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Embedment of Methylene Blue in natural and synthetic phillipsite

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ABSTRACT: Phillipsite was crystallized from a high siliceous aluminosilicate mixture containing Zn cations and methylene blue (MB). The presence of MB did not affect the crystallization, but it resulted in a substantial amount of dye being anchored to the zeolite, despite its narrow channels. Dye-free synthetic phillipsite modified with MB solution showed markedly lower dye content, which, however was considerably higher than those in the MB-treated natural phillipsite and mordenite. The ultra violet/visible (UV-vis) spectra of the dye-modified synthetic phillipsites indicated the presence of MB monomers and oligomers, whereas the spectra of the modified natural zeolites showed protonated MB also. The electron spin resonance spectra of samples crystallized with MB indicated the presence of paramagnetic species.

KEYWORDS: Methylene Blue, dye encapsulation, zeolite, phillipsite, mordenite.

Zeolites can be used among other important applications as substrates for intercalated molecules due to their rigid crystalline structure and uniform pore size. The intercalated guest molecules are highly dispersed inside the intra-crystalline channels and they often exhibit new catalytic, optical, electrical or magnetic properties. Unstable compounds such as sulfur anion-radicals in ultramarine blue may acquire remarkable stability after encapsulation, because they are well isolated and protected against reactive agents or light (Kowalak & Jankowska, 2009)

Methylene blue (MB, Fig. 1) is a widely used dye the molecules of which might be accommodated inside zeolite channels or cavities of appropriate size. The cationic nature of MB forms ionic bonds with the zeolite by replacement of extra-framework zeolite cations (Schultz-Ekloff *et al.*, 2002; Simoncic & Armbruster, 2005). Alternatively, MB may be incorporated into the zeolite during synthesis when added as the template to the synthesis batch (Hoppe at al., 1993; Lew at al., 2007). Crystallization of zeolite matrices in the presence of potential guest molecules is an interesting topic, but not always efficient, because the guest might affect the route of crystallization and disrupt the formation of the desired crystalline structure or even prevent crystallization. On the other hand, drastic crystallization conditions (e.g.

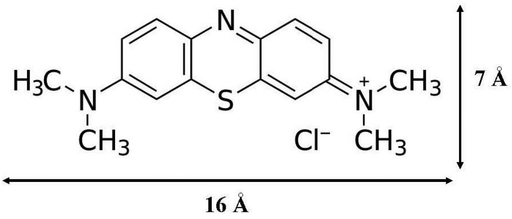

FIG. 1. Structural model of the MB molecule.

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high temperature, extreme pH values) may cause degradation of the compound to be encapsulated.

As MB contains two alkylammonium groups in its molecule it could be considered that the dye might act as a structure-directing agent, similar to many conventional templates. The synthesis of molecular sieves using organic structure-directing agents is a common and efficient procedure for facilitating crystallization and has allowed discovery of many novel structures. Most compounds used as templating agents contain alkylammonium groups. It is often assumed that the inorganic components of the initial crystallization mixture (e.g. Al species) interact with the amine groups and form the nucleation complexes of the resultant crystalline structure. The geometry of the organic template molecules helps control the size and shape of the porous structures formed. The organic templates are generally removed thermally after completion of the synthesis, rendering the molecular sieve suitable for adsorption or catalysis (Corma, 1997).

Recently, our group reported the attempted use of MB as a potential structure-directing agent for the synthesis of molecular sieves (Szyld *et al*., 2014). It was assumed that a novel structure templated by MB would confine the dye molecules very tightly and contribute to their perfect dispersion and isolation. The synthesis of aluminosilicate zeolites from mixtures containing MB showed no noticeable influence of the dye on the structure and yield of the products of crystallization. Similar attempts at synthesizing $AlPO_4$ structures with MB in the absence of conventional template agents yielded non-porous materials (Szyld *et al*., 2014). However, some of the syntheses of zincophosphate zeolite-like materials with the aid of MB showed that the presence of the dye in the starting mixture changed the direction of crystallization significantly (Szyld *et al*., 2014). Hence the initial mixture resulted in formation of a faujasite structure (FAU), but after addition of some MB the cancrinite structure (CAN) prevailed. Although novel structures were not observed, it was assumed that the modification of the crystallization route due to the contribution of MB could result from the affinity of Zn cations for the MB molecules. The Zn-MB complex might initiate nucleation and direct the crystallization towards different structures compared to experiments without use of this dye.

