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## ADSORPTION OF WATER AND BENZENE VAPOUR IN MESOPOROUS MATERIALS

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### Abstract

Mesoporous materials have attracted the attention of many researchers due to the potential applications promised by the materials. This article discusses adsorption of water and benzene vapour in mesoporous materials (mesoporous silica: MCM-41, MCM-48 and their modification). MCM-41 and MCM-48 were synthesized hydrothermally at 100 °C using cethyltrimethylammonium chloride or dodecyltrimethylammonium bromide for MCM-41 (C16) or MCM-41 (C12) respectively and a mixture of cethyltrimethylammonium bromide and Triton X-100 for MCM-48 as templates. Their modifications were conducted by silylation of MCM-41 (C16) and MCM-48 with trimethylchloro silane (MCM16-TMCS and MCM48-TMCS) and t-butyldimethylchloro silane (MCM16-TBDMCS and MCM48-TBDMCS). Results showed that MCM-41 and MCM-48 materials had hydrophobic features which were shown in the small amount of water adsorption at low  $P/P^0$ . The hydrophobicity of samples used in this study decrease in the sequence: MCM-41 (C16) > MCM-48 > MCM-41 (C12). The hydrophobicity increased when MCM-41 and MCM-48 were silylated with TMCS or TBDMCS. All unsilylated MCM materials show higher affinity to benzene at low  $P/P^0$  than the silylated samples. The results of water and benzene adsorption showed that silylated samples are promising candidates as selective adsorbents for organic compounds.

*Keywords:* Adsorption, water, benzene, MCM-41, MCM-48

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### 1. Introduction

Porous materials have attracted the attention of researchers due to their wide application for both commercial interest in chemical separations along with heterogeneous catalysis and scientific interest in the challenges posed by their synthesis, processing, and characterization.

Porous materials are most frequently characterized in terms of pore sizes derived from gas sorption data. IUPAC conventions [1] divided pores according to their diameter into 3 main classes as follows: micropores have diameters less than about 2 nm; mesopores have diameters between 2 and 50 nm; and macropores have diameters greater than about 50 nm.

In 1992, a new family of mesoporous materials designated as the M41S family was discovered by Mobil Corporation [2]. Since then, several additional mesoporous materials have been discovered, such as, FSM-16 [3], SBA-1, 2, 3 [4], MSU-1 [5], KIT-1 [6] SBA-11, 12, 15 [7], and SNU-2 [8].

These materials attracted the attention of many scientists working in areas, such as, the synthesis of

zeolites and related materials, catalysis and materials science. Therefore a large number of potential applications of the materials have been developed in the area of catalysis, adsorption and advanced materials.

M41S materials are mesoporous silica. There are three main classes of M41S materials firstly reported by Mobil group; a hexagonal phase denoted as MCM-41, a cubic phase with the space group of *Ia3d* designated as MCM-48 and a non-stable lamellar phase, MCM-50 [2].

This article discusses the vapour-solid interaction between adsorbates (water and benzene) and mesoporous materials, (MCM-41, MCM-48 and their modification).

### 2. Methods

**Synthesis of MCM-41 and MCM-48.** MCM-41 (C16) was synthesized following the procedure of Kim, *et. al.* [9]. A gel mixture of 46.9 g of 1 M aqueous NaOH and 14.3 g of Ludox HS40 were used to prepare a clear solution of sodium silicate with the Na/Si ratio of 0.5. The mixture was heated under stirring for 2 hours at 353 K. In a polypropylene bottle, 0.29 g of 28 % (w/w)  $\text{NH}_3$  solution and 20 g of 25 % (w/w) CTAC solution were

mixed. The cold sodium silicate solution was then added dropwise to the mixture, under vigorously stirring at room temperature. After being stirred for one more hour, the gel mixture was heated at 370 K for 24 h. The mixture in the polypropylene bottle was then cooled to room temperature, and pH of the mixture was adjusted to 10.2 by using 30 % (w/w) acetic acid under vigorous stirring. After the pH adjustment, the mixture was heated again to 370 K for 24 h and cooled to room temperature. The pH adjustment and the heating process was repeated twice more. The precipitated material was then filtered, washed with double distilled water and dried in an oven at 370 K.

