Adsorption of methanol on Si(1 0 0)/SiO$_2$ and mesoporous SBA-15

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Abstract

Adsorption of methanol on Si(1 0 0)/SiO$_2$ substrate and mesoporous SBA-15 has been studied by using Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). Contact angle technique is employed to study the adsorption kinetics of methanol on Si(1 0 0)/SiO$_2$ and thermal stability of adlayer. Thermogravimetric (TGA) technique is used to understand the thermal behavior of methanol layer on SBA-15. Adsorption kinetics fit fairly well with Langmuir isotherms giving adsorption rate constant, $k_a = 0.0021$ M^{-1} s^{-1}. FTIR results show formation of methoxy silicon (SiOCH$_3$), silicon polyhydride (SiH$_2$), carboxylate, molecular water and hydroxyl groups on Si(1 0 0)/SiO$_2$ surface and only methoxy silicon on SBA-15. XPS results confirm methanol adsorption and support FTIR results. The methanol adlayers are found to be thermally stable up to a temperature of ~262 °C on both Si(1 0 0)/SiO$_2$ and SBA-15 and decompose between 262 and 450 °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 technological applications [1]. The major applications include nano-technology, molecular electronics, nano-catalysis, non-linear optics, bio/chemical sensors; micro-electromechanical systems (MEMS), passivating layers, ultra fine scale lithography, corrosion resistant layers, preparation of new composite and functional materials [1–4]. Organic solvents are widely used in semiconductor technology for cleaning of semiconductor surfaces and for the synthesis of silicon carbide, a material widely used in microelectronic devices and in refractory material industry. The research on self-assembled monolayers on metal and other substrates is also based on interaction of organic molecules with inorganic surfaces and has grown exponentially in the recent years [2]. Adsorption of organic solvent-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 are 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]. Adsorption of methanol on MgO thin films has been studied [8,9]. Methanol adsorption on bulk SiO$_2$ powder has also been studied [10–18]. Methanol adsorption on silicon substrate with a thin oxide layer is important and has many applications like surface modification for wafer level anti-stiction application like MEMS in microelectronics. Methanol adsorption on silicon is also important because it is most widely used substrate in microelectronics. Methanol adsorption on SBA-15 is important because of its large surface area and therefore it is possible to study thermal behavior of adsorbed methanol by thermogravimetric technique. Such a technique cannot be employed for planer silicon substrate. The objective of this paper is to study methanol adsorption on Si(1 0 0)/SiO$_2$ and mesoporous SBA-15 surface and compare the results. Contact angle technique is used to study the adsorption kinetics of methanol on Si(1 0 0)/SiO$_2$ and thermal stability of adsorbed methanol layer. Thermogravimetric technique is employed to understand the thermal behavior of methanol layer on SBA-15. FTIR and XPS techniques are used to confirm the methanol adsorption.

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2. Experimental

2.1. Substrate preparation

Commercially available n-type silicon wafers of (1 0 0) orientation are used for adsorption study. These substrates (1 cm × 1 cm) are rinsed by milliQplus water, sonicated in ethanol and dried in a flow of nitrogen. The wafers are then soaked in 10:1 deionized water: HF solution for 30 s to remove native oxide layer. The wafers are then soaked in a piranha solution (7:3 concentration H_2SO_4:H_2O_2) for 30 min at 60 °C to grow fresh oxide layer. Piranha solutions are extremely energetic and remove organic impurities from the substrates [19]. At the same time they help to grow a thin oxide layer with lots of silanol (Si–OH) groups [20]. These groups are needed for adsorption. These wafers are then rinsed with deionized water, dried in the flow of nitrogen and used for adsorption study.

2.2. Preparation of mesoporous SBA-15

Mesoporous SBA-15 was synthesized by a standard method [21,22]. 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.

2.3. Adsorption study

Methanol (99.8%) obtained from Euclid is used for adsorption study. Few pieces of Si(1 0 0) with thin oxide layer and mesoporous SBA-15 powder of 0.3 g quantity are immersed in 10 ml methanol solvent for 24 h with intermediate stirring. After 24 h the silicon wafers are removed from methanol solvent and used for further characterization. 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. For adsorption kinetic study contact angle measurement technique is used. Si(1 0 0)/SiO_2 wafer is dipped in the solvent to start the adsorption reaction and removed from the solvent to terminate the reaction. The contact angle is measured and again the wafer is dipped to start the adsorption reaction.

2.4. Characterization

2.4.1. Contact angle measurement

The contact angle of methanol adlayer on Si(1 0 0)/SiO_2 was measured by using water sessile drop on RAME-HART NRL-Model CA goniometer. The contact angle was measured to test the adsorption as well as for the study of thermal stability. For thermal stability study, Si(1 0 0)/SiO_2 wafer with methanol layer was annealed for 5 min at different temperatures in air and contact angle measured after cooling to ambient temperature. The contact angle was measured at three different locations and the results were averaged.

2.4.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR of Si(1 0 0)/SiO_2 wafer and SBA-15 was carried out before and after methanol adsorption on Perkin-Elmer 1615 FTIR spectrometer equipped with DTGS detector and Ge-coated KBr beam splitter. The spectrum was recorded at a resolution of 4 cm^{-1} over 256 scans at ambient temperature.