Based on this observation, it was decided to conduct the synthesis of molecular sieves from the initial aluminosilicate mixture with addition of a zinc precursor and with MB as a potential structure-directing agent. The ordering of the symbols of the samples (e.g. ZAS, SAZ), refers to the (decreasing) proportions of the cations: zinc, aluminium or silicon in the samples. It was assumed that the presence of zinc in the starting mixture could be advantageous for forming new crystalline porous structures. As the phillipsite structure (PHI) was one that was obtained during the syntheses, the capacity to host MB was compared with that of natural phillipsite and mordenite. Natural zeolites play a very important role in agriculture, water purification, the building industry and environmental protection among other fields (Wise, 2013). The annual production of natural zeolites exceeds three million tones, more than the synthetic molecular sieves.

EXPERIMENTAL

Three series of syntheses were carried out. The principal reagents were water glass (supplied by Chempur, Poland) as Si precursor, potassium aluminate ($KAlO_2$) (Chemos, GmbH) as a source of Al and alkalis and $Zn(NO_3)_2$ (POCH, Poland) as a source of Zn. The chemical reagents were of analytical grade.

For the first series (sample SAZ-MB), the water glass was mixed with MB and then $Zn(NO_3)_2$ and $KAlO_2$ solutions were added to form the starting gel. The molar ratios of the components (Si:Al:Zn:Na:K:MB) in the mixtures are listed in Table 1.

For the other series, the MB was added to the gel (sample ZAS-MB). The same mixture as ZAS, but without MB, was prepared as a reference material and was denoted as ZAS-0. In the SAZ-MB series the Zn content in the mixture was half of that for the ZAS series.

All the above mixtures formed homogeneous gels that were crystallized in Teflon-lined autoclaves at 160ºC for 66 h (samples ZAS-MB and ZAS-0) or 45 h (sample SAZ-MB). The end products were washed with water and the blue products containing MB were extracted with distilled water and then with ethanol in a Soxhlet apparatus to remove the dye physically adsorbed on the outer surface of the zeolite sample.

The products were characterized using X-ray diffraction (XRD), Ultraviolet−visible spectroscopy (UV-vis), Fourier transform infrared spectroscopy

TABLE 1. Experimental conditions for the zeolite syntheses.

Sample	Molar ratio Al:Si:Zn:Na:K:MB	Temp. (ºC)	Time (h)	Structure
ZAS-0	1:15:0.1:15:0.2:0	160	66	PHI
ZAS-MB	1:15:0.1:15:0.2:0.01	160	66	PHI
SAZ-MB	1:15:0.2:15:0.2:0.01	160	45	PHI

(FTIR), Electron spin resonance (ESR) and elemental analysis. The XRD analysis was performed with a Bruker D8 Advance X-ray diffractometer using Ni-filtered Cu$K\alpha_1$ radiation over the 2θ angle range 6–60º. Diffuse reflectance UV-vis spectra were recorded with a Jasco V-670 spectrometer. The FTIR spectra of the synthetic zeolites were obtained in absorption mode in the frequency range 400–4000 cm^{-1} with a Bruker Tensor 27 FTIR spectrometer, on samples prepared with the KBr method. The ESR spectra were measured at liquid nitrogen temperature with an X-band SE/X 2547 spectrometer (Radiopan, Poland) at microwave frequency 8.9 GHz and magnetic modulation 100 kHz. The C, N, S and H contents of the zeolites treated with MB were determined with an Elementar Vario EL III CHNS analyser.

The natural phillipsite was obtained from the Marano Neapolitan Yellow Tuff (NYT). For terms of comparison, a natural mordenite was also used, because its larger channel size (0.7 nm × 0.65 nm) (Baerlocher *et al*., 2007) fits better with the size of the MB molecule than phillipsite and should affect the capacity of the MB introduced.

The quantitative mineralogical analysis of the raw and purified phillipsite is shown in Table 2. The purification procedure consisted of fine grinding and sieving of the starting material to recover the fraction between 60 and 120 mesh. Subsequently, the selected powder was purified with deionized water using ultrasonic treatment to remove the finer clay fraction (Ney Ultrasonik 300) followed by magnetic separation to remove the magnetic fraction (Frantz isodynamic magnetic separator). The purified sample contained >70% phillipsite (Fig. 2). The chemical composition is listed in Table 3.

The natural mordenite sample, which was donated by the Sails Company, Philippines, contained ~50% of mordenite with the composition shown in Table 3.

