Condensation of pyrrole with aldehydes in the presence of Y zeolites and mesoporous MCM-41 aluminosilicate: on the encapsulation of porphyrin precursors

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Condensation of pyrrole and benzaldehyde was carried out in isooctane or cyclohexane in the presence of MCM-41, HY (Si/Al 15) and CoY (Si/Al 2.6). In all cases, formation of tetraphenylporphyrin (TPP) was observed in the organic solutions, even after dissolving with hydrofluoric acid the resulting MCM-41 solid employed in the condensation. In addition, some reaction intermediates containing one to two pyrrole heterocycles were also characterized in these solutions. In spite of this, the diffuse reflectance and IR spectra of the organic material adsorbed in the aluminosilicates after the condensation reaction were remarkably different from those characteristic of TPP. This discrepancy indicates that the material adsorbed inside the solid pores is not TPP but most probably any of its immediate porphyrinogen precursors. In this regard, the coincidence of the diffuse reflectance spectra obtained after the synthesis with those characteristic of porphomethenes and porphodimethenes was noted. Condensation of pyrrole and acetaldehyde follows the same pattern: lack of formation of *meso*-tetramethylporphyrin (TMP) inside the pores according to diffuse reflectance and IR spectroscopies, but detectable amounts of TMP in the organic solutions.

Encapsulation of organic guests inside microporous supports has become a general methodology to increase and control their selectivity as catalysts.[1–3] The framework of the host defines a restricted reaction cavity[4] where the chemical transformation is forced to occur. In addition, confinement may also produce a higher stability of the active species, avoiding degradation pathways and leading to higher turnover numbers. Combination of these two effects (higher stability and selectivity) justifies the positive effect that heterogenization of the catalyst may have, compared with its activity in homogeneous media. A representative example of the above systems, which has attracted considerable interest recently, is the use of phthalocyanine complexes within faujasites as catalysts for hydrocarbon oxidations.[5,6]

Zeolites have been, in most cases, the supports of choice for this purpose. The reason is that they combine a high thermal and chemical stability with a crystalline structure formed by channels and cavities of strictly regular dimensions called micropores.[7] Depending on the dimensions of their apertures, zeolites have been classified as small, medium and large pore zeolites.[8,9] Large pore faujasites X and Y have been the most widely used zeolites to incarcerate organic guests. Their crystalline structure is formed by almost spherical supercages of 14 Å diameter interconnected tetrahedrally through smaller openings of 7.4 Å.[9]

In order to entrap within faujasites bulky molecules larger than 7.4 Å, but small enough to be accommodated inside the supercages (14 Å diameter), it is necessary to devise ship-in-a-bottle methodologies.[10–13] These strategies rely on the easy diffusion of smaller precursors that then react inside the micropores to form the bulky molecule immobilized within the cages.

As a continuation of our work aimed at the ship-in-a-bottle synthesis of organic compounds inside zeolite micropores,[10–12,14–16] we would like to report the results that we have obtained in the attempted preparation of *meso*-substituted porphyrins adsorbed within mesoporous MCM-41 aluminosilicate and Y zeolites. Tetraphenylporphyrin (TPP) is considered as one of the cleanest singlet oxygen photosensitizers,[17] and embedding it inside the supercavities of Y zeolite would provide a heterogeneous singlet oxygen sensitizer exhibiting high selectivity, similar to the thionin-based one recently reported.[18] Preparation of tetraaryl and tetramethyl *meso*-substituted porphyrins within the supercages of Y zeolites has been previously reported in the literature.[19–22] However, these reports were aimed at the study of the properties of zeolite-bound porphyrins as oxygen carriers and singlet oxygen generators and lacked a careful characterization of the guests. We have undertaken a detailed study of the samples by combining diffuse reflectance and IR spectroscopies with product studies. In addition, we have compared the spectroscopic properties with samples prepared by adsorbing authentic preformed porphyrins within novel mesoporous MCM-41 (30 Å diameter channels),[11,23] where incorporation of porphyrins should not be impeded by size. The results show that the species inside the faujasite cavities are not really porphyrins but more likely porphyrinogen precursors.