To improve the hydrothermal stability, 2.74 g of NaCl was added subsequently to the reaction mixture, after the first pH adjustment and heating process, then the mixture was heated again at 370 K for 24 h and cooled to room temperature before the second pH adjustment and heating process [10].

The product was washed with ethanol-hydrochloric acid mixture (0.1 mole of HCl/L of ethanol) by stirring at room temperature for 30 min to remove the template agent. At this stage, most of template was removed. Calcination was performed in air under static conditions using a muffle furnace. The temperature was increased from room temperature to 770 K over 10 h and maintained at 770 K for 24 h [9].

To synthesize MCM-41 (C12), the above procedure was used. However, 4.5 g of DTAB dissolved in 16.82 g water was utilized instead of 20 g of 25 % CTAC as the template agent.

The following procedure [6] was used to synthesize MCM-48. 14.3 g of Ludox HS40 solution was mixed with 45.25 g of 1 M NaOH solution. The surfactant mixture was prepared by dissolving 6.12 g of CTAB and 1.34 g of Triton X-100 simultaneously in 83.47 g of distilled water with heating. After cooling the sodium tetrasilicate solution and the surfactant solution to room temperature, both solutions were mixed quickly in a large polypropylene bottle. The bottle was immediately capped and shaken vigorously. The gel mixture obtained was heated under static condition at 373 K for 24 h. At this stage, the surfactant-silica mesophases were formed. To avoid separation of the mesophases at an early stage of heating, the bottle containing the mixture was sometimes agitated. The reaction mixture was then cooled to room temperature and acetic acid (30 %) was added subsequently into the mixture in order to adjust the pH to 10. After the pH adjustment, the mixture was heated again at 373 K for 24 h and cooled to room temperature. 2.95 g of NaCl was added into the mixture and the mixture was heated at 373 K for 1 more day. Synthesized MCM-48 was then filtered, washed with double distilled water and dried at 393 K in an oven.

The surfactant was removed from the product by washing with HCl-ethanol mixture, 1 g of MCM-48 was washed with 25 mL of 0.1 M HCl in 50 % aqueous ethanol solution. The precipitate was calcined in air under static condition in a muffle furnace. The temperature was raised from room temperature to 823 K at a ramp rate of 1 K/min and maintained at 823 K for 18 h.

**Silylation with TBDMCS.** Silylation with TMCS was done using the procedure of Fraile *et. al.* [11] with modification as follow: Calcined MCM-41 or MCM-48 was dried at 573 K under a vacuum system for 24 h. About 1 g of the dehydrated sample was weighed into a round bottom flask under dry condition. The dried sample was then suspended in TMCS solution (0.8 mL of TMCS in 40 mL of dried toluene/g sample) in a dry box. The mixture was refluxed overnight, filtered, washed with 3 x 50 mL of dichloromethane and dried at 413 K.

**Silylation with TBDMCS.** A modified procedure of Ren *et. al.* [12] was used to produce mesoporous materials silylated with TBDMCS. Calcined MCM-41 or MCM-48 was evacuated at 573 K for 24 h. 1 g of the dehydrated sample was weighed into a round bottle flask under dry atmosphere. 30 mL of dried toluene and 3 mL of triethylamine was added into the dried sample in a nitrogen dry box. A solution of TBDMCS (2.81 g TBDMCS in 10 mL of dried toluene) was added to suspend the sample. The suspension was then refluxed overnight, filtered and washed with 150 mL of toluene, then chloroform, tetrahydrofuran, acetonitrile and methanol, sequentially. The resulting white solid was then dried at 413 K.

Adsorption experiments were performed in a vacuum line where the vapour of adsorbates was allowed to be in contact with the mesoporous materials. A microbalance was used to monitor the amount of vapour adsorbed.

### 3. Results and Discussion

#### Adsorption of Water Vapour in Materials

**Adsorption of water vapour in MCM-41.** Water vapour was used to study the hydrophobicity features of mesoporous materials. Figure 1 shows the adsorption isotherm of water in MCM-41 materials, prepared from CTAC and DTAB, before silylation. Both materials exhibits Type V water adsorption isotherm, indicating an initial repulsive character followed by capillary condensation at higher pressures. Similar results have been reported by other researchers [13-15]. Monolayer adsorption on the inner and the outer surface occurred at low  $P/P^0$ . The low amount of monolayer adsorption suggests a weak interaction between the surface and water molecules; that is, some hydrophobic character.