For cation exchange of the phillipsite and mordenite samples, 1 g of each sample was mixed with 20 ml of aqueous MB (0.001 M) at ambient temperature. The exchange solution was changed three times before extracting the samples with water and then with ethanol (Soxhlet) until the super-

TABLE 2. Mineralogical composition of raw (NYT) and purified (PHI) natural phillipsite.

Mineral phases (%)	NYT	PHI
Phillipsite	56 (±2)	77 (±3)
Chabazite	4 (±1)	5 (±1)
Smectite	5 (±1)	1 (±1)
Analcime	3 (±1)	2 (±1)
Feldspar	21 (±3)	7 (±2)
Biotite	trace	–
Pyroxene	trace	–
Total	89 (±8)	92 (±8)
Amorphous	11	8

TABLE 3. Chemical composition (wt.%) of natural phillipsite and mordenite.

Element	PHI	MOR
SiO_2	52.48	61.5
Al_2O_3	18.11	11.6
CaO	2.51	4.3
Na_2O	2.03	2.28
K_2O	8.91	0.6
Fe_2O_3	0.13	3
H_2O	15.51	7.25
O	53.24	–
MgO	–	0.83

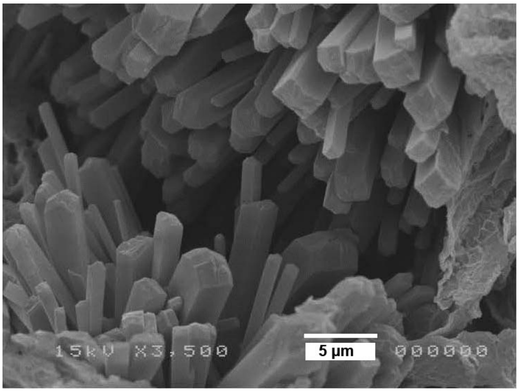

FIG. 2. SEM image of the natural phillipsite used in the experiments.

natant was colourless. These samples were denoted as: PHI nat. (IE) MB and MOR nat. (IE) MB.

RESULTS AND DISCUSSION

The XRD traces of samples ZAS-0, ZAS-MB and SAZ-MB (Fig. 3) show the presence of phillipsite (PHI), regardless of whether MB is present or not in the initial crystallization mixtures. This indicates that MB does not affect the crystallization of the studied mixtures under the applied conditions, suggesting that it does not act as a structure-directing agent. The samples crystallized in the presence of MB show intense blue colouration, which does not decrease significantly after extensive extraction with water and alcohol (Fig. 4).

The UV-vis spectra of the samples SAZ-MB and ZAS-MB (Fig. 4) contain three main absorption bands at 640, 600 and 560 nm, attributed, respectively to monomers, dimers and trimers of MB (Cenens & Schoonheydt, 1988; (Nicolai & Rubim, 2003), but the contribution of monomers is predominant (particularly in the sample SAZ-MB). This might suggest that a considerable number of the dye molecules are entrapped in the inner channels of the phillipsite structure, although their pore diameter ~0.4 nm (Baerlocher *et al*., 2007) is much smaller than the van der Waals width of a MB molecule, ~0.7 nm (Fig. 1), but closely resembles the largest cavity diameter of ~0.6 nm. Some of the dye might also be linked to the outer surface of the zeolite by ionic bonds. The IR spectra (Fig. 5) are not of particular importance because of the relatively small dye content, but the band at ~1600 cm^{-1} from MB is still noticeable in samples crystallized or modified with the dye solution.

After identification of the crystalline structure of the synthesized samples (ZAS-MB, SAZ-MB) their properties were compared with those of natural phillipsite. Of particular importance was the comparison of the ability of natural and synthetic zeolites to accommodate MB when in contact with MB aqueous solutions. The UV-vis spectra of the composites obtained by treatment of synthetic phillipsite (ZAS-0 (IE) MB) and natural zeolites (phillipsite and mordenite) with MB solutions (PHI nat. (IE) MB and MOR nat. (IE) MB) differ markedly from those crystallized in the presence of the dye (Fig. 6). Although they also show the

