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FTIR AND NMR STUDIES OF ADSORBED CETHYLTRIMETHYLAMMONIUM CHLORIDE IN MCM-41 MATERIALS

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ABSTRACT

The high use of surface-active agents (surfactants) by industry and households today leads to environmental pollution, therefore treatments are required to remove such substances from the environment. One of the important and widely used methods for removal of substances from solution is adsorption. In this research, MCM-41 and its modified product of MCM41-TMCS were used to adsorb cationic surfactants, cethyltrimethylammonium chloride, CTAC. FTIR and NMR methods were used to study the interaction between the surfactants and the adsorbents. MCM-41 was synthesized hydrothermally at 100 ^{o}C and its modification was conducted by silylation of MCM-41 with trimethylchloro silane (MCM41-TMCS). Both unmodified and modified MCM-41 can adsorb the surfactant. The interaction of CTAC with MCM-41 was mostly the electrostatic interaction between the electropositive end of the surfactant and MCM-41, whereas in modified MCM-41 hydrophobic interactions become more dominant. These hydrophobic interactions appear however to involve the methyl groups on the head group of the surfactant interacting with the modified surface.

INTRODUCTION

The high use of surface-active agents (surfactants) by industry and households today leads to environmental pollution. Therefore treatments are required to remove such substances from the environment. One of the important and widely used methods for removal of substances from solution is adsorption. It has been reported that activated carbon and graphite [1-3], unmodified and modified silica [4,5], silica gel [6,7], mica [8,9], clays [10-12], polymers [13-17), and modified zeolites [18] have all previously been used as adsorbents for the removal of surfactants and other organic pollutants from aqueous environments.

Mesoporous materials, such as mesoporous silica with diameters of 2 to 50 nm, show high promise to be used as adsorbents for such organic materials because of their high porosity and their large surface areas. One example of mesoporous silica is MCM-41, discovered in 1992 by Mobil Corporation [19, 20]. In this research, adsorption of cationic surfactant (cetyltrimethyl-ammonium chloride, CTAC) in MCM-41 and its modification will be discussed. The molecular structure of the surfactant is given in Fig 1.
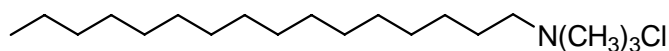

Fig 1. Structure of CTAC

Several methods have been tried in this study in order to measure the amount of surfactants adsorbed in mesoporous materials. Determination of concentration of surfactants can be quantitatively carried out using ATR FTIR spectroscopy as described elsewhere [21, 22] but there was a problem faced in this study due to adsorption of surfactants on the crystal of ATR cell. Therefore, it was difficult to accurately determine the concentration of surfactants. Another unsuccessful method tried in this study was conductometry. The problem with this method was that the surfactant used was ionic surfactants that can undergo ion exchange. The ion exchange can interfere with the measurement of the surfactant in the solution after adsorption. Furthermore, analysis of the surfactant content using UV-Vis spectrophotometer has been tried but it did not work well. To overcome the problems outlined above, the amount of surfactants adsorbed was measured from the carbon content of the adsorbent following adsorption.

^{13}C CP MAS NMR and FTIR spectroscopy was used to study the mechanism of interaction between the surfactant and mesoporous materials. The method used for adsorption of the surfactant in mesoporous materials was the stirring method, which has been described in detail elsewhere [23] in aqueous solutions for periods of 5 hours.

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EXPERIMENTAL SECTION

A hydrothermal method was used to synthesize MCM-41 as described in elsewhere [24] and trimethylchloro silane (TMCS) were used as reagents for silylation of MCM-41 using the procedure of Fraile *et al.* [25] with some modification to produce MCM41-TMCS. Hydrostability of MCM-41 was tested by making use of a Siemens D500 diffractometer using CuKα (λ = 1.5412 Å) as a radiation source. For in-situ experiments, a Bomem MB-100 Fourier Transform Infrared (FTIR) spectrometer equipped with a mercury cadmium telluride (MCT) detector was used to obtain infrared spectra of samples. The ^{29}Si spectra were measured on a Bruker MSL-300 NMR spectrometer, using a Bruker 4 mm 4WB-BL probe, a Larmor frequency of 59.61 MHz was used. The sample was spun at a spin rate of 3 kHz and an acquisition time of 21.5 ms.

