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NMR Study of Adsorbed Sodium Dodecylbenzene Sulphonate (SDBS) in MCM-41 Materials

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ABSTRACT
It is well known that the use of surface active agents (surfactants) by industries and households is very high. This can affect the environment especially aquatic environment. Anionic surfactants are the most widely used. Therefore, it is necessary to remove such substances from the environment. Adsorption is one of the important and widely used method for removal of substances from aquatic media. In this research, MCM-41 and its modification were used to adsorb anionic surfactant, sodium dodecylbenzene sulphonate. NMR method was used to study the interaction between the surfactant and the adsorbent. MCM-41 was synthesized hydrothermally at 100 °C and its modification was conducted by silylation of MCM-41 with trimethylchlorosilane (MCM41-TMCS) and t-butyldimethylchlorosilane, TBDMCS (MCM41-TBDMCS). Modified samples had higher capacity to adsorb the surfactant than unmodified MCM-41. The interaction of the surfactant and MCM41-TMCS is due to a hydrophobic interaction between SDBS and the trimethylsilyl group of MCM41-TMCS and the t-butyldimethylchlorosilane group of MCM41-TBDMCS. It is likely that the alkyl chain tail interacts with the alkylsilyl groups rather than the aromatic head groups.

Keywords
NMR, adsorbed SDBS, MCM-41 materials

1. INTRODUCTION
The widespread use of surfactants in industries as well as at home is producing an important environmental impact, especially in aquatic media. As a consequence, it is required to remove such substances from the environment. Anionic surfactants are the most widely used. It is well known that surfactants with ramified hydrocarbon chains show high resistance to biodegradation in aqueous media, causing the formation of long-standing foams. The complete biodecomposition of surfactants, requires several days or weeks. This process often initiates the formation of persistent and even toxic metabolites. Therefore, since the 1960s new formulas with more biodegradable surfactants with linear chains in their molecules, such as linear alkylbenzene sulfonates (LAS), were introduced. Typical representatives of these compounds are sodium dodecylbenzene sulfonate and sodium dodecyl sulfate. In general, detergents are not eliminated with conventional treatments of coagulation-flocculation, decantation, filtration, and chlorination. It is necessary to resort to foam formation, ozone treatment, or the adsorption on adsorbent materials. The adsorption of surfactants has been studied for many adsorbent systems including silica (Takada, 1987), layered double hydroxides (Gracia-Delgado, 1992), bentonite in a natural state or modified (Rodriguez-Sarmiento and Pinzón-Bello, 2001), and activated carbons (Wu and Pendleton, 2001, González-Garcia, et al., 2004). In addition, the simultaneous use of ozone and powdered activated carbon has been studied, with interesting advantages in removing sodium dodecylbenzene sulfonate (Rivera-Utiñula, et al., 2006).

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 (Beck, et al., 1992 and Kreese, et al., 1992). This material has silanol groups which can be modified using silylating agents (trimethylchlorosilane, TMCS and t-butyldimethylchlorosilane, TBDMCS) in order to make the material to be more hydrophobic.

In this research, adsorption of SDBS in MCM-41 and its modification was studied. The amount of surfactant adsorbed was measured from the carbon content of the adsorbent following adsorption. 13C CP MAS NMR spectroscopy was used to study mechanism of interaction between the surfactant and mesoporous materials.

2. EXPERIMENTAL SECTION
A hydrothermal method was used to synthesize MCM-41 as described in elsewhere [Kim, et al., 1995]. Template was removed by stirring at room temperature with ethanedioxide hydrochloric acid mixture (0.1 mole of HC1/L of ethanol) for 30 minute. 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. Trimethylchloro silane (TMCS) were used as reagents for silylation of MCM-41 using the procedure of Fraile, et al. (1997) with some modification to produce MCM41-TMCS.

A modified
procedure of Ren et al. (1995) was used to produce mesoporous materials silylated with t-butyldimethylchlororosilane, TBDMCS. Hydorostability of MCM-41 was tested by making use of a Siemens D500 diffractometer using CuKα (λ = 1.5412 Å) as a radiation source. The diffractometer was interfaced to a PC computer and the operating software used was Si=Tronic SIE 122D. Samples were put into an aluminum holder and the diffraction data were collected using a continuous scan mode with a scan rate of 1 degree 2-theta/min and a step size of 0.02 degree 2-theta. The slits used were 0.3′ divergence slits and 0.05′ receiving slit. A current setting of 30 mA and an accelerating voltage of 40 kV were used to scan a range from 0.8 to 10 degree 2-theta. The Si=Tronic XRD Trace software was used to process the data. 13C Cross Polarization spectra were recorded with a 7 mm MAS probe on a Varian Inova NMR 300 with a contact time of 2 or 5 ms. The spin rate was 3 kHz. These experiments were carried out in order to study how the surfactant interacts with mesoporous materials. The chemical shifts for 29Si and 13C spectra were referenced to Kaolin and Adamantane, respectively, as external standards.

