A spectroscopic study on the adsorption of cationic dyes into mesoporous AlMCM-41 materials

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Abstract

Mesoporous materials loaded with dyes are of interest with respect to novel optical applications. The spectral behaviors of some dyes in these materials are considerably affected by the presence of surfactants. A comparative study has been carried out on the adsorption of the methylene blue, rhodamine 6G and thionine dyes into a surfactant-free and surfactant-containing mesoporous AlMCM-41. The ion exchange method has been employed for incorporation of the dye molecules into the structure of MCM-41. The exchangeable sites in the MCM-41 were generated prior to dye loading by isomorphous substitution of aluminum for silicon in the structure of the mesoporous material during the synthesis procedure. Diffuse reflectance measurements indicate adsorption of methylene blue and rhodamine 6G dye molecules into AlMCM-41 taken place via ion exchange at room temperature. The spectra show presence of monomer and dimer aggregates of the dyes established into the pores and surface of AlMCM-41. The ratio of dimer to monomer forms of rhodamine 6G incorporated in the surfactant-free and surfactant-containing AlMCM-41 is about one which is higher than those observed in aqueous solutions. The surfactant-containing AlMCM-41 induced destabilization and decomposition of methylene blue while uploading the dye. Degradation of this dye produces intermediate species identified as demethylated forms of methylene blue adsorbed on AlMCM-41. Our experiments revealed that kinetics of ion exchange for thionine dye is very slow at room temperature, but it become faster at higher temperatures. The spectral properties of thionine in AlMCM-41 are close to that of thionine in an aqueous solution, possibly due to high pore space in a mesoporous molecular sieve. No adsorption of thionine was observed for surfactant-containing AlMCM-41 even at higher temperatures.

Keywords: AlMCM-41; Methylene blue; Rhodamine 6G; Thionine; Cationic surfactant; Mesoporous

1. Introduction

The regularly structured pores and cages of molecular sieves represent host systems where can accommodate dye molecules. Considerable researches were developed to find out appropriate conditions for an efficient incorporation of dyes in molecular sieves [1–5]. Recently, dye-containing molecular sieves have attracted interest for different applications such as photochromic or photocatalytic materials and optical sensors [1,6,7]. However, such application for zeolite molecular sieves are limited by their relatively small pore openings. Therefore, pore enlargement is one of the main aspects in developing new trends in the design of precise functionalities. In the past several years, there has been explosion growth in research on ordered mesoporous molecular sieves. Four international symposia on the mesoporous materials have been held since 1998 and the fifth one will be held in Shanghai on 2006, to explore their potentials as sorbents and host materials [8–11]. The mesoporous materials may be in any geometric form, but is preferably in the form of a film, fiber, powder or combinations thereof. The guest–host materials based on dyes loaded mesoporous will exhibit particular advantages for optical function in optical and optoelectronic devices, electrochromic materials and chemical...
sensors [12–19]. MCM-41 is a mesoporous molecular sieve and their dye-loaded forms can be prepared by addition of the dye into the sol–gel mixture arranged for the synthesis of mesoporous material [13,20,21]. However, incorporation of aluminum into the structure of MCM-41 materials via isomorphous substitution of aluminum for silicon, generate ion exchange sites in this mesoporous molecular sieves [22–24]. Therefore, cationic dyes such as methylene blue can be incorporated into AlMCM-41 by ion exchange method.

For the practical use of dye-loaded molecular sieves a pre-requisite is good dispersion of the dye species inside or on the surface of the host materials. Methods such as in situ synthesis (ship-in-the-bottle) [1,25] or crystallization inclusion during the hydrothermal synthesis [1,26,27] provide stable anchoring but fair dispersion on the molecular scale. However, by converting MCM-41 to AlMCM-41 and generating ion exchange sites, a better dispersion and therefore improved optical homogeneity can be achieved. The purpose of the present study is to obtain spectroscopic data on some of the dye-loaded AlMCM-41 materials where the incorporation of the dye molecules are attained by ion exchange method. We use the structurally different: methylene blue (MB), rhodamine 6G (R6G) and thionine (TH) dye molecules for our investigation. We will examine adsorption of dye molecules on both surfactant-free and surfactant-containing AlMCM-41 materials. Such a comparative study, to the best of our knowledge, has not been done so far. We have employed diffuse reflectance technique in our studies. This method is a reliable and sensitive approach to study dye-loaded molecular sieves [28–31].

