Intercalation of Methylene Blue into Mordenites: Role of Zeolite Acidity

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Abstract

The intercalation of methylene blue into mordenite zeolite was studied by diffuse reflectance spectroscopy. Methylene blue was incorporated into mordenite by ion exchange in the aqueous phase. Samples of sodium, calcium and protonated mordenite were subjected to methylene blue loading. The DR spectra observed shortly after mixing the dye with sodium mordenite are those of aggregated species adsorbed on the surface. The period of intercalation is very short (1 h) for protonated mordenite and is too long for calcium mordenite (7 days). The hydrated mordenite samples containing intercalated methylene blue show two 660 and 610 nm bands which are assigned to monomeric and dimeric species of methylene blue, respectively. Upon dehydration a new band at 745 nm is observed which corresponds to the protonated dye molecule. The intensity of this band increases with severity of dehydration. Those dehydrated samples containing merely aggregated dye molecules adsorbed on the surface do not show the 745 nm band. The protonation of methylene blue is reversible by the dehydration-hydration process.

Introduction

Dye molecules incorporated in molecular sieves find increasing attention for their potential application [1]. Molecular sieves provide regular pore and cage structures of different shapes allowing systematic ways to study the influence of void size and form on guest–host interaction. One practical interest from the industrial side is to use them as dye pigments [2–4]. The encapsulation of a cationic dye in a molecular sieve host has the advantage of enhanced stability against leaching with solvents [5]. For the uncharged dye molecules where the interaction between the dye and zeolite host is not strong, complementary techniques have been devised to increase the stability of dye-loaded zeolite against solvents [6].

Dye molecules can be incorporated into molecular sieves by four different methods, namely ion exchange, adsorption, *in situ* synthesis in channels of the zeolite and crystallization inclusion during the hydrothermal synthesis of the zeolite. Details of these methods have been well described [7–9]. The method to be used depends on the charge, stability and solubility of the guest molecules. Cationic guest molecules such as methylene blue can be incorporated *via* ion exchange [2, 3, 10]. The characterization of dye-loaded molecular sieves for control of dye inclusion and dye aggregation is very important. Diffuse reflectance spectroscopy has proven to be a fast and sensitive tool for identification and location of various forms of dyes under different conditions in different molecular sieves [1, 10–17]. There are a number of factors involved in the formation of monomers and aggregates of dye molecules incorporated into the zeolite. The presence or absence of coadsorbed water molecules in the channels or cavities of the molecular sieves is one of the important factors among them [10, 12]. There are also a limited number of reports on the effect of the acidity of zeolites on the adsorbed methylene blue dye [18–21]. However, these studies are not comprehensive and/or suffer from not employing a sensitive solid-state analyzing method.

The purpose of the present study is to obtain information on the forms of methylene blue molecules incorporated into mordenite zeolite. We have chosen this zeolite because mordenite with a Si/Al ratio of about 6.5 could be considered a strong acidic zeolite with a pore opening of 6.5×7.0 Å, which is close to the van der Waals radii of methylene blue [22, 23]. We will show that hydration-dehydration processes have great influence on the protonation of methylene blue molecules and that these can directly be observed by the DRS method.

Experimental

Sample preparation

Mordenite zeolite was prepared by a hydrothermal synthesis method based on the published recipe [24]. Mordenite was treated with 1 M NaCl solution at 25 °C for 5 h to ensure that all exchangeable cations consist of Na^+. The exchanged mordenite was washed several times with deionized water and dried at 100 °C. This sample is called NaMOR. To ob-

tain the protonated form of the zeolite, 2.0 g of the NaMOR sample was stirred in 100 mL of ammonium chloride solution at room temperature for 24 h. The solid product was separated by centrifugation, washed with hot deionized water several times and finally dried at 110 °C. This sample (NH$_4$MOR) was converted to acidic mordenite (HMOR) by heating it in a muffle furnace in air at a rate of approximately 2 °C per minute up to 550 °C, keeping at this temperature for 5 h. In a separate experiment, 2 g of the NaMOR sample was added to 100 mL of a 1M solution of CaCl$_2$ and stirred at room temperature for 48 h to obtain calcium exchanged mordenite (CaMOR) sample. This sample was recovered, washed and dried the same as NaMOR.

Methylene blue loaded samples (MBNaMOR, MBHMOR, MBCaMOR) were prepared by ion exchange method. 1.0 g of either NaMOR, HMOR or CaMOR was dispersed in 50 mL of $\sim 10^{-5}$ M aqueous solution of MB. The suspension was shaken for 1 hour to 12 days at room temperature in the dark. Then the solution was decanted and the solid was dried at 100 °C for 5 h. A Soxhlet extractor was used for purification of the samples. The MB loaded samples were extracted with ethanol. The extraction step was continued until the solvent became colorless. Only minor amount of dye were extracted from all of the samples.

