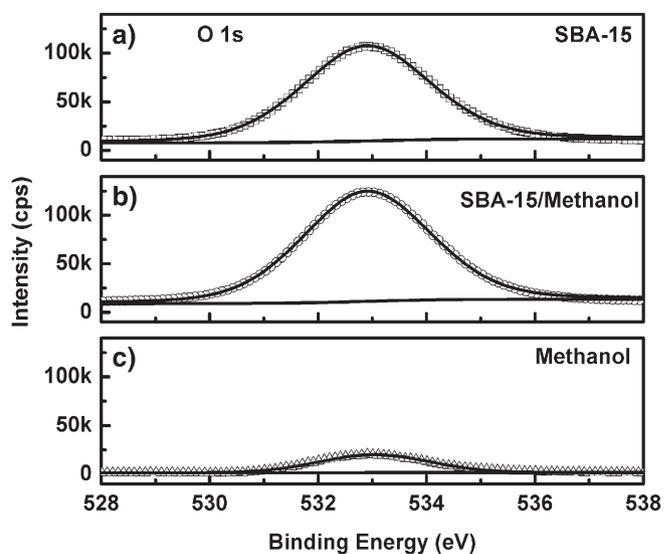


Fig. 5. X-ray photoelectron spectra showing O 1s binding energy range of: a) SBA-15 before methanol adsorption, b) SBA-15 after methanol adsorption and c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption spectra, adsorption time=1 day.

3.3. Fourier transform infrared spectroscopy

The FTIR spectra of the mesoporous SBA-15 before and after methanol adsorption are shown in Fig. 3. The FTIR spectrum of the parent SBA-15 gives a narrow band at 3724 cm⁻¹ and a broad low-frequency band at 3400 cm⁻¹. The band at 3724 cm⁻¹ can be assigned to the symmetrical stretching vibration mode of O–H from isolated terminal silanols (Si–OH) groups. The broad low frequency band at 3400 cm⁻¹ is due to those silanols groups or silanols nests with cross hydrogen bonding interactions in between [22–24]. Appearance of strong IR bands at 2862 and 2964 cm⁻¹ due to methyl (—CH_3) symmetric and asymmetric stretching demonstrate the presence of methanol and evidence of successful methanol adsorption [16]. After methanol adsorption the bands at 3400 and 3724 cm⁻¹ get

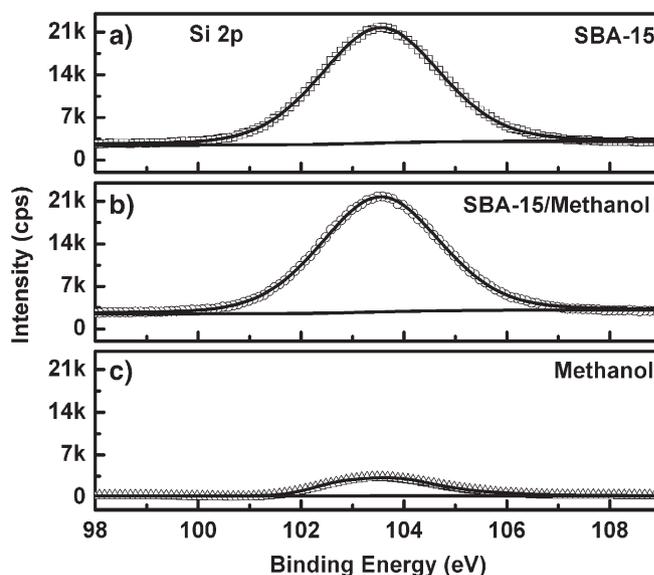


Fig. 6. X-ray photoelectron spectra showing Si 2p binding energy range of: a) SBA-15 before methanol adsorption, b) SBA-15 after methanol adsorption and c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption spectra, adsorption time=1 day.

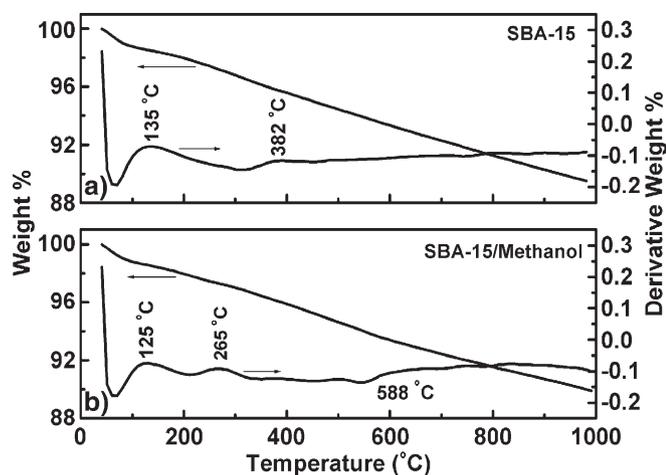


Fig. 7. Thermogravimetric analysis of SBA-15, a) before and b) after methanol adsorption.

broadened indicating the involvement of silanols in the adsorption mechanism. Absence of methoxy ($\text{O}-\text{CH}_3$) band in the FTIR spectra suggests that the methanol adsorption is not through the formation of SiOCH_3 groups. The results indicate molecular bonding of methanol similar to methanol adsorption on mica surface [7].