3. RESULT AND DISCUSSION

Adsorption of Sodium Dodecylbenzene Sulphonate 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 as can be seen in Figure 1. 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 this condition.

The adsorption of sodium dodecylbenzene sulphonate was carried out at concentration above critical micelle concentration (cmc) which was 10^{-1} M. Figure 2 displays the amount of SDBS adsorbed in unmodified and modified MCM-41 at this concentration. It can be seen that unmodified MCM-41 can not adsorb SDBS, whereas the modified materials can adsorb the surfactant. The different results were observed when cetyltrimethylammonium chloride, CTAC, (cationic surfactant) were used as adsorbate as has been reported before (Taba, et al, 2008). Both unmodified and modified MCM-41 can adsorb well CTAC where the amount adsorbed in unmodified MCM-41 was higher than that in modified materials.

![Figure 1. 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.](image1)

![Figure 2. Adsorption of SDBS in MCM-41, MCM41-TMCS and MCM41-TBDMCS](image2)

NMR Studies of Adsorbed Sodium Dodecylbenzene Sulphonate in MCM-41 Materials

There was no peak observed in 13C CP NMR spectrum (not shown) after adsorption of SDBS in MCM-41. This indicates that MCM-41 adsorbs no SDBS which is in a good agreement with the result of carbon content measurements.

Figure 3 illustrates the 13C NMR spectra of modified MCM-41 after adsorbed SDBS. an intense peak at -1.5 ppm is observed, which is due to the methyl groups of the

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trimethylsilyl group, (CH$_3$)$_3$Si-, in MCM41-TMCS. The peak of MCM41-TMCS shifts from -1.5 ppm to -1.1 ppm and a new peak at 0.8 ppm appears. Peaks attributed to adsorbed SDBS at 32.4, 30.7, 23.1 and 14.0 ppm were also found after adsorption. These peaks are shifted by about 0.2 - 0.7 ppm relative to the peaks of SDBS in solution. Other peaks, expected for adsorbed SDBS, especially those belong to carbon atoms of the benzene ring are not observed. Similar evidence is seen when SDBS is adsorbed by MCM41-TBDMCS. The peak of MCM41-TBDMCS at -5.1 ppm is perturbed and shifted to -4.0 ppm. The peak at 24.2 ppm also shifts to 25.1 ppm with a shoulder at 24.3 ppm. New peaks at 31.8, 29.7 and 13.9 ppm appeared after adsorption of SDBS. Those peaks are attributed to C8, C16, C10-C15 and C18 of SDBS, respectively. From the evidence that the peaks of trimethylsilyl and t-butyldimethylsilyl groups, shifted to higher chemical shifts, it can be concluded that there is a hydrophobic interaction between SDBS and trimethylsilyl groups of MCM41-TMCS or t-butyldimethylsilyl groups of MCM41-TBDMCS.

The most striking change in the spectra of adsorbed SDBS is the disappearance of the peaks due to aromatic carbons. Proton cross-polarization to the aromatic carbons will not occur efficiently in the adsorbed species if the aromatic groups are undergoing significant motion on the NMR time scale. The absence of these peaks in the cross-polarized spectra therefore indicates that the aromatic head group of SDBS is undergoing motion within the pores of modified MCM-41. It is likely therefore that it is the alkyl chain tail that is interacting with the alkylsilyl groups rather than the aromatic head groups. The small shifts in the alkyl chain resonances on adsorption support this argument.

In situ FTIR measurements were also measured for unmodified and modified MCM-41 after adsorption of SDBS. There are no C-H stretching or bending bands observed in the FTIR spectra of unmodified MCM-41. When the measurements were done on modified MCM-41, the increase in the intensities of C-H stretching and bending peaks was quite large after adsorption of SDBS. This is supported by the fact that carbon content of modified MCM-41 after adsorption of SDBS is higher than unmodified MCM-41.

![Figure 3. $^{13}$C NMR of (a) SDBS solution (b) MCM41-TMCS, (c) MCM41-TMCS after adsorbed $10^{-1}$ M SDBS, (d) MCM41-TBDMCS, and (e) MCM41-TBDMCS after adsorbed $10^{-1}$ M SDBS. The solid samples (b, c, d and e) were measured with $^1$H cross polarization.](image-url)
4. CONCLUSION
From the results observed above, it can be summarized that unmodified MCM-41 can not adsorb the anionic surfactant (SDBS), whereas modified MCM-41 (MCM41-TMCS and MCM41-TBDMCS) can adsorb the surfactant. For modified samples, SDBS interacts with alkylsilyl groups mostly through hydrophobic interaction. It is likely that the alkyl chain tail interacts with the alkylsilyl groups rather than the aromatic head groups of SDBS.

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6. REFERENCES