The hydrated samples were left in a desiccator containing saturated ammonium nitrate solution for at least 48 h. The dried samples were kept dehydrated in a desiccator over P$_2$O$_5$. For severe dehydration , the sample was heated in a special cell connected to a vacuum system. These samples were heated at 120 °C under reduced pressure of 10^{-2} Torr for 10 h.

The zeolite Y used in this study as a reference material was from Union Carbide with Si/Al ratio of 2.56. All the procedures to convert it to MBNaY and MBHY were similar to the ones used for mordenite zeolite. For dealumination, zeolite HY was heated in a muffle furnace in air at a rate of $\sim$5 °C /min up to 550 °C, keeping at this temperature for 12 h.

Characterization

The crystallinity of all the samples was checked by X-ray diffractometer (Philips PW 1840) with Cu-Kα radiation at room temperature. 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 was used in all measurements. The spectra were recorded against barium sulfate at room temperature and plotted in terms of absorbance.

Specific pore volume was calculated based on the specific surface area measured by a Sibata Surface Area Apparatus 1100. All of the samples were first degassed at 250 °C for two hours.

Chemical analysis of the mordenite was done by energy dispersive X-ray analysis (EDX) joined to a Philips XL 30 scanning electron microscope. The water content of the sample was determined by gravimetry.

Table 1. Sample designation, color and pore volume for different treated zeolites

Sample	Ion exchange duration in MB solution	Color	Pore volume cm^3/g
NaMOR	–	White	0.140
MBNaMOR-1	1 h	Purple	0.153
MBNaMOR-2	10 h	Purple	0.151
MBNaMOR-3	4 days	Blue	0.129
MBNaMOR-4	12 days	Blue	0.129
HMOR	–	White	0.165
MBHMOR-1	1 h	Blue	0.140
MBHMOR-2	4 days	Blue	0.117
CaMOR	–	White	0.138
MBCaMOR-1	4 days	Purple	0.151
MBCaMOR-2	7 days	Blue	0.132
HY	4 days	White	–
MBHY	4 days	Blue	–
MBDHY	4 days	Blue	–

From EDX data unit cell composition of the NaMOR zeolite was deduced as follow Na$_{7.4}$ [(AlO$_2$)$_{7.4}$ (SiO$_2$)$_{40.6}$] · 23.7 H$_2$O.

Results and discussion

The modification of the as-synthesized mordenite including its exchange with Na$^+$, Ca^{2+}, MB$^+$ and its conversion to protonated form along with their designation are summarized in Table 1. The Si/Al ratio for NaMOR sample as determined by EDX/SEM was 6.5. The unit cell composition of this sample was also calculated from EDX data. This is shown in the footnote to Table 1.

X-ray diffraction patterns of the NaMOR and all of the samples studied demonstrate the high purity and high crystallinity of the products. All of them belong to the MOR crystallographic designation for mordenite zeolite [25]. The dehydrated and protonated samples preserve their purity and crystallinity upon heating. Figure 1 shows XRD patterns of the original and acidic mordenite samples before and after dye loading. Similar diffraction patterns observed for NaMOR and MBNaMOR-4 and also for HMOR and MBHMOR-2 in Figure 1 indicate that methylene blue does not form crystals of appreciable size and is well dispersed in the zeolite.