2.4.3. X-ray photoelectron spectroscopy (XPS)

XPS of Si(1 0 0) with thin oxide layer and SBA-15 was done before and after methanol adsorption using VG Micro Tech ESCA 3000 instrument at a pressure, below 10^{-9} Torr. The samples were 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 [23] software to obtain peak information. A Shirley's base line was used in the fitting process.

2.4.4. 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. Adsorption kinetics

Contact angle measurement technique is used to study the adsorption kinetics of methanol on Si(1 0 0)/SiO_2 [24]. Si(1 0 0) wafer with a thin oxide layer is dipped in the methanol solvent to start the adsorption reaction and removed from the solvent to terminate the reaction. The contact angle is measured and again the wafer is dipped to start the adsorption reaction. The variation of contact angle as a function of dipping time (adsorption reaction time) is shown in Fig. 1a. The initial adsorption is very fast. The contact angle value reaches to a value of ~36° in about 60 s of adsorption reaction time, it reaches to ~44° in 10 min of adsorption time, and thereafter it increases slowly and reaches to a value of ~55° in 24 h of adsorption reaction time. The fractional coverage of methanol, θ, a unit less quantity, which also represents the fraction of available sites that have reacted is obtained by dividing the contact angle values with the maximum contact angle value obtained in 24 h dipping time. The results are shown in Fig. 1b (scattered graph). The Langmuir kinetic equations are used to analyze the data. According to Langmuir
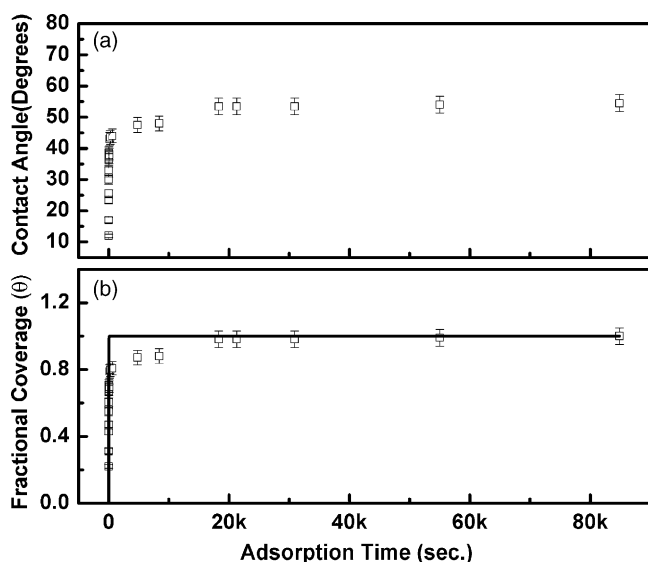
Fig. 1. (a) Variation of water contact angle as a function of adsorption time of methanol adsorption on Si(1 0 0)/SiO$_2$; (b) Variation of fractional coverage as a function of adsorption time of methanol adsorption on Si(1 0 0)/SiO$_2$, solid line is a fit to Langmuir isotherms.

isotherms the rate of surface reaction is given by

$$\frac{d\theta}{dt} = k_a (1 - \theta) C - k_d \theta \tag{1}$$

where θ is the fraction of surface covered and $(1 - \theta)$ the fraction of surface exposed, C the methanol concentration and k_a and k_d are the adsorption and desorption rate constants, respectively. Integration of Eq. (1) gives the time dependence of the adsorption [25].

$$\theta(t) = K' \left[1 - \exp(-k_{obs}t) \right] \tag{2}$$

where

$$K' = \frac{C}{C + (k_d/k_a)} \tag{3}$$

and

$$k_{obs} = k_a C + k_d \tag{4}$$

Since, we are using pure methanol solvent for adsorption study; the concentration 'C' is very large, therefore we can put $k_d = 0$ as an approximation [26]. With this, Eq. (1) becomes:

$$\theta(t) = 1 - \exp(-k_{obs}t) \tag{5}$$

and Eq. (4) becomes:

$$k_{obs} = k_a C \tag{6}$$

Our experimental data in Fig. 1b is fitted with Eq. (5), using k_{obs} as fitting parameter. The fitting is fairly good with a chi-square value of 0.03. The, k_{obs} value obtained is $0.068 \pm 0.0016\,s^{-1}$. The adsorption rate constant, k_a, obtained using this value in Eq. (6) is $0.0021\,M^{-1}\,s^{-1}$. This proves methanol adsorption on Si(1 0 0)/SiO$_2$. Fitting with Eq. (5) is same as fitting with Eq. (2) with $K' = 1$. Any deviation from this value gives a bad fit.

Therefore it confirms desorption rate constant, $k_d \approx 0$. In our previous study of toluene adsorption on Si(1 0 0)/SiO$_2$ we got a very small value of adsorption constant, $k_a = 0.000054\,M^{-1}\,s^{-1}$ [26]. Adsorption of methanol is through its –OH group [10–18] and adsorption of toluene is through aromatic electrons [27]. Relatively large value of adsorption constant in case of methanol adsorption may suggest adsorption through –OH group is stronger than through aromatic electrons in toluene. Toluene with a benzene ring has more chemical stability then methanol. Since adsorption is a type of chemical reaction, the remarkable stability of benzene ring in toluene might affect the adsorption reaction. More energy may be required for toluene then methanol for adsorption. This could be another reason for larger value of adsorption constant in case of methanol then in case toluene.