2. Experimental

2.1. Sample preparation

The MCM-41 and AlMCM-41 materials were synthesized by a room temperature method with some modification in the described procedure in the literature [32]. We used tetraethyloorthosilicate (TEOS, Merck, 800658) as a source of silicon and hexadecyltrimethylammonium bromide (HDTMABr, BDH, 103912) as a surfactant template for preparation of the mesoporous materials. The detail of the procedure has been described elsewhere [24]. The molar composition of the reacting mixture was as follows:

\[ \text{SiO}_2:1.6\text{EA}:0.215\text{HDTMABr}:325\text{H}_2\text{O}:0.1\text{Al}_2\text{O}_3 \]

EA stands for ethyleneamine. Part of the as-synthesized AlMCM-41 sample was calcinated at 550 °C for 5 h to decompose the surfactant. Both surfactant-containing and surfactant-free materials are white. These powder samples were used for loading the dyes. For this purpose, about 0.1 g of the calcined (surfactant-free) or as-synthesized (surfactant-containing) materials were treated in 100 ml of \(~1.0 \times 10^{-5}\) M of either methylene blue, rhodamine 6G or thionine. The suspension was stirred for 6 h at room temperature in the dark. Then the solution was decanted and the solid dried at 100 °C for 5 h.

2.2. Characterization

X-ray diffraction (XRD) measurements were performed on a Philips PW 1840 diffractometer with Cu-Kα radiation (40 kV, 40 mA), scan rate 0.02 2\(^\circ\)/s within a range of 20 of 1–10\(^\circ\). XRD patterns were recorded using an automatic divergence slit system. Diffuse reflectance spectra were recorded by a UV-2100 Shimadzu Spectrophotometer, equipped with an integrating sphere assembly. A special cell, loaded with the solid sample and covered by a quartz window, was used in all measurements. All the spectra were recorded at room temperature against barium sulfate and were plotted in terms of absorbance. Energy dispersive X-ray analysis (EDX) jointed to a XL-30 scanning electron microscope was used to calculate Si/Al ratio of the aluminum containing MCM-41. Specific surface area based on nitrogen physisorption was measured by a Sibata Surface Area Apparatus 1100. The samples were first degassed at 250 °C for 2 h. The dye contents of the materials were determined by spectrophotometric method. The amount of the adsorbed dye was calculated from the difference measurement of the concentration of dye in the solution before and after ion exchange treatments. Since the absorption maxima of the solutions containing methylene blue prior and after ion exchange with surfactant-containing AlMCM-41 do not coincide, the dye content was determined from sulphur for this sample.

3. Results and discussion

Aluminum incorporation into the structure of MCM-41 is due to isomorphous substitution mechanism. Quantitative data for estimation of aluminum incorporation was obtained by EDX/SEM. The analysis was made upon several parts of the sample observed by scanning electron microscopy, to measure amounts of silicon and aluminum. The mean of the separate analyses was taken. The silicon and aluminum contents of the as-synthesized sample are 17.6% and 3.2%, respectively (results are in atomic percent). According to the chemical composition employed for the synthesis of our AlMCM-41, we expected a nominal value of Si/Al ratio five in our material. However, the real Si/Al ratio in the as-synthesized AlMCM-41 is a little higher than that (Si/Al = 5.5). This indicates that amount of aluminum incorporated in the structure is a little less than the predicated from the composition of the synthesis mixture. We have shown previously that most of the aluminum atoms presented in the reacting mixture will incorporate into the AlMCM-41 framework [24]. They are clearly identified by an intense 200 nm band in the diffuse reflectance spectra. This band is attributed to a charge transfer transition of framework tetrahedral aluminum atoms [24]. These aluminum atoms are responsible for generating the ion exchange capacity in the high-quality AlMCM-41 materials [33].