3.4. X-ray photoelectron spectroscopy

Figs. 4, 5 and 6 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. In all the figures part a) shows the spectra before methanol adsorption, part b) shows the spectra after methanol adsorption and part c) shows the contribution from methanol alone, obtained after subtracting before adsorption spectra from after adsorption spectra. Before adsorption of methanol, the C 1s XPS spectra shows two peaks, the low energy peak at 281.3 eV and high energy peak at 284.8 eV. The low energy peak is attributed to residual carbon from the decomposed triblock copolymer used for the synthesis of mesoporous SBA-15 and the high energy peak is attributed to residual triblock copolymer itself, which has not been decomposed. After methanol adsorption the integrated area of carbon peak at ~ 284.8 eV increases by 2.22 times, that validates methanol adsorption. The peak at 281.3 eV remains unchanged. After subtraction of before adsorption data from after adsorption data, we get only one peak at ~ 284.8 eV as shown in Fig. 4c).

Before methanol adsorption O 1s peak appears at a binding energy of 532.9 eV. The contribution for this peak is due to oxygen from SBA-15 mesoporous SiO_2 . After methanol adsorption the integrated area of O 1s peak increases, this confirms methanol adsorption. The increase of integrated area of O 1s peak is larger as compared with C 1s peak; this could be because methanol has more oxygen weight percentage than carbon, this also confirms methanol adsorption. Before methanol adsorption silicon Si 2p peak appears at 103.5 eV. The contribution for this peak is due to silicon from SBA-15 mesoporous SiO_2 . After methanol adsorption the integrated area of silicon peak increases slightly. After subtracting before adsorption spectra from after adsorption data the Si 2p obtained is shown in Fig. 6c). The increase of integrated area of Si 2p peak due to methanol adsorption can be explained in the following way. The surface of SBA-15 consists of free silanols and these free silanols attenuate photoelectrons from SiO_2 (SBA-15). Adsorption of methanol has been found to eliminate these silanols

[25,26]. Because of this the attenuation of photoelectrons has been stopped and hence the increase of the integrated area of Si 2p peak after methanol adsorption. This also confirms methanol adsorption.

3.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of SBA-15 powder before and after methanol adsorption is shown in Fig. 7a) and b) respectively. The thermal analysis was carried out in the temperature range from 30 to 1000 °C, in air at a heating rate of 10 °C/min. The TGA pattern of SBA-15 demonstrates that there are two observable weight loss regions. The first region is from ambient to ~ 135 °C and the second region is from ~ 135 °C to ~ 382 °C. The first region can be attributed as due to the loss of physically bound water and breakup of hydrogen bonded network. The second region can be associated with desorption of the adsorbed water as well as water generated by the condensation of part of free silanols [27]. The continued weight loss beyond this temperature can be attributed to decomposition of residual triblock copolymer, conversion of residual carbon from triblock copolymer into carbon dioxide and carbon monoxide, increase of siloxane bridges ($\text{Si}-\text{O}-\text{Si}$) due to isolated silanol condensation [29] and breakdown of mesoporous network due to sintering of SBA-15 [30].

A multi step weight loss is observed in case of methanol adsorbed on SBA-15. The weight loss occurred in three distinct regions. The first region is from ambient to ~ 125 °C; the second region is from ~ 125 °C to 265 °C and the third region is from 265 °C to 588 °C. The first region has been assigned to the loss of physically bound water and breakup of hydrogen bonded network. This region has been shifted by about 10 °C towards lower temperature side as compared to pure SBA-15, may be because of the modification of the surface properties due to methanol adsorption. The second region can be associated with desorption of the adsorbed water as well as water generated by the condensation of part of free silanols. The third region is attributed as due to methanol desorption or decomposition. It starts at a temperature of ~ 265 °C and ends at a temperature of ~ 588 °C. The decomposition of methanol is known to take place between the temperatures 200–550 °C [28]. Though BET surface area results show about 0.06 g methanol adsorption per one gram of SBA-15 ($\sim 6\%$) the TGA results show only about $\sim 0.5\%$ weight loss of SBA-15/methanol as compared with bare SBA-15 sample. The reason for this could be due to incomplete decomposition of methanol or decomposition in several steps like oxidation of methanol into formaldehyde (HCHO) and then formic acid (HCOOH) like in the case of methanol adsorption on MCM-48 and $\text{U}_3\text{O}_8/\text{MCM-48}$ [28]. The methanol and its converted or decomposed products like HCHO, HCOOH and carbon itself may be locked inside the mesopores due to sintering of SBA-15 [30] as a result further weight loss may not occur. The TGA of methanol adsorbed deep inside the mesopores is like burning of methanol in a closed atmosphere deficient in oxygen. Therefore, carbon residues are most likely to remain inside the mesoporous.

4. Conclusions

All our measurements clearly show methanol adsorption on mesoporous SBA-15. Decrease of surface area, pore volume and size after methanol adsorption reveals the surface modification inside the primary mesopores of SBA-15. XPS results show increase of carbon and oxygen content on the surface of SBA-15. FTIR results clearly show methyl ($-\text{CH}_3$) stretching bands confirming methanol adsorption. Thermogravimetric analysis shows that the methanol adsorbed on SBA-15 are stable up to a temperature of 265 °C and that the methanol adlayers decompose between 265 and 588 °C.

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