RESULT AND DISCUSSION

Adsorption of Surfactants in MCM-41 Materials

Before adsorption experiments were undertaken, the hydrostability of MCM-41 was tested by stirring the materials in water at room temperature for certain periods of time and then the XRD patterns of the materials were recorded and are shown in Fig 2. It is clear that the structural order of MCM-41 remained unchanged after a stirring period of 5 h, therefore the adsorption can be performed under these condition.

The adsorption of CTAC was carried out at concentrations both below and above critical micelle concentration (cmc) for CTAC. Fig 3 displays the adsorption as a function of concentration of CTAC.

It can be seen that the amount of CTAC adsorbed below the cmc is about 0.33 mmol/g, and the amount of the surfactant adsorbed above the cmc is considerably higher than that below the cmc. This suggests that MCM-41 has a higher affinity for the
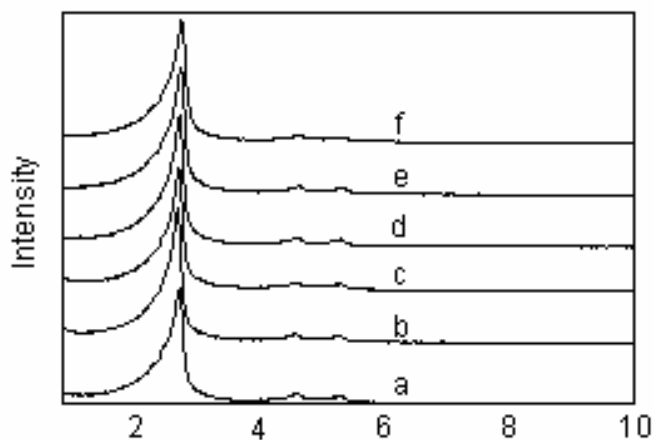
micellar form of CTAC than for single molecules of the surfactant. For the purposes of comparing the amount of the surfactant adsorbed by unmodified and modified MCM-41, a standard surfactant concentration of 10^{-1} M was employed in experiments. The amount of surfactants adsorbed in unmodified and modified MCM-41 at this concentration is presented in Table 1.

Table 1. The uptake of CTAC in MCM-41 and MCM41-TMCS on a pore volume basis together with the surfactant uptakes in mmol per gram and $mmol/cm^3$.

Samples	Pore Volumes (cm^3/g)	Amount of CTAC adsorbed	
		mmol/g	$mmol/cm^3$
MCM-41	1.09	1.39	1.28
MCM41-TMCS	0.69	0.68	0.99