3.2. Fourier transform infrared spectroscopy

FTIR spectra of Si(1 0 0)/SiO$_2$ wafer is taken before and after methanol adsorption. Fig. 2 shows the spectra after background subtraction. The assignments of the observed frequencies of vibrational modes are listed in Table 1. The IR band appearing at 2961 and 2882 cm^{-1} are attributed to methoxy, methyl C–H asymmetric/symmetric stretch. The band at 2085 cm^{-1} (inset a) shows the formation of silicon polyhydride (SiH$_2$) [28]. The presence of C–H stretching band at 2820 cm^{-1} (inset b) shows the formation of methoxy silicon (SiOCH$_3$) [18]. FTIR results also indicate presence of carboxylate species. The IR band at 1535 and 1381 cm^{-1} are the features associated with ν_{as} and ν_s modes of carboxylate. The band at 1705 cm^{-1} also indicates the presence of carboxylic acid. The band at 3161 and 3526 cm^{-1} show the formation molecular water. The bands at 3692 and 3776 cm^{-1} indicate the presence of free silanol groups.

To explain the formation of methoxy silicon (SiOCH$_3$), silicon polyhydride (SiH$_2$), molecular water and hydroxyl (–OH) species on the Si(1 0 0)/SiO$_2$ surface a simple model as shown in Fig. 3 is proposed. Fig. 3a) shows Si(1 0 0)/SiO$_2$ surface and
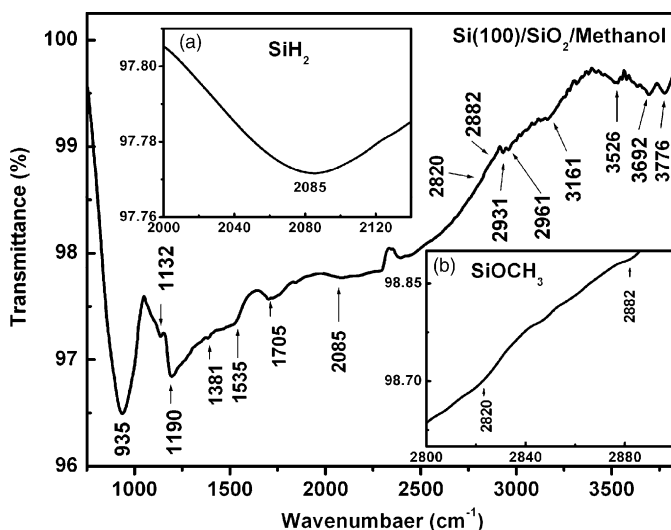

Fig. 2. FTIR spectra of methanol adsorbed on Si(1 0 0)/SiO$_2$, inset shows: (a) SiH$_2$ bonding; and (b) SiOCH$_3$ bonding.

Table 1
Observed frequencies for methanol adsorption on Si(1 0 0)/SiO$_2$ and vibrational assignments

IR frequency	Assignment
935	Stretching vibrations of free silanol groups on SiO$_2$
1132, 1190	Asymmetric stretching vibrations of Si–O–Si bridging sequences
1381	Carboxylate symmetric stretch
1535	Carboxylate asymmetric stretch
1705	Carboxylic acid
2085	Stretching modes of SiH$_2$
2820	Methoxy, methyl C–H stretch
2882	Methoxy, methyl C–H symmetric stretch
2931	Overtones or combinations of methyl deformation modes
2961	Methoxy, methyl C–H asymmetric stretch
3161, 3526	Molecular water
3692, 3776	Free Si–OH groups

four methanol molecules, M1-M4 before adsorption. Fig. 3b) shows Si(1 0 0)/SiO$_2$ surface after methanol adsorption.

A thin oxide layer is grown on Si(1 0 0) surface using piranha treatment, therefore, Si(1 0 0)/SiO$_2$ surface can be assumed to consist of sites with vacancies (site i, ii, iii, and iv) and sites occupied by hydroxyl groups (site vi and vii) as shown in Fig. 3a. The vacant sites are the active sites for surface reaction. The vacant sites will have affinity for oxygen or/and hydrogen. Since methanol has oxygen, its (M1 and M2) interaction with silica surface at vacant site (i and ii) leads to its dissociation into methoxy (–OCH$_3$) and hydrogen [1]. Methoxy groups adsorb to silicon forming SiOCH$_3$ (site i and ii, Fig. 3b) and hydrogen's adsorb to vacant site iii where two vacancies are available forming silicon polyhydride. A single methoxy silicon can also form as in site iv and a single hydrogen can bond to site v as shown in Fig. 3b, forming a silanol group due to adsorption of methanol molecule, M3. If methanol (M4) interacts with a location where there are majority of silanol groups (site vi and vii) then it gets dissociated