Results and Discussion

Molecular modelling has proven to be a powerful and reliable tool to predict the possibility of incorporating a guest within the zeolite voids.[24,25] Molecular sizes of TPP and tetramethylporphyrin (TMP) were calculated by the molecular mechanics Discover 3.1 program package and the results are presented in Fig. 1. The diameters of TPP and TMP are 18.44

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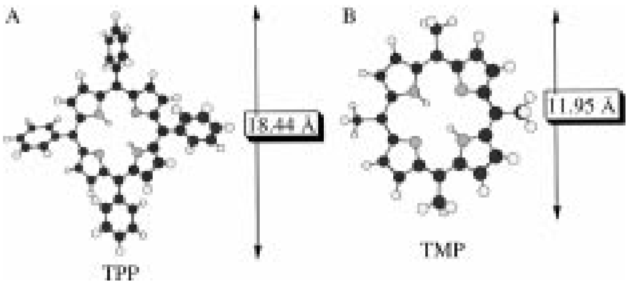


Fig. 1 Molecular mechanics modelling of TPP (A) and TMP (B)

and 11.95 Å, respectively. Therefore, it is clear that neither TPP or TMP can enter through the 7.4 Å windows of the faujasite supercages and only TMP can be accommodated within the large cavitites of faujasites. In view of these simple calculations, incorporation of tetrapyridylporphyrin (similar dimensions as TPP) within NaY by mere ion exchange, as it has been reported,[20] appears to be highly unlikely and only deposition on the external surface of the particles seems to be reasonable. On the other hand, our calculations support the previous assumption that TMP can fit into the faujasite supercages.[19] However, in this case a successful ship-in-a-bottle synthesis is still necessary to achieve the encapsulation of TMP, since its entrance through the cage apertures is not possible. Based on the relative sizes of the porphyrins and MCM-41 hexagonal channels, molecular modeling also predicts that no restrictions on the diffusion of TPP or TMP into the extra-large channel system of MCM-41 aluminosilicate need to be expected.

To study the possibility of synthesizing these porphyrins from less bulky precursors, the spectroscopic properties of two MCM-41 samples, one prepared by adsorbing preformed TPP from an organic solution and the other by treating a mixture of pyrrole and benzaldehyde in the presence of MCM-41, were compared. It is known that TPP can be obtained in the liquid phase by heating a solution of pyrrole and benzaldehyde in the presence of acids.[26] In our case, the acid sites of MCM-41 could act as a catalyst for the condensation.[27,28]

The diffuse reflectance and IR spectra of authentic TPP adsorbed on MCM-41 are presented in Fig. 2 and 3, together with the spectra of TPP in acid solution or as a KBr disc. As it can be seen in Fig. 2, the UV/VIS absorption spectrum of TPP in acid EtOH solution shows remarkable coincidences with the diffuse reflectance of the TPP-MCM-41 sample in the shape of the series of Q bands and the λ_{max} of the Soret band. These patterns are quite different from those corresponding to neutral TPP (not shown in the figure). Likewise, the FT-IR spectrum of TPP upon adsorption on MCM-41 does not coincide with that of neutral TPP recorded in a KBr disc (Fig. 3).

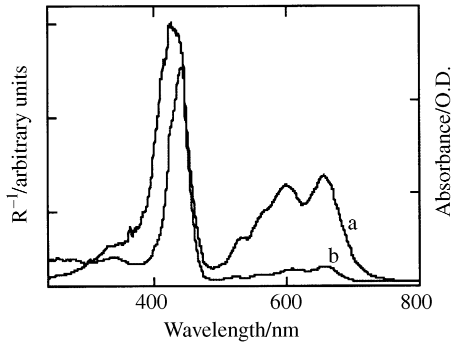


Fig. 2 Trace a: Diffuse reflectance spectrum (inverse of reflectance, R^{-1}) of TPP-MCM-41 prepared by adsorbing TPP onto dehydrated MCM-41. Trace b: UV/VIS absorption spectrum of a solution of TPP in ethanol containing hydrofluoric acid