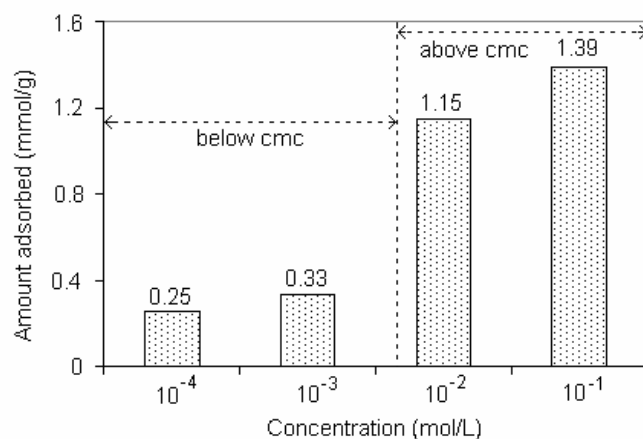**Fig 3.** Adsorption of CTAC in MCM-41 as a function of concentration.
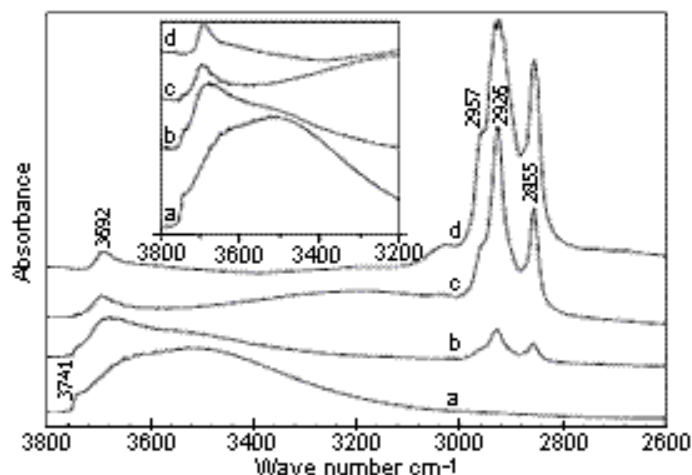

Fig 4. In situ FTIR spectra of (a) calcined MCM-41, (b) MCM-41 after adsorption of 10^{-4} M CTAC, (c) MCM-41 41 after adsorption of 10^{-1} M CTAC and (d) as-synthesized MCM-41. The inset shows expansion of the ν(OH) region. In all spectra, samples were outgassed in vacuum at 373 K.

Fig 2. XRD Patterns of MCM-41 stirred in water at room temperature for (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h and (f) 5 h

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Modification of MCM-41 with TMCS decreased slightly the uptake of the surfactant. This is due to the decrease of pore volume of the surfactant after being modified with TMCS.

FTIR and NMR Studies of Adsorbed CTAC in MCM-41 Materials

Fig 4 illustrates in situ FTIR spectra of unmodified MCM-41 after adsorption of CTAC together with the spectra of the as-synthesized and the calcined samples.

It is noteworthy that before adsorption, there is a peak at 3741 cm^{-1}, which is due to the isolated and/or geminal silanol groups. After adsorption of 10^{-4} M CTAC solution, the intensity of this peak reduces and is further reduced after adsorption of 10^{-1} M CTAC solution. The peak does not appear at all in the as-synthesized MCM-41 as can be seen in Fig 4(d). This demonstrates that the isolated or geminal silanol groups play a key role for the interaction of CTAC with MCM-41. From the carbon content experiments, it was found that the amount of CTAC adsorbed in MCM-41 at 10^{-1} M was about 60 % of the total CTAC in the as-synthesized material. The result is in good agreement with the intensities of the ν(CH) bands in the infrared spectra.

The differences between the infrared spectra of MCM-41 after adsorption of 10^{-4} M and 10^{-1} M CTAC are in the intensities of the ν(CH) bands (at ca. 2957 cm^{-1}, 2926 cm^{-1} and 2855 cm^{-1}) of the adsorbed surfactant and in the extent of perturbation of the hydroxyl bands. As the amount of adsorbed surfactant increases, the frequency of the perturbed hydroxyl bands shifts downwards. At 10^{-4} M CTAC, the frequency is about 3650cm^{-1}, whereas at 10^{-1} M it shifts to about 3200 cm^{-1}. In the as-synthesized MCM-41, on the other hand, there are very few hydroxyl groups. The FTIR spectra thus point to the importance of hydroxyl groups in the adsorption of surfactant, but do not explain why the uptake is so much higher above the cmc. It is well known, from previous studies on surfactant adsorption [26 – 29] that there is a difference in the adsorption mechanism of cationic surfactants below and above the cmc. The difference was that below the cmc, the interaction between the cationic surfactant and the surface of the adsorbent with an opposite charge was due to electrostatic binding between both charges. Above the cmc, the interaction was both the electrostatic

binding between the head groups and the adsorbent surface as well as the hydrophobic interaction between the tail groups of surfactants. The hydrophobic interaction between the tail groups appears, in the case of MCM-41, to be a major driving force for adsorption.