into –H and –OCH$_3$ [28]. Silanol group (Si–OH) also dissociates its –OH group (Site vi). Methoxy group adsorbs to silicon forming SiOCH$_3$ (site vi, Fig. 3b) and –H from methanol and –OH from silanol combine to form molecular water (Fig. 3b). This explains the generation of methoxy silicon, silicon polyhydride, molecular water and hydroxyl groups. Generation of carboxylate or carboxylic acid species can be explained by using the model of Davis and Barteau [29]. According to this model, methanol sequentially losses hydrogen and eventually yield CO. The model has been proved to be valid for methanol reaction on all the faces of group VIII and 1b metals. Such a model may work for Si(1 0 0)/SiO$_2$ surface also. Particularly at locations, where large number of vacancies are present, methanol can dissociate all its hydrogen resulting in the generation of CO. CO thus generated can interact with silanol groups to give carboxylate (–COOH) or it can interact with methanol to give carboxylic acid (CH$_3$COOH). Since a thin oxide layer is generated on Si(1 0 0) using piranha solution, the surface of Si(1 0 0)/SiO$_2$ can have silicon, oxygen and silanol endings. Therefore, different kinds of adsorption mechanisms can work at different locations of the surface. Methanol adsorption on Si(1 0 0)/SiO$_2$ is a kind of surface chain reaction. The FTIR results are the observations at equilibrium after 24 h of adsorption reaction. Adsorption of methanol thus produces SiOCH$_3$, SiH$_2$, and carboxylate species. Hydroxyl (–OH) groups are also generated but used again and again in the adsorption reaction. At the end of 24 h of reaction some molecular water and hydroxyl groups may still remain on the substrate as residues. Molecular water may remain on the substrate due to its physisorption.

SBA-15 is a pure SiO$_2$ material and since no piranha solution treatment is given the surface will have only natural silanol groups. Unlike Si(1 0 0)/SiO$_2$ surface, the surface of SBA-15 can have only oxygen and silanol endings. XPS results (Section 3.3) show a large integrated area for O 1s peak of SBA-15 as compared with Si(1 0 0)/SiO$_2$ surface, indicating surface of SBA-15 with more oxygen endings. Therefore the mechanism that works for methanol adsorption on Si(1 0 0)/SiO$_2$ surface may not work for SBA-15. Particularly the mechanism of methoxy generation at the silicon ending (site i and ii, Fig. 3) may not work for methanol adsorption on SBA-15. An FTIR spectrum of SBA-15 taken before and after methanol adsorption is shown in Fig. 4(a) and (b), respectively. After methanol adsorption, methyl C–H asymmetric and symmetric stretching bands are observed at 2964 and 2862 cm^{-1} and methyl C–H asymmetric bending is observed at 1466 cm^{-1} demonstrating methanol adsorption. The presence of C–H stretching band at 2811 cm^{-1} (inset, Fig. 4b) that is associated with methoxy (O–CH$_3$) shows generation of methoxy species due to methanol adsorption [18]. The FTIR spectrum of the parent SBA-15 also shows a narrow band at 3731 cm^{-1} and a broad low-frequency band at 3400 cm^{-1}. The band at 3731 cm^{-1} can be assigned to the symmetrical stretching vibration mode of O–H from isolated silanol (Si–OH) groups. The broad low frequency band at 3400 cm^{-1} is due to those silanol groups or silanol nests with cross hydrogen bonding interactions in between [30–32]. After methanol adsorption the bands at 3400 and 3731 cm^{-1} get broadened indicating the involvement of silanols in the adsorption mechanism.
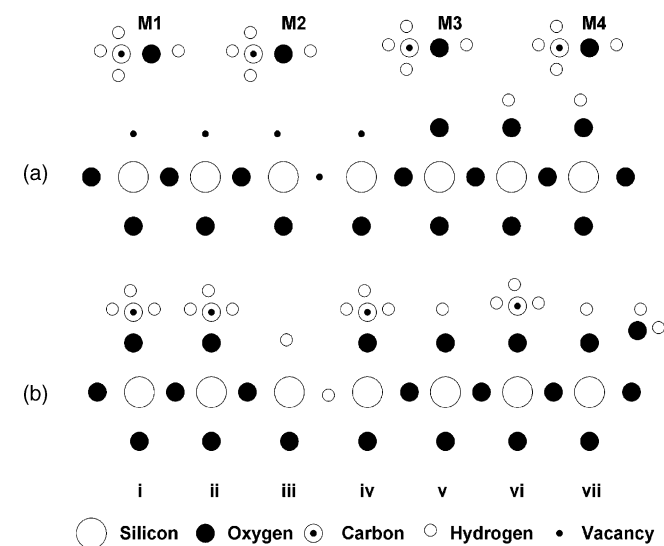