According to Zhao and Lu [14], hydrogen bonding between the surface silanol groups and water molecules caused water adsorption over MCM-41 materials. This theory is supported by the FTIR spectrum of MCM-41 (Figure 2). The broad peak centered at  $3396\text{ cm}^{-1}$  with a shoulder at  $3638\text{ cm}^{-1}$  is attributed to physically adsorbed water associated with hydrogen bonding. Generally, the maximum amount of water adsorbed in MCM-41 (C16) is higher than that in MCM-41 (C12). This difference in water adsorption is due to difference in pore diameter of the materials, which can clearly be seen from the inflection point of adsorption curve for MCM-41 (C16), which is 0.12 higher than that for MCM-41 (C12). These results are in agreement with the adsorption isotherms of nitrogen in both samples reported in elsewhere [16].

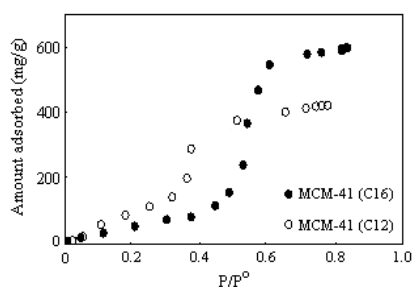


Figure 1. Water adsorption isotherms of unsilylated MCM-41 materials; (a) MCM-41 (C16) and (b) MCM-41 (C12)

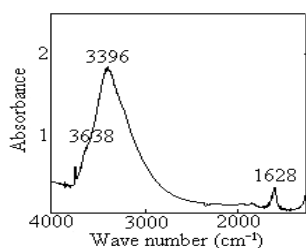


Figure 2. FTIR spectrum of MCM-41

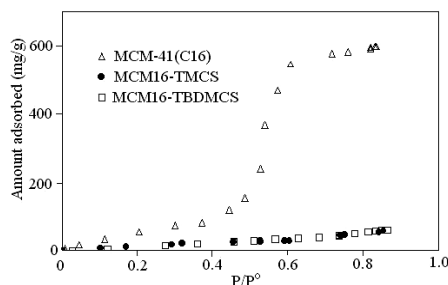


Figure 3. Water adsorption isotherms of silylated MCM-41 samples with TMCS and TBDMCS together with the parent sample

The amount of water adsorbed below the inflection point in MCM-41 (C12) is more than that in MCM-41 (C16), showing that MCM-41 (C16) is more hydrophobic than MCM-41 (C12).

Adsorption isotherms of silylated MCM-41 materials and the parent sample are illustrated in Figure 3. The type of isotherms for silylated MCM-41 with TMCS is Type III without any observation of capillary condensation, which has been observed in an earlier study [14,17]. Similar isotherm, Type III, is also observed in MCM16-TBDMCS. The amount of water adsorbed in the silylated samples is extremely low, not only at low relative pressure but also at high relative pressure. There was no great apparent increase in the adsorption even at  $P/P^0 = 0.85$ , as observed in previous work [14, 17-18]. The results indicate that both internal and external surface of samples becomes more hydrophobic after silylation either with TMCS or TBDMCS. According to Zhao *et. al.* [7], the small amount of water, adsorbed by silylated samples, is probably caused by the interaction between the residual SiOH sites through hydrogen bonding and/or the strained siloxane bridged by rehydroxilation.

**Adsorption of water vapour in MCM-48.** Water adsorption isotherms of MCM-48 before and after silylation are illustrated in Figure 4.

Like in MCM-41, the adsorption isotherm of MCM-48 is of Type V, whereas those of the silylated samples are of Type III. The amount of water adsorbed by MCM48-TMCS or MCM48-TBDMCS is considerably less than that by MCM-48, indicating that the surface of silylated samples is more hydrophobic than the unsilylated sample. There is a slight increase in water adsorption in MCM48-TMCS at  $P/P^0 = 0.85$ , which is not the case in MCM48-TBDMCS. These results show that MCM-48-TBDMCS is more hydrophobic than MCM48-TMCS.