^{13}C NMR spectroscopy was also used to study the interaction mechanism of the surfactant adsorbed in the mesoporous material. Fig 5 displays ^{13}C NMR spectra of MCM-41 after adsorption of CTAC in solutions of 10^{-4} and 10^{-1} M. The spectra of CTAC solution (25 wt %) and the as-synthesized material are also presented.
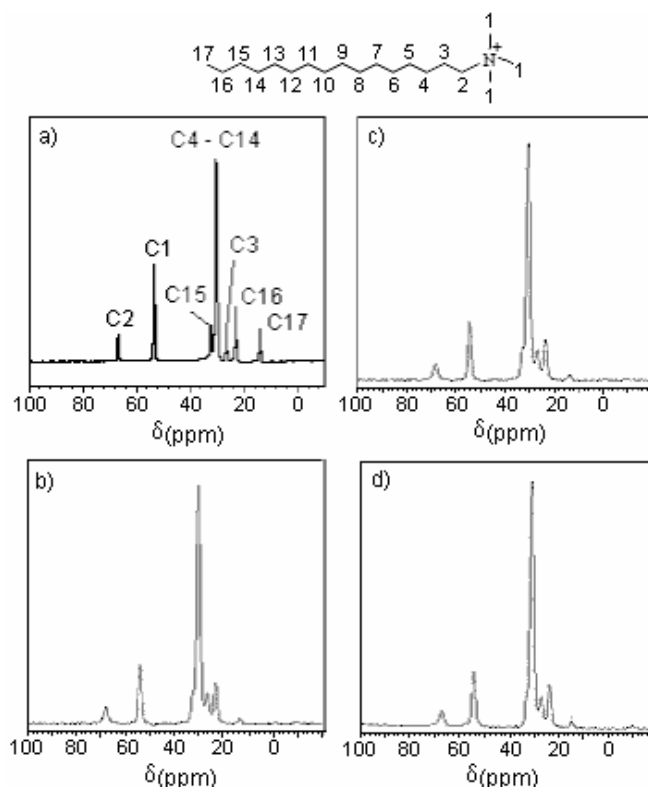

Fig 5. ^{13}C NMR spectra of (a) 25 wt % CTAC aqueous solution, (b) MCM-41 after adsorption of 10^{-4} M CTAC and (c) calcined MCM-41 after adsorption of and 10^{-1} M CTAC and (d) as-synthesized MCM-41. The solid samples (b, c and d) were measured with ^{1}H cross polarization.

Table 2. Chemical shifts of CTAC peaks in as-synthesized, calcined MCM-41 after adsorbed 10^{-4} and 10^{-1} M CTAC and in 25 wt % CTAC solution.

Spectra	Chemical shift (PPM)						
	C1	C2	C3	C4-C14	C15	C16	C17
25 % CTAC Solution	53.4	66.9	26.7	30.6	32.5	23.3	14.3
MCM-41 after absorbed 10^{-4} M CTAC	54.1	67.9	26.8	30.4	32.8	23.4	13.5
MCM-41 after absorbed 10^{-4} M CTAC	54.1	67.9	26.8	30.4	32.8	23.4	13.5
As synthesized	54.3	67.3	27.0	30.7	32.8	23.5	14.7

Uncertainty in chemical shift = $\pm$ 0.30 ppm

There are several features of the ^{13}C NMR spectra of CTAC solution observed in Figure 5(a). According to Wang *et al.* [30], the peak at 14.3 ppm is attributed to the terminal methyl group (C17), whereas C16 and C15 are observed as a peak at 32.5 and a shoulder at 23.3 ppm, respectively. The peak at 26.7 ppm is due to the methylene group (C3). The N-methylene group (C2) is observed at 66.9 ppm, which is weak and broad. Peak at 53.4 is assigned to the N-methyl group (C1). Other internal methylenes (C4-C14) give the broad peak centered at 30.6 ppm.