Fig. 3. A model that explains generation of methoxy silicon, silicon polyhydride, hydroxyl groups and molecular water as a result of methanol adsorption on Si(1 0 0)/SiO$_2$.
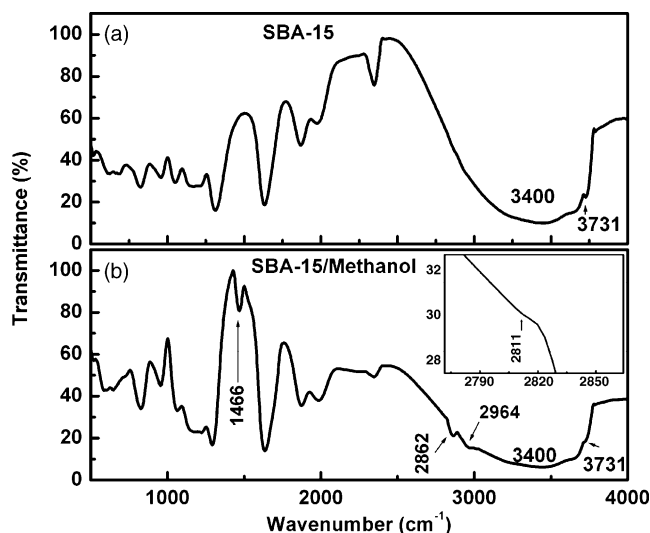
Fig. 4. FTIR spectra of SBA-15: (a) before; and (b) after methanol adsorption.

3.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectra in the C 1s binding energy range before and after methanol adsorption on Si(1 0 0)/SiO$_2$ for adsorption duration of 24 h is shown in Fig. 5. Similar data for methanol adsorption on SBA-15 is shown in Fig. 6. In both figures, part (a) shows the XPS spectra of sample before methanol adsorption, part (b) shows the spectra after adsorption and part (c) shows the contribution from methanol alone, obtained after subtracting before adsorption spectra from after adsorption spectra. The results clearly show methanol adsorption on both Si(1 0 0)/SiO$_2$ and SBA-15. The integrated area of C 1s spectra increases by ∼2.26 and ∼2 times after adsorption of methanol on Si(1 0 0)/SiO$_2$ and SBA-15, respectively. The integrated area of C 1s spectra due to methanol adsorption on Si(1 0 0)/SiO$_2$ is (∼16,550) larger by 4.8 times the methanol adsorption on SBA-15 (∼3400). Though SBA-15 is a large sur-
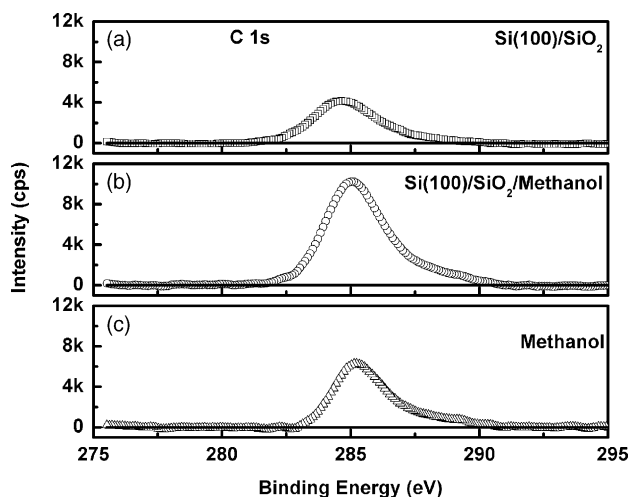

Fig. 5. X-ray photoelectron spectra showing C 1s binding energy range of Si(1 0 0)/SiO$_2$: (a) before; (b) after methanol adsorption; and (c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption data. Adsorption time = 24 h.
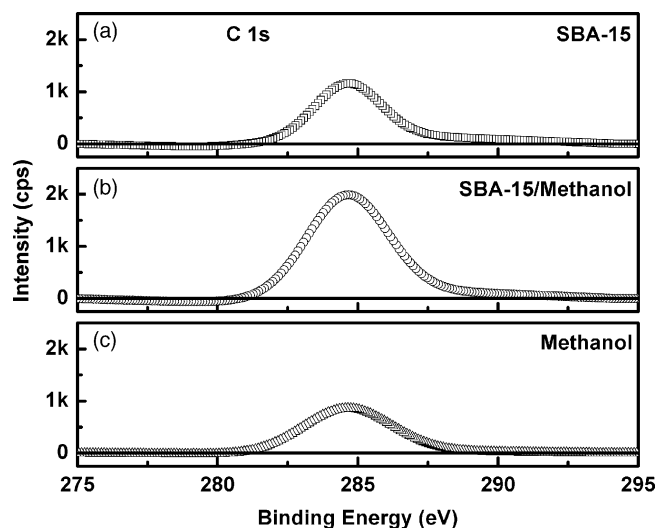

Fig. 6. X-ray photoelectron spectra showing C 1s binding energy range of mesoporous SBA-15: (a) before; (b) after methanol adsorption; and (c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption data. Adsorption time = 24 h.