The diffuse reflectance spectra of the hydrated MBNaMOR samples are shown in Figure 2. The NaMOR contains no methylene blue, it is white and therefore does not show any absorption band in the visible region of the spectra. The DR spectra of the MBNaMOR samples show significant difference among them. The colored MBNaMOR-1 MBNaMOR-2 solids are purple whereas MBNaMOR-3 and MBNaMOR-4 are blue. The DR spectra of MBNaMOR-1 and MBNaMOR-2 consist of three bands at about 655, 600 and 555 nm. The 655 nm band is assigned to monomer form of MB and the two 600 and 555 nm bands belong to the aggregated forms [26–28]. As can be seen from Figure 2, the forms of MB in MBNaMOR-3 and MBNaMOR-4 are mainly restricted to monomeric and dimeric species with the absorption bands at about 655 and 600 nm, respectively. The bands are broadened and the maxima are blue-shifted as
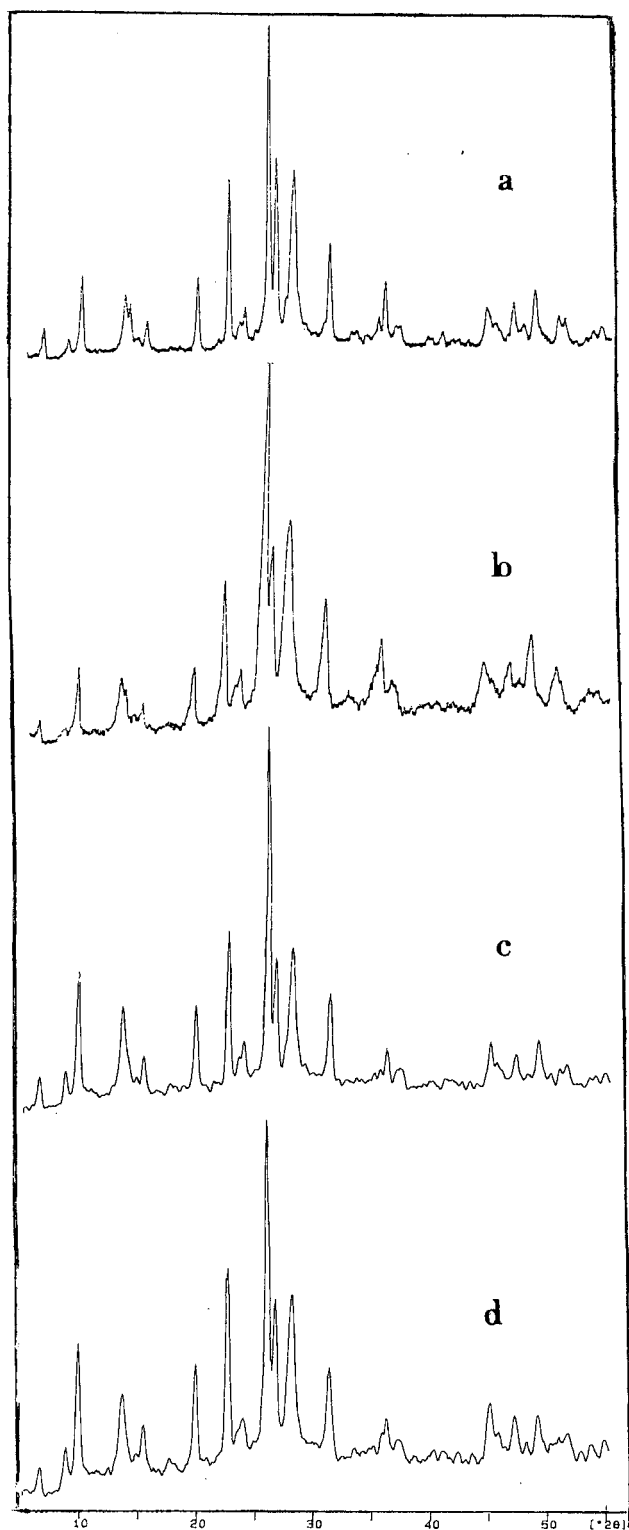
Figure 1. X-ray diffraction patterns of: (a) NaMOR, (b) MBNaMOR-4, (c) HMOR and (d) MBHMOR-2.
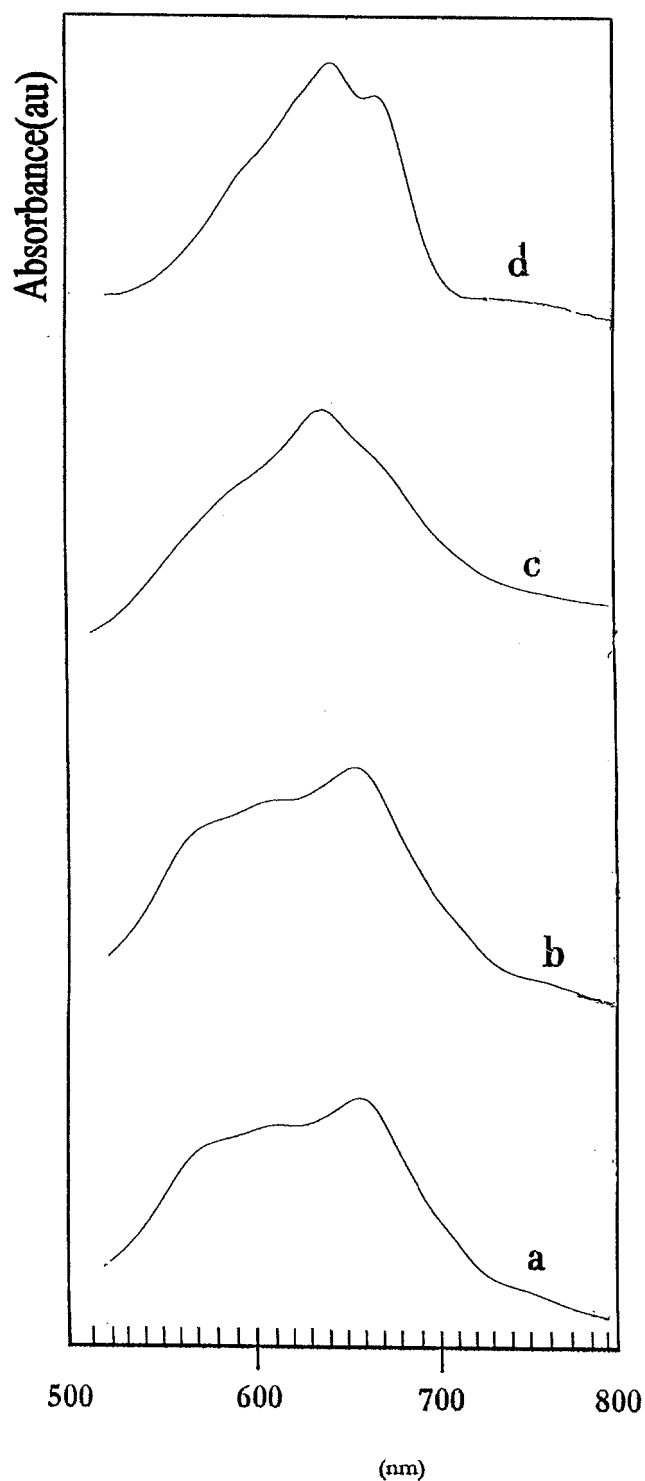