Fig. 1 shows the powder X-ray diffraction patterns of the as-synthesized and calcined AlMCM-41 materials.
The XRD patterns of these materials show a typical characteristic four-peak pattern with a very strong one at a low 2θ and three weaken peaks at higher 2θ values [34,35]. The calcined AlMCM-41 preserves its purity and crystallinity upon heating (Fig. 1(b)). The calcined AlMCM-41 has a specific surface area of 940 m²/g (Table 1). This is a little lower then the surface area of 1027 m²/g found for our aluminum-free MCM-41. This means that incorporation of aluminum into the MCM-41 is accompanied by a decrease in surface area and therefore a decrease in pore volume due to pore wall thickness. The pore size of the AlMCM-41 powder can be calculated from the X-ray diffraction interplanar spacing using the equation [36]

\[ W_d = cd(\rho V_p/(1 + \rho V_p))^{1/2} \]

where \( W_d \) is the pore size, \( V_p \) is the pore volume (0.33 cm³/g from our nitrogen physisorption, equivalent to a surface area of 940 m²/g), \( \rho \) is the pore wall density (ca. 2.2 cm³/g for siliceous materials), \( d \) is the XRD(100) interplanar spacing (33.5 Å for our AlMCM-41 sample), and \( c \) is a constant dependent on the assumed pore geometry and is equal to 1.155 for hexagonal models. From the equation, the pore size of our AlMCM-41 is 24.4 Å. This value is equal to 25.3 Å for aluminum-free MCM-41 (surface area = 1027 m²/g and \( d = 32.8 \) Å). Therefore, aluminum incorporation does not alter considerably the pore size of the AlMCM-41.

Our inspection for the XRD patterns of all the dye-loaded AlMCM-41 materials including those of surfactant-free and surfactant-containing materials demonstrate that the crystallinity and the structure order remain intact. Table 1 shows the designation, color, surface area and dye content of the dye-loaded samples. There are great differences among these dye-loaded AlMCM-41 materials upon adsorption of the dye molecules into either of the surfactant-free or surfactant-containing materials. The specific surface area decreased proportionate to the dye content for the surfactant-free MB-AlMCM-41 and R6G-AlMCM-41 samples compared to that of 940 m²/g obtained for the calcined dye-free AlMCM-41 (Table 1). However, this proportionality cannot be envisaged for TH-AlMCM-41. Although, the dye content is less for TH-AlMCM-41 compared to those of MB-AlMCM-41 and R6G-AlMCM-41 but a lower surface area has been obtained for the thionine-loaded sample. An explanation for this problem is that the stability of mesoporous MCM-41 materials decreases upon hydrothermal treatment and consequently a reduction in surface area is resulted [37]. Therefore, performing the ion exchange treatment for AlMCM-41 in thionine solution at 70 °C may caused this considerable reduction in surface area for TH-AlMCM-41.

The diffuse reflectance spectrum of the MB-AlMCM-41 is shown in Fig. 2(a). The DR spectrum consists of two bands at about 645 and 600 nm. The 645 nm band is assigned to monomer form of MB and 600 nm band belongs to the dimeric form of it [28,38]. The 645 nm band is blue-shifted as compared to that of MB spectrum in aqueous solution [39]. The optical spectrum of MB in water shows two 665 and 610 nm bands. This blue shift is due to host–guest interaction which is often observed for dyes on solid hosts [40]. On the other hand, the spectrum of MB-AlMCM-41(S) shows quite different features (Fig. 2(b)) compared to that of the surfactant-free, MB-AlMCM-41 sample described above. The spectrum consists of three 615, 525 and 485 nm bands. The occurrence of 525 and 485 nm bands has never been mentioned for any species of methylene blue in literature. The trimers and higher aggregated forms of methylene blue ([(MB)ₙ⁺, \( n \geq 3 \)]) on clay particles gives absorption band around 570–580 nm [41]. Therefore, the observed bands on surfactant-containing MB-AlMCM-41(s) cannot be related to any aggregated forms of methylene blue formed into the channels or on the surface of the mesoporous material. Recently, Czimerova et al. reported that a high-charge density surface of smectite clay mineral induced destabilization and decomposition of thionine on the clay surface [42]. We consider that the space in the pores or surface of MB-AlMCM-41(S) does not provide enough space for adsorption of MB⁺ molecules (as most of those are occupied by surfactant molecules). Therefore, a tension between some of the pre-adsorbed dye aggregate are raised which leads to their destabilization. The destabilization of MB⁺ leads to the formation of some intermediate species produced from degradation of methylene blue. These species are most likely demethylated forms of methylene blue encountered by Schafeer and Zimmermann while investigating the