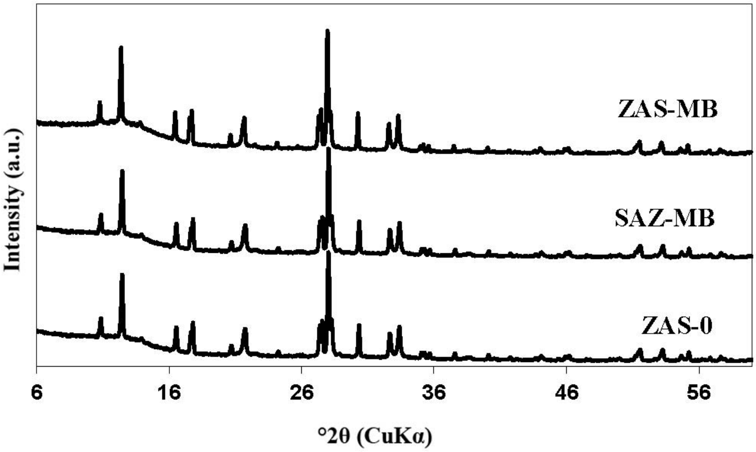

FIG. 3. XRD patterns of the products crystallized with MB (ZAS-MB, SAZ-MB) and without MB (ZAS-0).

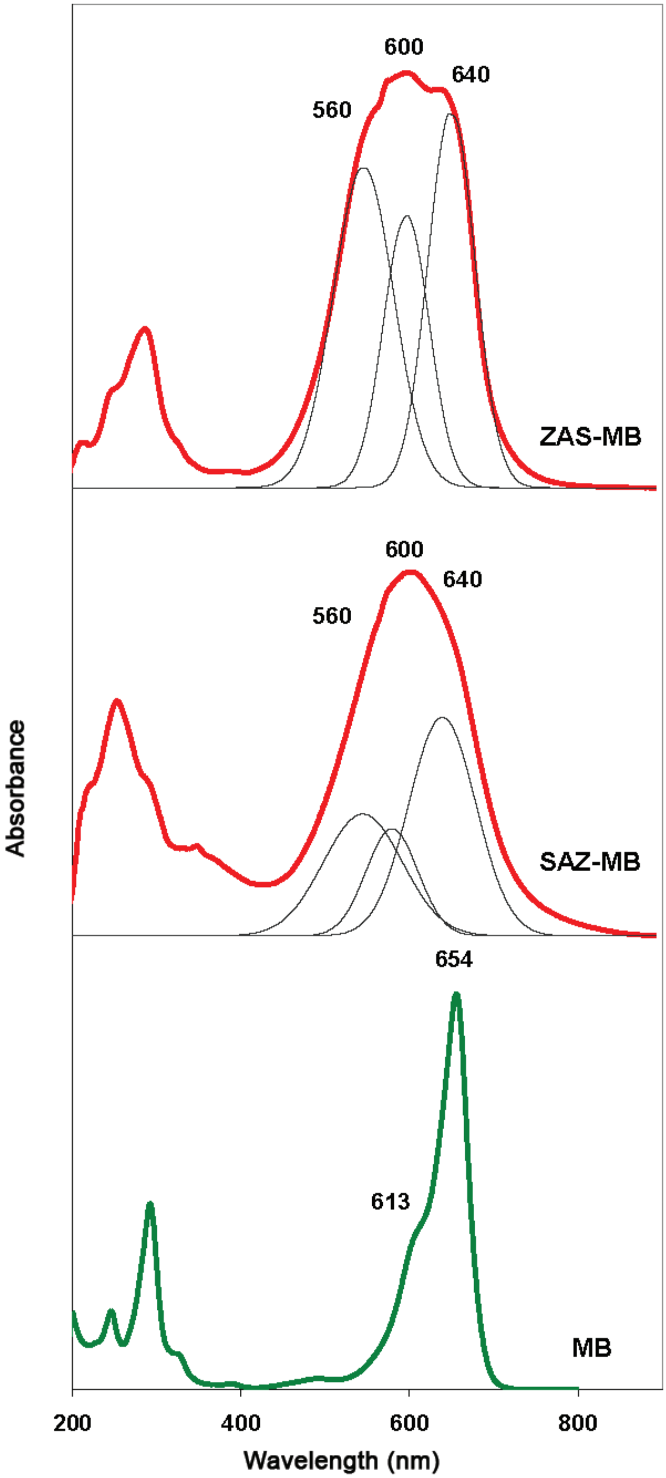

FIG. 4. UV-vis spectra of the phillipsites crystallized with MB.