Figure 2. Diffuse reflectance spectra of the hydrated samples: (a) MB-NaMOR-1, (b) MBNaMOR-2, (c) MBNaMOR-3 and (d) MBNaMOR-4.

compared to the MB spectra in aqueous solution (Figure 3). The optical spectrum of MB in water shows two 665 and 610 nm bands which correspond to the monomeric and dimeric forms of MB in water, respectively. The host–guest interaction might be responsible for the blue-shift of the absorption bands that is often observed for dyes on mineral carriers [27, 28].
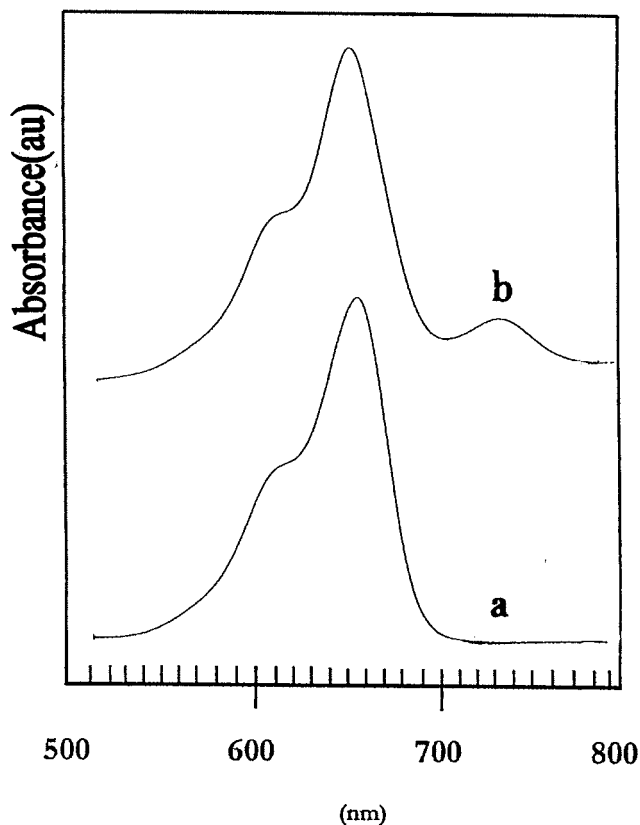
Figure 3. Electronic spectra of MB in: (a) water and (b) hydrochloric acid.

The dehydrated MBNaMOR-3 and MBNaMOR-4 samples show quite different features compared to the hydrated ones, whereas the DR spectra of the dehydrated MBNaMOR-1 and MBNaMOR-2 remain unchanged upon dehydration. A distinct band at 745 nm (Figure 4c and d) is the result of the transformation of some of the MB^+ to HMB^{2+}. No such intense band is observed for either the dehydrated MBNaMOR-1 or MBNaMOR-2. Protonation of methylene blue as evidenced by spectral bands has been observed for the dehydrated and dealuminated zeolite Y [10]. The appearance and intensity of this band in dehydrated samples strongly depend on the sample and its dehydration treatment. Figure 4e shows MBNaMOR-4 sample dehydrated in a vacuum system. The severe dehydration of this sample results in a much higher intensity of the 745 nm band. Comparison of the MB spectrum of MBNaMOR-4 to that in a 2.5 M aqueous HCl solution (Figure 3b) shows that the acidity MB sense in MBNaMOR-4 is much higher than the acidity it senses in a 2.5 M HCl solution.