face area material the adsorption is more on silicon substrate. The possible reason for this could be presence of large amount of silanols (Si–OH) due to treatment of silicon substrate in piranha solution [20]. Such treatment is not given to SBA-15. This result implies that the presence of –OH groups on the surface increases the adsorption. The –OH group in methanol is known to take part in the mechanism of adsorption [10–18]. The presence of –OH groups, on Si(1 0 0)/SiO$_2$ surface are mandatory for adsorption of organic compounds like octadecyltrichlorosilane (OTS) [2]. Adsorption of OTS is also through –OH groups. This suggests that the adsorption mechanism of methanol is similar to OTS adsorption. There are different adsorption mechanisms for methanol. Methanol adsorbs via oxygen atom and then dissociates into Si–OCH$_3$ and H [1]. Another mechanism suggests dissociation of methanol into OH and CH$_3$ and adsorption of these fragments [5]. A simple model proposed as shown in Fig. 3 also explains more methanol adsorption on silicon substrate then on mesoporous SBA-15. The C 1s peak width in case methanol adsorption on SBA-15 is (≈3.16 eV) larger than that adsorbed on Si(1 0 0)/SiO$_2$ (≈2.2 eV). This could be due to discrete nature of SBA-15 due to which methanol adsorbed will be less densely packed as compared with Si(1 0 0)/SiO$_2$.

X-ray photoelectron spectra in the O 1s binding energy range before and after methanol adsorption on Si(1 0 0)/SiO$_2$ for adsorption duration of 24 h is shown in Fig. 7. Similar data for methanol adsorption on SBA-15 is shown in Fig. 8. In both figures, part (a) shows the XPS spectra of sample before methanol adsorption, part (b) shows the spectra after adsorption and part (c) shows the contribution from methanol alone, obtained after subtracting before adsorption spectra from after adsorption spectra. The O 1s spectra observed in case of Si(1 0 0)/SiO$_2$ before methanol adsorption can be attributed to thin SiO$_2$ layer present on silicon substrate. SBA-15 is a pure SiO$_2$ material and therefore the O 1s spectra can be attributed to oxygen in SiO$_2$. Before methanol adsorption the integrated area of O 1s
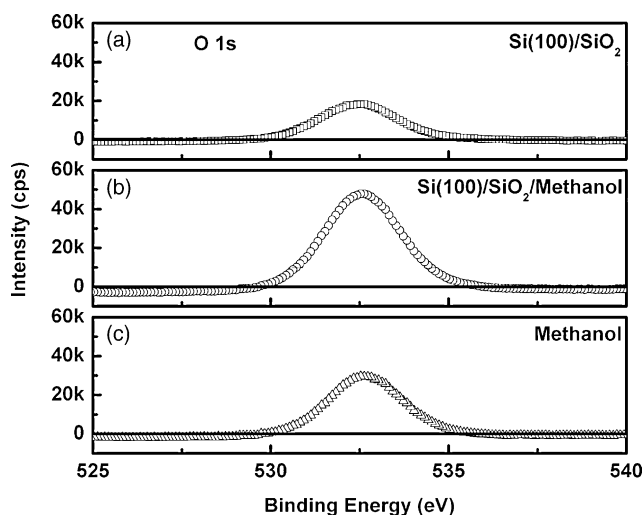
Fig. 7. X-ray photoelectron spectra showing O 1s binding energy range of Si(1 0 0)/SiO₂: (a) before; (b) after methanol adsorption and (c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption data. Adsorption time = 24 h.

Fig. 9. X-ray photoelectron spectra showing Si 2p binding energy range of Si(1 0 0)/SiO₂: (a) before; (b) after methanol adsorption; and (c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption data. Adsorption time = 24 h.

spectra of SBA-15 is (∼286000) 5.5 times larger than that of Si(1 0 0)/SiO₂ (∼52,000). This can be due to pure SiO₂ of SBA-15 as compared with thin SiO₂ layer on silicon substrate. This also suggests that the SBA-15 surface has more oxygen endings then silicon substrate. This result supports our model as shown in Fig. 3 and helps in the explanation of more methanol adsorption on silicon substrate then on SBA-15. The integrated area of O 1s spectra increases by ∼2.5 and ∼1.2 times after methanol adsorption on Si(1 0 0)/SiO₂ and SBA-15, respectively. The integrated area of O 1s spectra due to methanol adsorption on Si(1 0 0)/SiO₂ is (∼80,500) larger by ∼1.7 times the methanol adsorption on SBA-15 (∼48,000). Like C 1s spectra O 1s spectra also shows more methanol adsorption on Si(1 0 0)/SiO₂ then on SBA-15. Therefore, the justification given their also holds here.