The chemical shifts of the peaks are summarized in Table 2. There is a shift in C1 by about 0.9 ppm downfield, for the as-synthesized MCM-41 and by 0.7 ppm downfield for MCM-41 materials after adsorption of CTAC solutions. There is also a substantial broadening of all the observed peaks. This downfield shift results from the electrostatic binding between the electropositive end of the surfactant and silanol groups of MCM-41.

The result is in a good agreement with what was found by Wang *et al.* [30] apart from the observation of an additional peak at ~ 57.4 ppm (C1') for the ordered mesophase silicate synthesized by Wang *et al.* [30] and the peak of C15, observed in the spectrum of the material prepared by the authors, was well resolved.

According to Wang *et al.* [30], the splitting of C1 in the ordered mesophase silicate, was due to the loss of stereochemical symmetry of the methyl groups next to the head group. This loss of symmetry was as a result of the intermolecular interaction in the ordered mesophase silicate. Such splitting was not seen in this study.

The sequence of chemical shift of C17 is as-synthesized > in solution > in calcined MCM-41 after adsorption of 10^{-4} M and 10^{-1} M CTAC solutions. According to Wang *et al.* [30], C17 was the most mobile segment compared to the other segments of the surfactant. In this study, the difference in the chemical shift of C17 in as-synthesized MCM-41 and in solution is just 0.4 ppm. But for CTAC adsorbed in MCM-41 (CTAC-MCM-41), the difference is about 0.8 ppm. This might be caused by the difference in rigidity of C17 of CTAC in the different environments. In CTAC solution, the concentration of CTAC was 0.76 M, which was considerably higher than the concentration of CTAC used for adsorption (10^{-4} and 10^{-1} M). Therefore, the rigidity of C17 of CTAC in calcined MCM-41 after adsorption is less than that in the 0.76M CTAC solution.

Söderlind *et al.* [31] investigated adsorbed [2]H-Labeled surfactants at the solid/water interface using NMR spectroscopy in order to study molecular dynamics and order at the solid/water interface. It was found that the adsorbed surfactants had relatively high local motional freedom and a mobility gradient along the hydrocarbon chain, increasing toward the methyl end-group [31]. In the case of as-synthesized MCM-41, the concentration of CTAC used in the synthesis was also

0.76 M and the amount of CTAC, measured from the carbon content experiment, was 1.7 times higher than in the calcined MCM-41 after adsorbed 10^{-1} M CTAC. As a consequence, the rigidity of C17 in as-synthesized MCM-41 was higher than that in calcined MCM-41 after CTAC adsorption.

Results for CTAC adsorption in modified samples are illustrated in Fig 6 and Fig 7 for in situ FTIR and ^{13}C CP NMR spectra, respectively.

MCM41-TMCS adsorbed CTAC as can be seen in an increase in the intensities of C-H stretching bands. The intensities of C-H bending band below 1500 cm^{-1} (not shown) also increased. The modified samples contain small residual concentrations of hydroxyl groups, and these appear to interact with surfactant, as for the unmodified MCM-41.
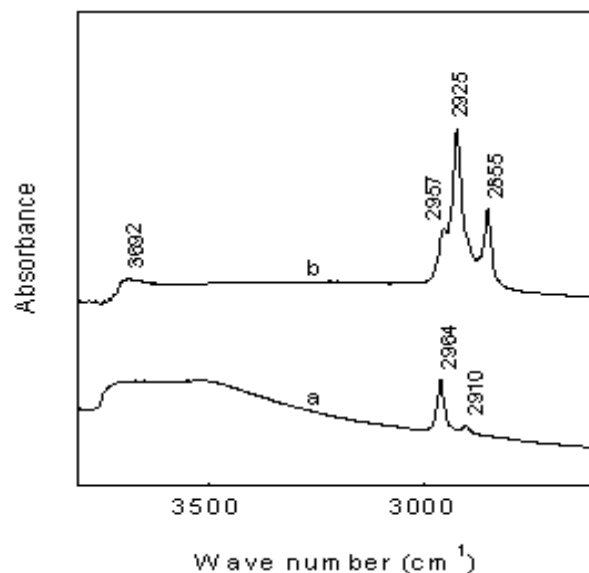