Our interpretation from the above observation is that treatment of MB in mordenite suspension for the longer times of 4 and 12 days provides a condition for intercalation of the surface-adsorbed dye into the zeolite channels. The differences in behavior of the two MBNaMOR-1 and MBNaMOR-2 samples with that of MBNaMOR-3 and MBNaMOR-4 are in accord with their position in the structure. The van der Waals radii of the methylene blue molecule is about 7×16 Å [23]. This suggests that it might fit into the main channel of mordenite which has an opening of about
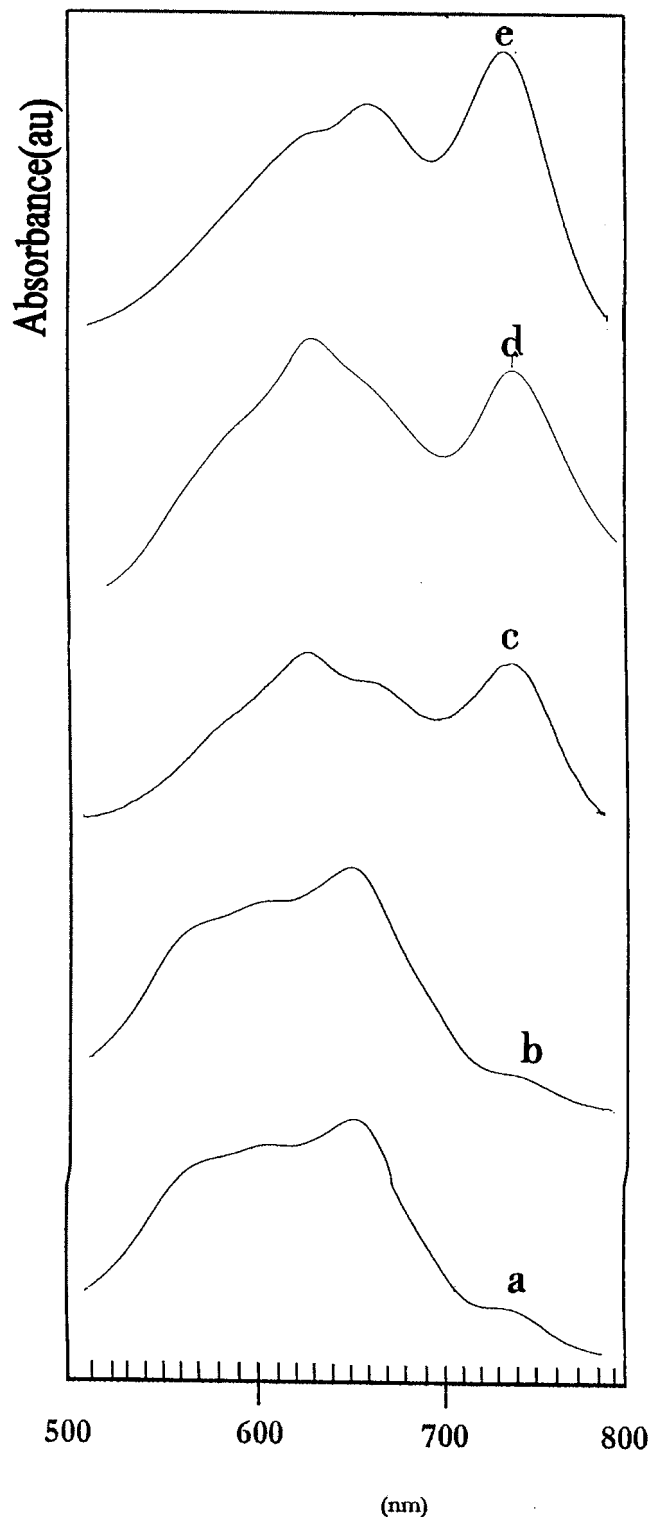

Figure 4. Diffuse reflectance spectra of the dehydrated samples: (a) MBNaMOR-1, (b) MBNaMOR-2, (c) MBNaMOR-3, (d) MBNaMOR-4 and (e) vacuum dehydrated MBNaMOR-4.
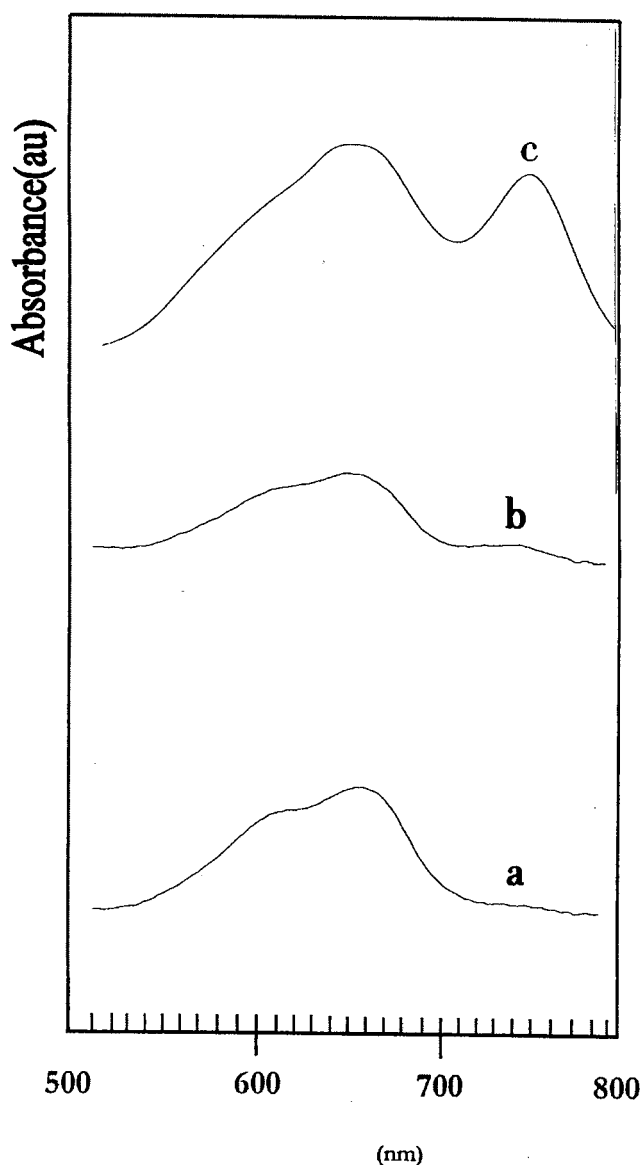
Figure 5. Diffuse reflectance spectra of (a) hydrated MBHY, (b) dehydrated MBHY and (c) dehydrated MBDHY.