A comparison of the isotherms of MCM-48 and MCM-41 (C16) can be seen in Figure 5. The surface hydrophobicity of MCM-41 (C16) is similar to that of MCM-48, reflected by their adsorption amounts at lower relative pressure ( $P/P^0 < 0.5$ ). However, it is clear that the inflection point of MCM-48 is higher than that of MCM-41 (C16). This result is unexpected since the inflection point of MCM-48 obtained from the nitrogen adsorption isotherm is lower than that of MCM-41. It is also clear that the amount of water adsorbed by MCM-48 at higher relative pressure ( $P/P^0 > 0.6$ ) is considerably higher than that adsorbed by MCM-41. One explanation for this observation is that MCM-48 contains higher amount of silanol groups than MCM-41 as shown in Figure 6. The intensity of the FTIR peak of the isolated silanol groups at about  $3745\text{ cm}^{-1}$  in MCM-48 is 1.6 times higher than that in MCM-41 (C16). This

indicates that the internal surface of the former is higher than the latter.

Table 1 summarizes the inflection point of the adsorption branches of the nitrogen and water isotherms as well as the pore diameter of mesoporous materials used in this study. Pore diameter was estimated using Kelvin equation:

$$\ln\left(\frac{P}{P^0}\right) = \frac{-2\gamma V_L}{RT} \times \frac{1}{r^k} \dots\dots\dots (1)$$

where  $\gamma$  and  $V_L$  are the surface tension and volume molar of water, respectively.  $\gamma$  for water equals 72.6 mN/m and  $V_L$  equals  $18.07 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ .  $T$  is the absolute temperature (298 K) and  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). According to Naono *et. al.* [19], when the Kelvin equation is used, the contact angle,  $\theta$ ,

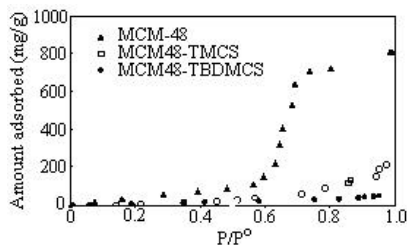


Figure 4. Water adsorption isotherms of unsilylated MCM-48 and silylated MCM-48 with TMCS and TBDMCS.

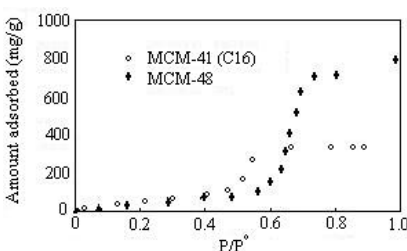


Figure 5. Water adsorption isotherms of MCM-41 (C16) and MCM-48

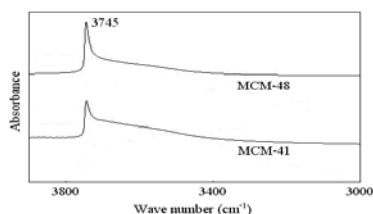


Figure 6. In situ FTIR spectra of MCM-41 (C16) and MCM-48 evacuated at 673 K

Table 1. The inflection point and the pore diameter of mesoporous materials calculated using Kelvin equation (based on water and nitrogen adsorption branch)

Samples	P/P <sup>0</sup> at inflection point		Pore diameter (D <sup>p</sup> ) nm	
	H <sub>2</sub> O Adsorption	N <sub>2</sub> Adsorption	H <sub>2</sub> O Adsorption	N <sub>2</sub> Adsorption
MCM-41 (C12)	0.32	0.20	1.88	2.62
MCM-41 (C16)	0.44	0.30	2.61	3.40
MCM16-TMCS	N/A	0.26	N/A	2.92
MCM16-TBDMCS	N/A	0.20	N/A	2.62
MCM-48	0.56	0.29	3.69	3.06
MCM48-TMCS	N/A	0.25	N/A	2.86
MCM48-BDMCS	N/A	0.21	N/A	2.66

Uncertainty in inflection point = ± 0.01

between the adsorbed film and the capillary condensate can be assumed to be zero because the pore surface of the rehydroxilated MCM-41 samples become hydrophilic.