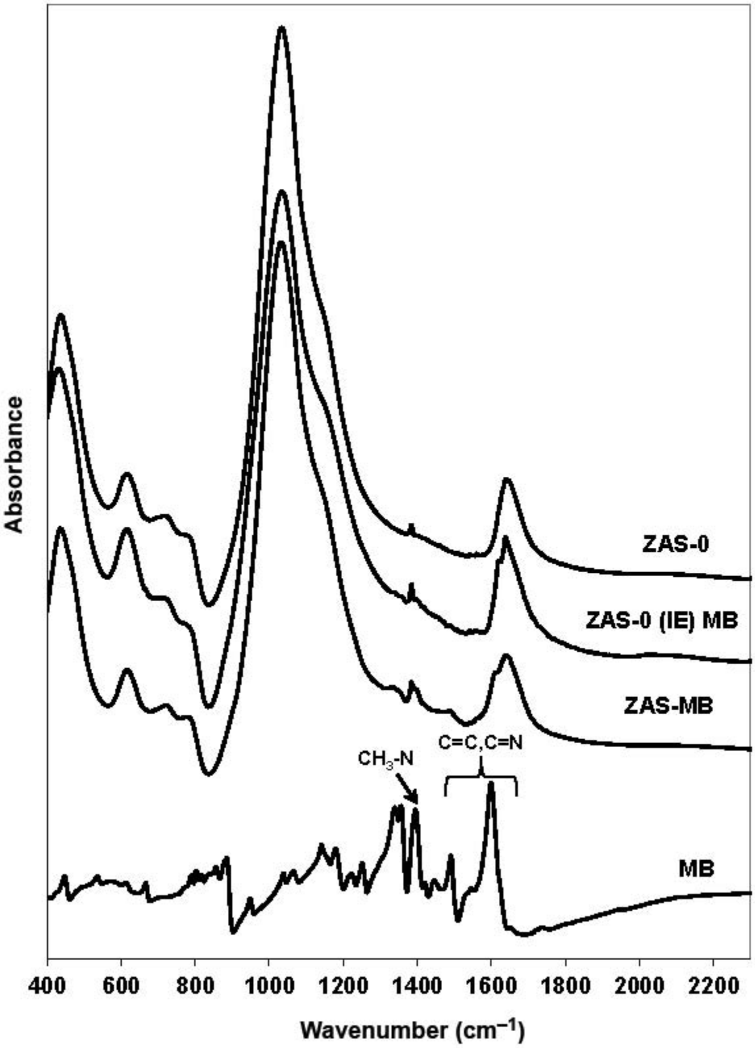

FIG. 5. FTIR spectra of the zeolite samples.

presence of monomers and oligomers, the modified samples of natural zeolites display an additional absorption band at ~760 nm, which is attributed to protonated MB (Cenens & Schoonheydt, 1988). The protons might have formed by hydrolysis of polyvalent cation impurities (e.g. Fe^{3+}) in natural zeolites.

The elemental analysis of the resultant pigments showed that the sample SAZ-MB has the largest dye content (~4.1 wt.% of MB). The sample ZAS-MB has a considerably smaller dye content (0.8 wt.% of MB). The synthetic phillipsite (ZAS-0-(IE) MB) modified with MB by ion-exchange contained ~0.6 wt.% of MB, whereas the MB-modified natural phillipsite (PHI nat. (IE) MB) has a smaller MB content (0.3 %). The modified natural mordenite (MOR nat. (IE) MB) has an even smaller MB content (0.25%), in spite of the larger channels compared to phillipsite, probably due to the smaller zeolite content in the mordenite sample.

The ESR spectra of the MB-bearing samples show distinct signals in the synthetic samples that reflect the presence of paramagnetic species in the composites (Fig. 7). These signals were not observed in the samples modified with MB aqueous solutions, although some small signals are