X-ray photoelectron spectra in the Si 2p binding energy range before and after methanol adsorption on Si(1 0 0)/SiO₂ for adsorption duration of 24 h is shown in Fig. 9. Similar data for methanol adsorption on SBA-15 is shown in Fig. 10. In both figures, part (a) shows the XPS spectra of sample before methanol adsorption, part (b) shows the spectra after adsorption and part (c) shows the contribution from methanol alone, obtained after subtracting before adsorption spectra from after adsorption spectra. XPS spectra of Si(1 0 0)/SiO₂ shows two peaks. The peak observed at ≈ 99 eV is due to elemental silicon (Si^0) and the peak observed at ≈ 103 eV is due to SiO₂ (Si^{+4}). In case SBA-15 only Si^{+4} peak is observed because it is pure SiO₂ material. After methanol adsorption on Si(1 0 0)/SiO₂ the integrated area of Si^0 and Si^{+4} peaks increase by ∼3.6 and 2.4
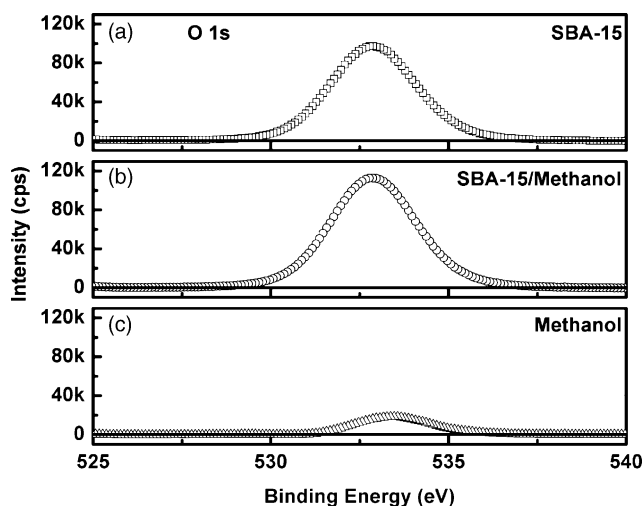

Fig. 8. X-ray photoelectron spectra showing O 1s binding energy range of mesoporous SBA-15: (a) before; (b) after methanol adsorption; and (c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption data. Adsorption time = 24 h.
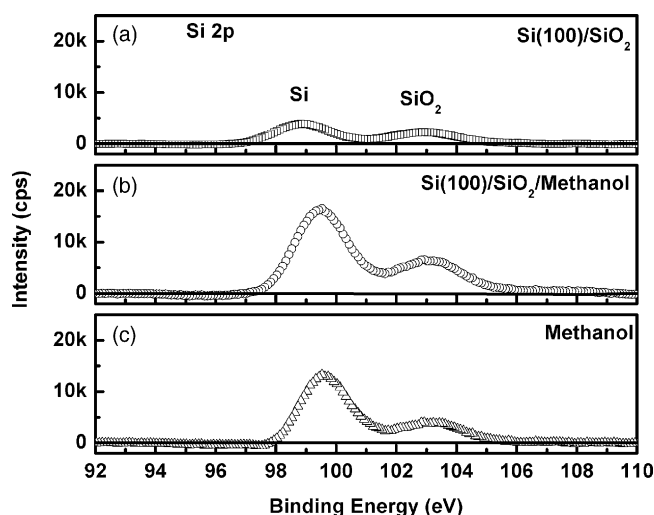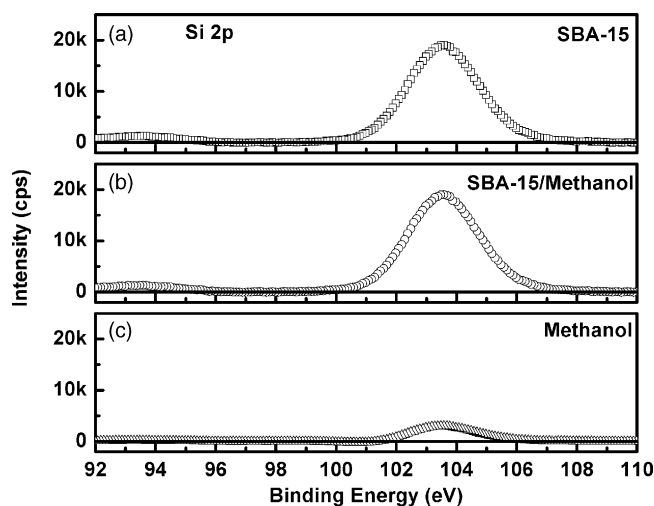

Fig. 10. X-ray photoelectron spectra showing Si 2p binding energy range of mesoporous SBA-15: (a) before; (b) after methanol adsorption; and (c) contribution from methanol obtained after subtracting before adsorption spectra from after adsorption data, Adsorption time = 24 h.

Table 2
XPS peak parameters before and after methanol adsorption on Si(1 0 0)/SiO$_2$ and SBA-15

Peak	Peak parameter	Si(1 0 0)/SiO$_2$	Si(1 0 0)/SiO$_2$/methanol	SBA-15	SBA-15/methanol
C 1s	BE (eV)	284.6	285	284.6	284.6
	FWHM	2.51	2.26	2.76	3.38
	Integrated area	13340	30100	3700	7400
O 1s	BE (eV)	532.4	532.54	532.83	532.83
	FWHM	2.61	2.53	2.77	2.79
	Integrated area	52000	132000	286000	332000
Si 2p (Si^0)	BE (eV)	98.86	99.49	–	–
	FWHM	2.17	2.02	–	–
	Integrated area	9400	34000	–	–
Si 2p (Si^{+4})	BE (eV)	102.81	102.97	103.41	103.54
	FWHM	2.64	2.45	2.78	2.74
	Integrated area	6000	14600	52000	60000