Calculation of the pore diameter using the nitrogen isotherms was carried out according to the corrected form of the Kelvin equation proposed by Kruk, *et. al.* [20]. The  $t$  value of nitrogen was obtained from the standard data for the adsorption of nitrogen [21], whereas  $t$  of water was calculated using the equation given by Chevrot, *et. al.* [22].

$$t = 0.0044\left(\ln\frac{P}{P^0}\right)^4 + 0.046\left(\ln\frac{P}{P^0}\right)^3 + 0.1792\left(\ln\frac{P}{P^0}\right)^2 + \left(\ln\frac{P}{P^0}\right) + 0.321 \dots\dots\dots (2)$$

It is clear from Table 1 that the pore diameter obtained from nitrogen adsorption isotherms for both MCM-41 (C16) and MCM-41 (C12) is higher than that obtained from the water adsorption. On the other hand, the pore diameter calculated from the inflection point of water adsorption for MCM-48 is considerably higher than the one calculated from the inflection point of nitrogen adsorption.

**Adsorption of benzene vapour in mesoporous materials**

Benzene is a non-polar aromatic adsorbate, which has some advantages as an alternative adsorbate to nitrogen. One advantage is that benzene can condense at a lower relative pressure therefore larger pores can be readily characterized by benzene adsorption [23]. Benzene is therefore one of the frequent probe molecules used in adsorption studies. Benzene adsorption in MCM-41, and MCM-48 materials will be discussed in detail.

**Adsorption of benzene vapour in MCM-41**

Benzene adsorption isotherms of MCM-41 (C16) and MCM-41 (C12) can be seen in Figure 7. The shapes of both isotherms are of Type IV as reported by other researchers [7, 14]. The amount of benzene adsorbed in

MCM-41 (C12) below the inflection point is smaller than that in MCM-41 (C16), which is in good agreement with the water adsorption isotherm of both samples. This result shows that MCM-41 (C16) is more organophilic than MCM-41 (C12).

Benzene adsorption isotherms of silylated MCM-41 samples and the parent sample can be seen in Figure 8.

The shapes of the isotherms for the silylated samples remain the same as the parent sample. The amount of benzene adsorbed below the inflection point for the silylated samples is smaller than that for the unsilylated sample. Similar results were reported in the previous work [24].

According to Zhao *et al.* [17], an explanation for this result could be that benzene adsorption in silylated samples are affected not by the surface chemistry of samples but by the pore configuration. Diffusion resistance due to attachment of trimethyl silyl and *t*-butyldimethyl silyl groups plays an important role in controlling the pore filling of benzene. Zhao *et al.* [17] reported that for benzene molecule having a ring-like structure, the spatial resistance due to attachment of alkyl groups, could largely hinder the diffusion of benzene molecules. This steric hindering resulted in a shift of the inflection point to the right. The decrease in the amount of benzene adsorbed at the low relative pressure for the modified sample was also explained as a result of the reduced surface silanol sites. According to Gregg and Sing [21] and Zhao *et al.* [17], the  $\pi$  electrons of benzene molecules could interact with the surface hydroxyl groups.

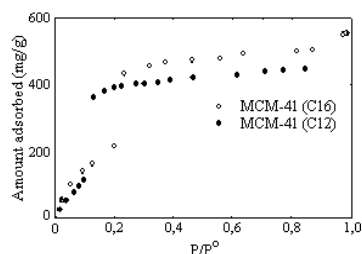


Figure 7. Benzene adsorption isotherms of MCM-41 (C16) and MCM-41 (C12)

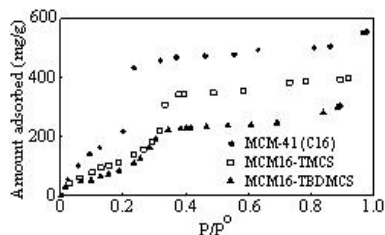


Figure 8. Benzene adsorption isotherms of unsilylated and silylated MCM-41 (C16)

MCM16-TMCS has higher capacity to adsorb benzene than MCM16-TBDMCS as shown in their isotherms. One explanation for this result is that the size of TBDMCS is bigger than that of TMCS. Hence, a steric effect played an important role in the interaction of MCM16-TBDMCS with benzene.