![Fig. 1. Powder XRD patterns of (a) as-synthesized AlMCM-41 and (b) calcined AlMCM-41.](image-url)
dye-amine systems in the dark [43]. They described that the degradation of methylene blue in a media containing amine is due to a base-catalysed self-oxidation or disproportion of the dye molecules followed by hydrolysis of the oxidized species to the demethylated forms of the dye (Scheme 1). Demethylation may be continued with a slower rate to form the species with less methyl groups. The pale red color and the absorption band at ~560 nm reported by Schafeer and Zimmermann for the demethylated methylene blue are close to our results and provide more confirmation for our assignment. It should be noted that our system of dye-solid might be responsible for the blue shift for this absorption band in MB-AlMCM-41(S). This is often observed for dyes in minerals and denoted as metachromasy [39,44].

We found that upon addition of methylene blue into the synthesis mixture of AlMCM-41(S) the same destabilization feature but in a lower level is produced (Fig. 2(c)). Certainly, presence of ethylamine and cationic surfactant into the pores of MB-AlMCM-41(S) is responsible for the destabilization of MB+. We should remind that in an aqueous solution of MB in HDTMABr, we did not observe any significant perturbation to the spectrum of methylene blue in water. Cationic surfactants in submicellar or micellar concentration dose not affect the spectral characteristics of some cationic dyes such as methyl violet [45]. This indicates that the presence of ethylamine in the reaction mixture is partly involved in destabilization and decomposition of MB+.

The spectra of R6G dye molecules incorporated into surfactant-free and surfactant-containing AlMCM-41 are shown in Fig. 3. Here, the two spectra are very similar (in contrary to the features observed in MB-loaded samples) except that the spectrum of R6G in the calcined form of AlMCM-41 (Fig. 3(a)) is more intense and more broaden than that of R6G in the surfactant-containing one (Fig. 3(b)). Both spectra have two absorption bands at about 535 and 500 nm. For R6G in aqueous solution the 526 and 500 nm bands were assigned to monomeric and dimeric form of rhodamine 6G, respectively [46–48]. The spectra in Fig. 3 demonstrate that the amount of dimeric (and higher aggregated forms of R6G) is comparable to that of monomeric form. However, the ratio of monomeric to dimeric forms of R6G in aqueous solution (with the same concentration of R6G in solution) is much higher [49]. This suggests that mesoporous AlMCM-41 materials favors the R6G aggregation and therefore impedes its removal from the structure. This interpretation is in agreement with the conclusion drawn for those microporous materials that formation of mesopores is observed for them [50].

Although, incorporation of a cationic dye such as R6G in surfactant-containing AlMCM-41 is much less than that of the calcined one (Table 1), but still it requires an explanation for the adsorption of this dye in a mesoporous