6.5 × 7 Å [22]. In sharp contrast to MBNaMOR-1 and MBNaMOR-2 of which we have not been able to observe the intense band of the protonated form of the dye, the 745 nm band is very strong in MBNaMOR-3 and MBNaMOR-4. This might be convincing proof that MB molecules are intercalated in these samples.

Dehydration causes dissociation of water molecules by the electrostatic field of the zeolite cations [29]. This field is very weak in low silica zeolites such as X or Y containing monovalent cations like Na^+. But the field is stronger in high silica zeolites like mordenite. That is the reason why Ehrl *et al.* have not observed protonated form of MB in zeolite Y [10]. We prepared protonated Y zeolite (HY) and then we heated it at 550 °C for dealumination. Upon this treatment, the Si/Al ratio and hence the electrostatic field increases which leads to 745 nm band formation in the DR spectrum (Figure 5).

To focus on the study on acidity, we examined MB loading into protonated mordenite. A remarkable observation was made when MB was exchanged into acidic mordenite. The DR spectrum recorded for MBHMOR-1 of which the ion exchange condition was performed in 1 h is not the same as that of MBNaMOR-1 or MBNaMOR-2 (compare Figure 2a or b with Figure 6a). We think that upon calcination of ammonium mordenite to produce acidic zeolite, framework fragmentation could occur. The partially broken openings enhance and facilitate sorption of MB molecules into the zeolite channel. A relatively strong 745 nm band was also observed. A longer period for exchange of MB with HMOR (two days) results in a more intense HMB^{2+} band and a lower amount of monomeric methylene blue.

The micropore volume of the samples, presented in Table 1, could also be interpreted as the intercalation of MB molecules in the channels of the zeolite. The considerable reduction of the pore volume of MBNaMOR-3 and MBNaMOR-4 compared to NaMOR, MBNaMOR-1 and MBNaMOR-2 supports the idea that in MBNaMOR-3 and MBNaMOR-4 some methylene blue molecules are entrapped in the channels of the mordenite. The decrease is highest in MBHMOR-2, due to fragmentation of the framework and therefore easier and faster sorption of MB molecules into the channels of the zeolite.

Figure 6 also shows the DR spectra for the hydrated and dehydrated MB-loaded CaMOR samples. We did DRS studies on CaMOR samples to inspect the acidity generated upon dehydration of a divalent cation (i.e., Ca^{2+}). The concentration of the acidic sites is related to the polarizing power of the cation in the zeolite [29, 30]. We noticed a slower diffusion of MB molecules into the zeolite channels for MB-CaMOR compared with that of MBNaMOR samples. In fact a DR spectrum similar to MBNaMOR-3 will be acquired when the treatment procedure of the suspension of the solid in MB solution is continued for 7 days. This time is much longer than the time used to prepare MBNaMOR-3 (4 days). This lower rate of intercalation of MB into the zeolite is related to the larger effective diameter of the hydrated Ca^{2+} compared to that of Na^+. We did not observe considerable difference in the intensity of 745 nm in MBCaMOR after replacement of some of the sodium with calcium ions. Although we believe that the polarizing power of Ca^{2+} is higher than that of Na^+, the semblance in the intensities of 745 nm in these two samples could be related to the lower amount of calcium ions in the unit cell of the mordenite, because each Ca^{2+} replaces two Na^+ ions.

Figure 7 illustrates disappearance of the 745 nm band in the DR spectra of rehydrated samples. This indicates that protonation and deprotonation of MB molecules intercalated into the mordenite samples is a reversible process, proceeded by the dehydration-rehydration steps.