times, respectively. In case of methanol adsorption on SBA-15, Si^{+4} peak integrated area increases but marginally. Methanol molecule does not contain silicon but still the integrated area of silicon peaks increase after methanol adsorption. The reason for this could be due to formation of new bonds viz., methoxy silicon (SiOCH$_3$) and silicon polyhydride (SiH$_2$). A large increase of integrated area of silicon peaks in case of methanol adsorption on Si(1 0 0)/SiO$_2$ and a marginal increase in case of SBA-15 can be explained by the model shown in Fig. 3. FTIR results show formation of methoxy silicon on SBA-15 due to methanol adsorption but do not show silicon polyhydride formation. On silicon substrate methanol adsorption can be due to –OH groups as well as due to vacancies at the silicon endings. For generation of silicon polyhydride vacancies at silicon endings are necessary. Since SBA-15 lacks such endings, the adsorption can be only at naturally available silanols. Therefore, methanol adsorption on SBA-15 generates only methoxy silicon. And since SBA-15 has a low density of silanols as compared with silicon substrate the density of SiOCH$_3$ will also be low. XPS results are summarized in Table 2.

3.4. Thermal stability

Fig. 11 shows water contact angle as a function of annealing temperature for methanol adsorbed on Si(1 0 0)/SiO$_2$. The contact angle value increases slightly with increase of annealing temperature, reaches to a maximum value of 61° at a temperature of 262 °C and then starts decreasing. The contact angle value becomes 25° (near hydrophilic) after annealing at 450 °C. The slight increase of contact angle value could be due to realignment of adsorbed methanol. The methanol adsorbed on Si(1 0 0)/SiO$_2$ is therefore, stable up to a temperature of 262 °C and decomposes or detaches from the surface in the temperature range 262–450 °C. This result also indicates that the methanol adsorption is due to chemisorption reaction because physisorbed methanol will boil and evaporate at the boiling point of methanol (∼65 °C). Consequently, methanol adlayer can be used to change the surface properties of Si(1 0 0)/SiO$_2$.

Thermogravimetric analysis of SBA-15 before and after methanol adsorption is also shown in Fig. 11. TGA pattern

of SBA-15 shows two weight loss regions. 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 water molecules [33,34]. The initial weight loss up to a temperature of 120 °C can be associated with breakup of hydrogen bonded network and removal of adsorbed water from silica. The second stage of weight loss from 120 to 400 °C can be associated with desorption of the adsorbed water as well as water generated by the condensation of part of free silanols [35]. After methanol adsorption the TGA weight loss pattern changes drastically between the temperature 217 and 363 °C. The derivative weight percentage starts increasing at a temperature 217 °C and reaches to a maximum value at ∼262 °C and then starts decreasing. This pattern is analogous to contact angle thermal stability data. The methanol desorption stars at ∼262 °C and continuous up to 450 °C. The TGA data and contact angle data closely match. The results match with the reported thermal stability data of adsorbed methanol [36].
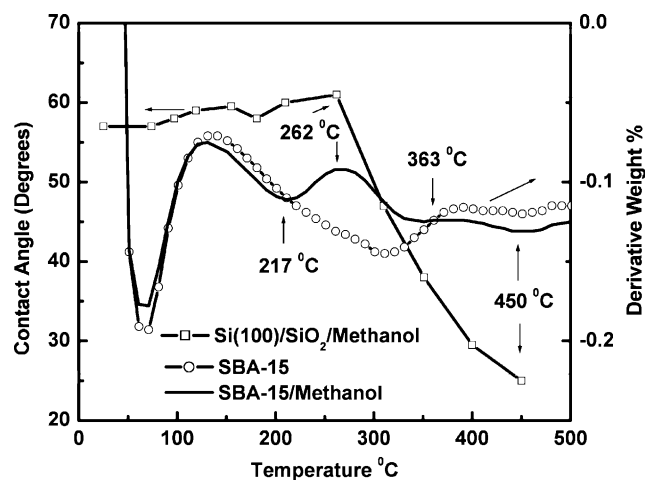

Fig. 11. Variation of water contact angle as a function of annealing temperature of methanol adsorbed on Si(1 0 0)/SiO$_2$ and thermogravimetric analysis of SBA-15 before and after methanol adsorption.

4. Conclusions

All our measurements clearly show methanol adsorption on Si(1 0 0)/SiO$_2$ and mesoporous SBA-15. The initial adsorption is very fast. The contact angle value increases from 12° (bare silicon) to 36° in about 60 s, 44° in 10 min and thereafter it increases slowly and reaches to a value of 55° in 24 h of adsorption reaction time. FTIR results show formation of methoxy silicon (SiOCH$_3$), silicon polyhydride (SiH$_2$), carboxylate, molecular water and hydroxyl groups on Si(1 0 0)/SiO$_2$ surface and only methoxy silicon on SBA-15. The XPS results confirm methanol adsorption and support FTIR observations. The methanol adlayers are found to be thermally stable up to a temperature of ∼262 °C on both Si(1 0 0)/SiO$_2$ and SBA-15 and decompose between 262 and 450 °C. Methanol adsorption can be useful in microelectronics for the growth of ultra thin SiO$_2$ layer on silicon substrate by cleavage of silanol groups. It is also useful for surface modification up to a temperature of 262 °C.

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