### Table 1
Designation and some characteristics of the dye-containing Al MCM-41 materials

<table>
<thead>
<tr>
<th>Samplea</th>
<th>Dye</th>
<th>Color</th>
<th>Surface area (m²/g)</th>
<th>Dye content (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlMCM-41</td>
<td>–</td>
<td>White</td>
<td>940</td>
<td>–</td>
</tr>
<tr>
<td>MB-AlMCM-41</td>
<td>Methylene blue</td>
<td>Blue</td>
<td>850</td>
<td>2.8 × 10⁻³</td>
</tr>
<tr>
<td>TH-AlMCM-41</td>
<td>Thionine</td>
<td>White</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TH-AlMCM-41(S)</td>
<td>Thionine</td>
<td>Purple</td>
<td>667</td>
<td>2.3 × 10⁻³</td>
</tr>
<tr>
<td>MB-AlMCM-41(S)</td>
<td>Methylene blue</td>
<td>Pink</td>
<td>–</td>
<td>1.5 × 10⁻³b</td>
</tr>
<tr>
<td>TH-AlMCM-41(S)</td>
<td>Thionine</td>
<td>White</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

a (S) Stands for surfactant-containing AlMCM-41, (70) stands for the temperature of ion exchange treatment in °C.

b MB content was measured from sulphur by chemical analysis.

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**Fig. 2.** Diffuse reflectance spectra of (a) MB-AlMCM-41, (b) MB-AlMCM-41(S) and (c) MB-AlMCM-41(S) while the dye was added to the synthesis solution.
material containing cationic surfactant. Our inspection of the literature for this matter revealed that positively charged species might be incorporated in the mesoporous materials containing cationic surfactant. Ganschow et al. reported that a large substituted phthalocyanine Zn complex exhibiting positive charge is incorporated into the mesopores of SiMCM-41 during hydrothermal synthesis in presence of surfactant [51]. They have presented a schematic picture of localization of a positively charged species that is anchored between the positively charged head groups of the surfactant. This may justify our observation, although, further work is required to clarify this matter in more details.

The ion exchange treatment of AlMCM-41 in an aqueous solution of thionine (at the similar temperature and concentration condition as was employed for the two other previously described MB and R6G dyes), did not lead to adsorption of TH\(^+\) into the solid. The color of TH-AlMCM-41 is white (Table 1) and no absorption peak is recorded for it (Fig. 4(a)). We performed the exchange process at room temperature for 6 h for thionine and other dyes in this study. However, it seems that the exchange kinetics is slow at room temperature in the case of thionine. We repeated the ion exchange treatment of AlMCM-41 in TH\(^+\) solution at a higher temperature of \(~70\) °C. This time, the TH-AlMCM-41(70) solid separated from the solution is colored (purple) and gives spectrum as shown in Fig. 4(b). The spectrum consists of two bands at about 595 and 560 nm. The 595 nm band is assigned to monomer form of thionine and the 560 nm band belongs to the dimeric and aggregated forms [42,52,53]. Comparison of
the thionine spectrum of TH-AlMCM-41(70) to that in an aqueous solution (Fig. 4 (c)) shows that the maxima are at about the same wavelength. However, the spectrum of thionine in TH-AlMCM-41(70) is more broaden reflecting the inhomogeneous distribution of TH into our sample. The surfactant-containing sample TH-AlMCM-41(S) did not adsorb thionine neither at room nor at higher temperatures. Possibly, the amount adsorbed is so little that cannot be probed by diffuse reflectance spectroscopy.

4. Conclusion

It is found that incorporation of methylene blue into surfactant-containing AlMCM-41 leads to dye decomposition. Presence of ethylene amine and the surfactant as preadsorbed molecules into the mesopores or as free molecules in the reaction media are responsible for decomposition of methylene blue. But the decomposition taken place within the mesoporous host is more severe than those taken place in the reaction media. The demethylated forms of methylene blue are likely to be the species produced by decomposition of the dye molecules. Methylene blue forms monomer and dimers with surfactant-free AlMCM-41. Rhodamine 6G exist in monomer and aggregates in both surfactant-containing and surfactant-free AlMCM-41. The concentration of incorporated dye is much more in the surfactant-free material. The amount of aggregated R6G is about the same as that of its monomer in both surfactant-containing and surfactant-free AlMCM-41. Therefore, larger amount of R6G molecules presents as aggregates compared to that of the dye in aqueous solution. Thionine does not incorporate into the structure of surfactant-free AlMCM-41 at room temperature, but the ion exchange rate increases at higher temperatures.

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References