Conclusion

This paper demonstrates that it is possible to use methylene blue as a probe molecule to evaluate acidity of mordenite
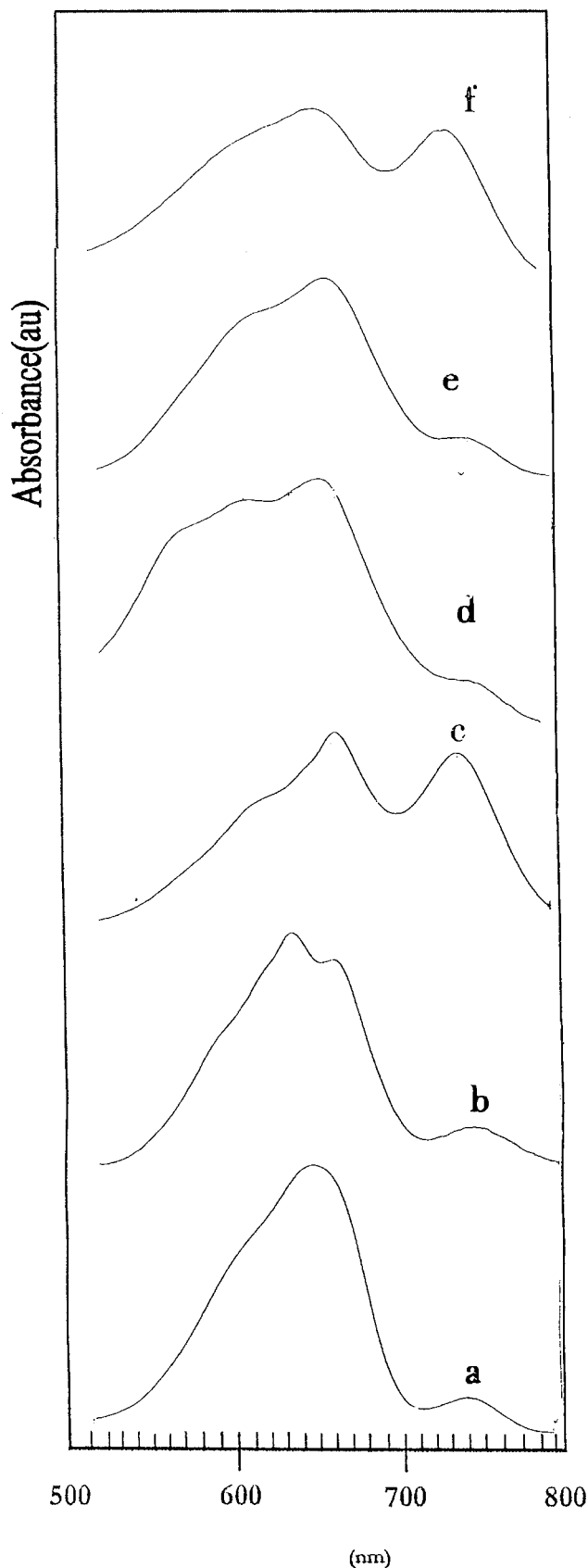
Figure 6. Diffuse reflectance spectra of (a) hydrated MBHMOR-1, (b) hydrated MBHMOR-2, (c) dehydrated MBHMOR-2, (d) hydrated MBCaMOR-1, (e) hydrated MBCaMOR-2 and (f) dehydrated MBCaMOR-2.
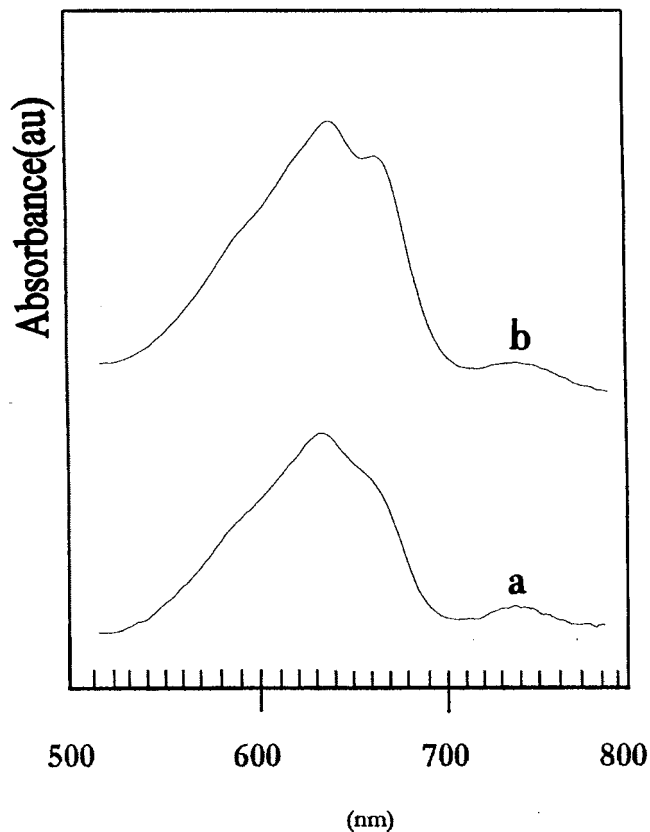

Figure 7. Diffuse reflectance spectra of rehydration of dehydrated (a) MBNaMOR-3 and (b) MBNaMOR-4.

samples under different conditions. By employing a diffuse reflectance spectroscopic technique we were able to correlate the spectral properties of incorporated dye to its molecular structure involving its protonated form. We determined the effect of dehydration on the acidity generated in different sodium, calcium and proton exchanged mordenite samples. It was observed that intercalation into protonated mordenite is nearly completed within 1 h. However, for the calcium mordenite it took about 7 days. The appearance of a strong band at 745 nm in dehydrated samples is characteristic for protonated methylene blue intercalated into mordenite samples. Those samples containing merely aggregated dye adsorbed on the sample do not show this band upon dehydration.