Fig 6. In situ FTIR of MCM41-TMCS (a) before and (b) after adsorbed 10^{-1} M CTAC solution.
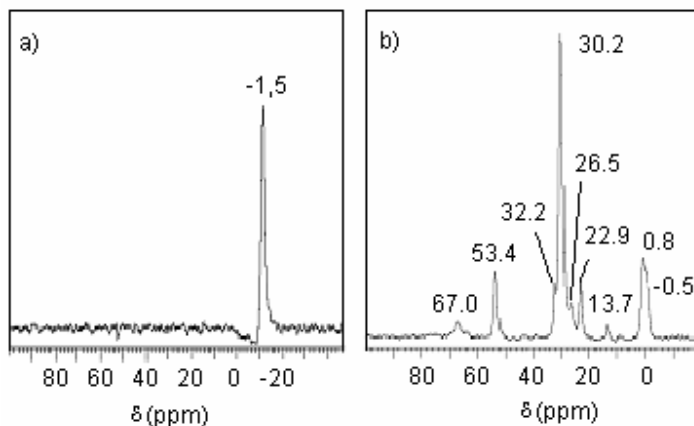

Fig 7. ^{13}C CP NMR spectra of (a) MCM41-TMCS, (b) MCM41-TMCS after adsorption of 10^{-1} M CTAC.

In Fig 7(a), an intense peak at -1.5 ppm is observed, which is due to the methyl groups of the trimethylsilyl a group, $(CH_3)_3Si$-, in MCM41-TMCS. After adsorption of 10^{-1} M CTAC this peak shifts to 0.8 ppm with a shoulder at ~ -0.5 ppm. The chemical shift of C1 is similar to that in CTAC solution. These results suggest that there is a hydrophobic interaction between CTAC and the trimethylsilyl groups in MCM41-TMCS.

The question then arising is whether the interaction is with the hydrocarbon tail of the surfactant or the methyl groups of the head group.

Manne and Gaub [32] studied the interaction of quaternary ammonium surfactants, especially CTAB, on hydrophobic graphite by atomic force microscopy. It was found that hydrophobic substrates interact primarily with the surfactants tail groups, not only through the hydrophobic interaction, but also through the van der Waals interaction [32]. For CTAC in TMCS modified MCM-41, however, the largest differences in chemical shifts between CTAC in the modified and unmodified MCM-41 are in the C1 and C2 carbons attached to the quaternary nitrogen head group rather than in those in the hydrocarbon tail. Accordingly, the interaction of the surfactant with the modified MCM-41 surface is believed to occur through the methyl groups in the head group rather than involving formation of a reverse micelle. That is the hydrophobic interactions between the hydrocarbon tails that are sufficiently strong to retain the normal micelle structure in the TMCS modified MCM-41.

CONCLUSION

From the results observed above, it can be summarized that both unmodified and modified MCM-41 can adsorb cationic surfactant. The interaction of CTAC with MCM-41 was mostly the electrostatic interaction between the electropositive end of the surfactant and MCM-41, whereas in modified MCM-41 hydrophobic interactions become more important. These hydrophobic interactions appear however to involve the methyl groups on the head group of the surfactant interacting with the modified surface, rather than the hydrocarbon tail.

ACKNOWLEDGEMENT

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