#### Adsorption of benzene vapour in MCM-48

Figure 9 shows benzene adsorption isotherms of unsilylated MCM-48 and its modified products. The amount of benzene adsorbed in silylated samples is smaller than that in the parent sample, similar to that observed in MCM-41 materials.

The difference between MCM-41 and MCM-48 materials is in the silylated samples. In MCM-41 materials the amount of benzene adsorbed in the sample silylated with TMCS is higher than that in the sample silylated with TBDMCS. On the other hand, in MCM-48 materials the amount adsorbed in MCM-48 silylated with TMCS is less than that in MCM-48 silylated with TBDMCS. Taba [16] has found that the surface coverage of TBDMCS in MCM-48 was smaller than that in MCM-41 by a factor of 60%. As a result, the steric effect in MCM48-TBDMCS is less than that in MCM16-TBDMCS. In other words, the organophilicity is the more important factor in the interaction of MCM48-TBDMCS with benzene. Table 2 shows a comparison of the inflection point and the pore diameter at the inflection point estimated from nitrogen and benzene isotherms.

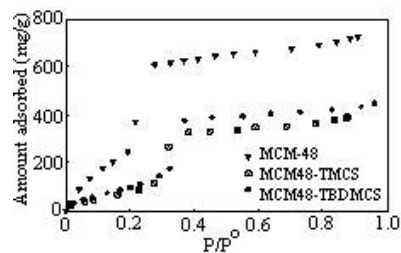


Figure 9. Benzene adsorption isotherm of unsilylated MCM-48 and silylated MCM-48

Table 2. Inflection point and pore diameter of mesoporous materials calculated by Kelvin equation (based on  $C_6H_6$  and  $N_2$  adsorption)

Samples	P/P <sup>0</sup> at inflection point		Pore diameter (D <sup>p</sup> )	
	Benzene adsorption	Nitrogen adsorption	Benzene adsorption	Nitrogen adsorption
MCM-41 (C12)	0.10	0.20	2.24	2.62
MCM-41 (C16)	0.20	0.35	3.16	3.40
MCM16-TMCS	N/A	0.26	N/A	2.92
MCM16-TBDMCS	N/A	0.20	N/A	2.62
MCM-48	0.19	0.29	3.08	3.06
MCM48-TMCS	N/A	0.25	N/A	2.86
MCM48-TBDMCS	N/A	0.21	N/A	2.66

Uncertainty in inflection point =  $\pm 0.01$

The relation between  $r_k$  (Kelvin radius) and  $P/P^0$  at 298 K is given by the equation:

$$\ln(P/P^0) = -2.05/r_k \text{ (nm)} \dots\dots\dots (3)$$

where 28.35 mN/m and  $89.43 \times 10^{-6} \text{ m}^3/\text{mol}$  were used as the surface tension and the molar volume of benzene, respectively. The adsorbed thickness of benzene was obtained from the table proposed by Naono *et. al.* [19].

As can be seen from Table 2, the pore diameter at the inflection point of benzene isotherm for MCM-41 (C12) is considerably lower than that of nitrogen isotherm. Difference between the pore diameter calculated from benzene and nitrogen isotherms for MCM-41 (C16) is about 0.14, whereas there is no significance difference between the pore diameters calculated from both benzene and nitrogen isotherms for MCM-48. There is no obvious explanation for these differences at present. They may reflect difficulties with the macroscopic models used to interpret the isotherms but further work would be needed to understand this problem.

#### 4. Conclusion

From the results above, it can be concluded that MCM-41 and MCM-48 materials have hydrophobic features which are shown in the small amount of water adsorption at low  $P/P^0$ . The hydrophobicity of samples used in this study decrease in the sequence: MCM-41 (C16) > MCM-48 > MCM-41 (C12). The hydrophobicity increased when MCM-41 and MCM-48 were silylated with TMCS or TBDMCS. The surface chemistry of mesoporous materials plays an important role in water adsorption.

All unsilylated MCM materials show higher affinity to benzene at low  $P/P^0$  than the silylated samples. In this case, the pore configuration is more important in influencing the adsorption of benzene. The results of water and benzene adsorption show that silylated samples are promising candidates as selective adsorbents for organic compounds.

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