Acknowledgement

References

1. G. Schulz-Ekloff, D. Wöhrle, B.V. Duffel and R.A. Schoonheydt: *Micropor. Mesopor. Mater.* **51**, 91 (2002).
2. G. Calzaferri and N. Gfeller: *J. Phys. Chem.* **96**, 3428 (1992).
3. R. Hoppe, G. Schulz-Ekloff, D. Wöhrle, E.S. Shpiro and O.P. Tkachenko: *Zeolites* **13**, 322 (1993).
4. W. Hölderich, G. Lauth, G. Wagenblast and E. Schefcizk: Ger. Pat. DE 4207339 assigned to W. Hölderich, 1992.

5. D. Wöhrle, A. Sobbi, O. Franke and G. Schulz-Ekloff: *Zeolites* **15**, 540 (1995).
6. W. F. Hölderich, N. Rohrlich, P. Bartl and L. Chassot: *Phys. Chem. Chem. Phys.* **2**, 3919 (2000).
7. D.E. DeVos and P.A. Jacobs: *Stud. Surf. Sci. Catal.* **137**, 957 (2001).
8. D. Wöhrle and G. Schulz-Ekloff: *Adv. Mater.* **6**, 875 (1994).
9. F. Bedioui: *Coord. Chem. Rev.* **144**, 39 (1995).
10. M. Ehrl, H.W. Kindervater, F.W. Deeg and C. Bräuchle: *J. Phys. Chem.* **98**, 11756 (1994).
11. S. Wohlrab, R. Hoppe, G. Schulz-Ekloff and D. Wöhrle: *Zeolites* **12**, 862 (1992).
12. V. Ramamurthy, D.R. Sanderson and D.F. Eaton: *J. Am. Chem. Soc.* **115**, 10438 (1993).
13. I. Braun, G. Schulz-Ekloff, M. Beckstette and D. Wöhrle: *Zeolites* **19**, 128 (1997).
14. M. Ganschow, D. Wöhrle and G. Schulz-Ekloff: *J. Porphyrins Phthalocyanine* **3**, 299 (1999).
15. M. Wark, M. Ganschow, Y. Rohlfing, G. Schulz-Ekloff and D. Wöhrle: *Stud. Surf. Sci. Catal.* **135**, 160 (2001).
16. A. Ghanadzadeh and M.A. Zanjanchi: *Spectrochimica Acta A* **57**, 1865 (2001).
17. B. Onida, B. Bonelli, M. Lucco-Borlera, L. Flora, C. Otero Areán and E. Garrone: *Stud. Surf. Sci. Catal.* **135**, 364 (2001).
18. G.P. Handreck and T.D. Smith: *J. Chem. Soc. Faraday Trans. 1* **84**, 4191 (1988).
19. J.R. Anderson, Y.F. Chang and A.E. Hughes: *Catal. Lett.* **2**, 279 (1989).
20. M. Susic, N. Petranovic and B. Miocinovic: *J. Inorg. Nucl. Chem.* **34**, 2349 (1972).
21. D.H. Park, K.W. Lee and S.J. Choe: *Bull. Korean Chem. Soc.* **16**, 467 (1995).
22. Ch. Baerlocher, W.M. Meier and D.H. Olson: *Atlas of Zeolite Framework Types*, 5th Ed., Elsevier, 191 (2001).
23. E. Rabinowithch and I.F. Epstein: *J. Am. Chem. Soc.* **63**, 69 (1941).
24. A.A. Shaikh, P.N. Joshi, N.E. Jacob and V.P. Shiralkar: *Zeolites* **13**, 511 (1993).
25. M.M.J. Treacy and J.B. Higgins: *Collection of Simulated XRD Powder Patterns for Zeolites*, 4th Ed., Elsevier, 243 (2001).
26. R. Hoppe, G. Schulz-Ekloff, D. Wöhrle, M. Ehrl and C. Bräuchle: *Stud. Surf. Sci. Catal.* **69**, 199 (1991).
27. K. Bergmann and C.T. O'konski: *J. Phys. Chem.* **67**, 2169 (1963).
28. J. Cenens and K.A. Schoonheydt: *Clays and Clay Minerals* **36**, 214 (1988).
29. D.W. Breck: *Zeolites Molecular Sieves*, Wiley-Interscience, 462 (1974).
30. J.W. Ward: *J. Phys. Chem.* **72**, 4211 (1968).