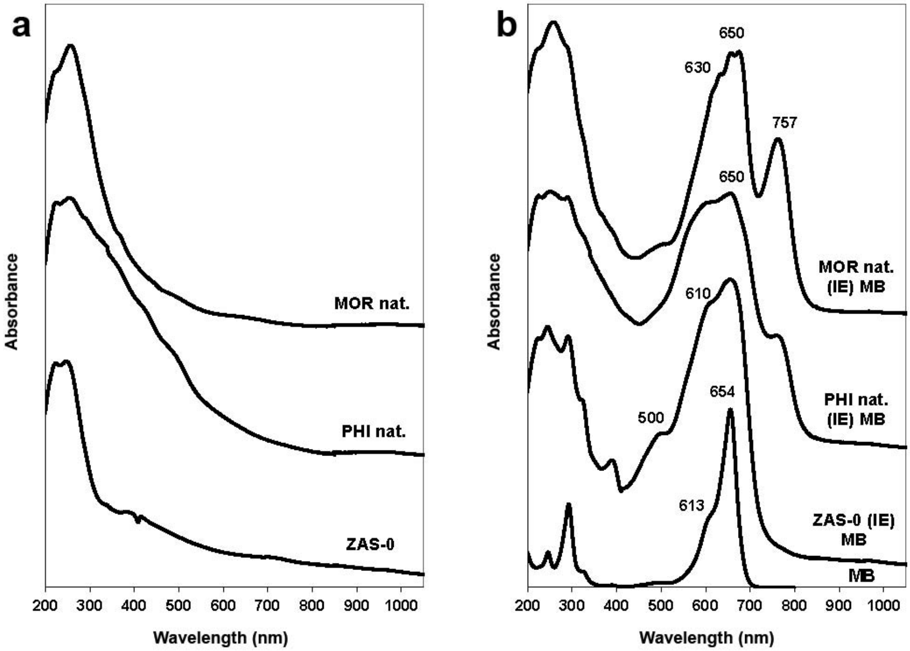

FIG. 6. UV-vis spectra of natural and synthetic zeolites (a) and of the pigments obtained by ion exchange of the zeolites with MB (b).

also visible in the modified natural phillipsite (PHI nat. (IE) MB). The ESR signals of the solid MB and condensed aqueous solutions with g value = 2.0036 are ascribed to MB oligomers, whereas the methanol solutions or monomers attached to the matrix show no signal (Eltantawy, 1979).

CONCLUSIONS

Methylene blue can be entrapped inside phillipsite either by ion exchange or by zeolite synthesis, despite its relatively narrow channel size. The PHI was obtained by hydrothermal crystallization of an aluminosilicate gel containing zinc cations either

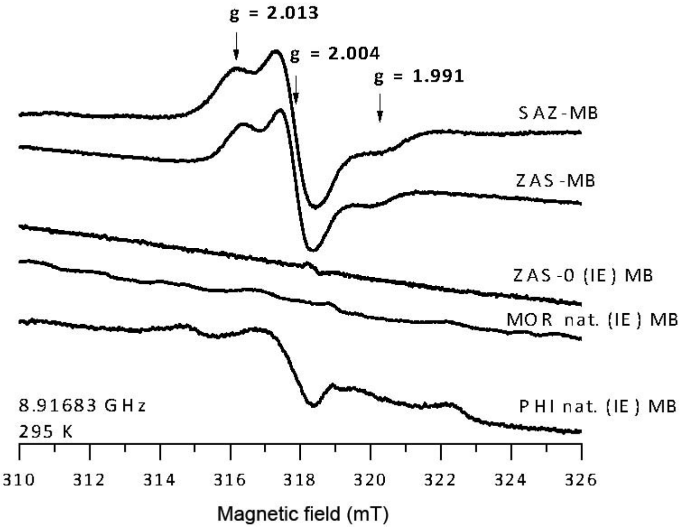

FIG. 7. ESR spectra of the zeolite samples.

with or without the presence of MB. Hence the MB does not act as a structure-directing agent and does not affect noticeably the crystallization route in this study. The zeolites synthesized in the presence of MB contain considerable amounts of dye, especially when MB was added to the Si source before formation of the crystallization gel. The dye content was considerably larger than that in the synthetic phillipsite modified with MB solution and even higher than in natural phillipsite. However, the natural phillipsite sorbed a higher amount of MB from solution than the natural mordenite, despite the larger size of channels of the latter. The lower capacity of mordenite compared to phillipsite is attributed to the lower zeolite content of the sample used.

The UV-vis spectra of the zeolites containing entrapped MB showed mainly the presence of MB monomers, with some MB dimers and trimers. The presence of MB oligomers might suggest a localization of the dye at the outer surface of the zeolites. The additional absorption band at ~760 nm in the natural zeolites, is attributed to protonated MB; the protons being formed from higher-valent metal cation impurities. The ESR spectra of the products obtained by zeolite crystallization and in the natural phillipsite modified by ion exchange contain a distinct signal due to paramagnetic species. This signal is absent from the other samples prepared by ion exchange. The detailed explanation of the results above will be the subject of a further study.

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