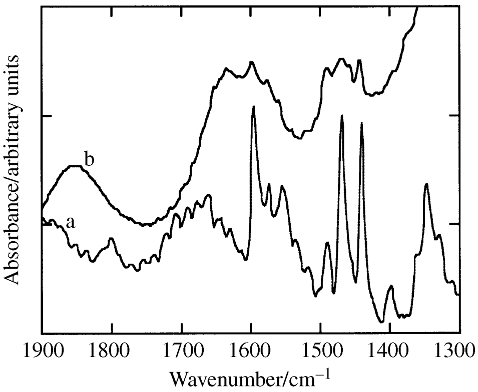


Fig. 3 Aromatic region of the FT-IR spectra of TPP in a KBr disc (trace a) and a self-supported TPP-MCM-41 sample (trace b) obtained by adsorbing preformed TPP onto dehydrated MCM-41. The spectra were recorded at room temperature. Before obtaining the spectrum of TPP-MCM-41, the sample was pumped out at 200 °C under 10^{-2} Pa for 1 h

The UV/VIS spectrum of recovered TPP from the supernatant solution after adsorption onto MCM-41 showed no changes in the wavelength maxima of the Soret absorption and in the relative intensity of the Q bands with respect to a neutral solution of TPP. This may be taken as a proof that no chemical changes have occurred to TPP during the simple adsorption procedure used here. In contrast to TPP-MCM-41, the diffuse reflectance spectrum of TPP adsorbed on silica (not shown) is exactly the same as that recorded for TPP in CH_2Cl_2 solution. We noticed that the changes in the pattern of the Q bands observed when TPP is adsorbed on MCM-41 are compatible with those previously observed in solution or in other heterogeneous media for the diprotonated form of TPP ($TPPH_2{}^+$).[29] This would indicate that protonation of the nitrogen electron lone pair of the porphyrin macrocycle has occurred upon adsorption of TPP on MCM-41, but not for TPP deposited on silica, in agreement with the higher acid strength of MCM-41 compared with neutral silica.[28]

We were interested in determining if the same spectroscopic properties can be observed in MCM-41 when mixtures of pyrrole and benzaldehyde in isooctane are treated at 80 °C in the presence of this mesoporous aluminosilicate. It has to be remarked that the thermal treatment necessary to dehydrate MCM-41 (see *Experimental*) is expected to generate non-framework aluminum species from partial removal of tetracoordinated aluminium from the walls.[28,30,31] After the reaction, the solid was filtered and exhaustively extracted with CH_2Cl_2 to desorb reagents and adventitious byproducts. The diffuse reflectance spectrum of the resulting MCM-41 sample, after the attemped TPP synthesis from pyrrole, was totally different from that of TPP-MCM-41 and exhibits a single broad absorption at about 500 nm (Fig. 4).[32,33]

The FT-IR spectrum of this MCM-41 sample (Fig. 5) is also different from that recorded for TPP-MCM-41 (Fig. 3b). Comparison of the two spectra of Fig. 4 and 5 with those of Fig. 2 and 3 indicates that the organic material adsorbed on MCM-41 after treatment with pyrrole and benzaldehyde is definitely not TPP.

However, UV/VIS spectroscopy and thin layer chromatography (tlc) of the organic phase and of the extracts from the MCM-41 employed as a catalyst for the condensation of pyrrole and benzaldehyde showed unambiguously the presence of TPP. We noticed that the intensity of the Soret band for these solutions, after filtration in air of the catalyst and thus in the absence of MCM-41 steadily increased, within minutes until a maximum was reached (see Fig. 7 for the case

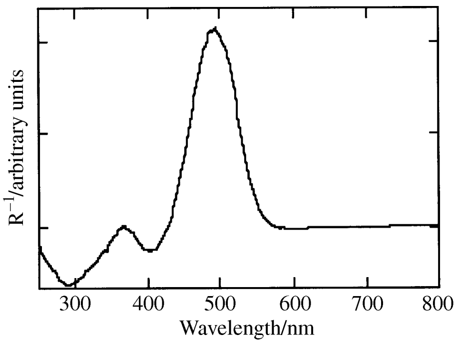


Fig. 4 Diffuse reflectance spectrum (inverse of reflectance, R^{-1}) of a MCM-41 solid, used as the catalyst for the condensation of pyrrole and benzaldehyde, after exhaustive solid/liquid extraction

of HY). This observation would indicate that a precursor of TPP, presumably with the same macrocyclic structure, was already present in the solution. This precursor would undergo an aerobic oxidation to generate increasing concentrations of TPP, being the typical behavior of porphyrinogens.[29] Besides, we were able to isolate by tlc a fraction whose UV/VIS spectrum recorded immediately after isolation matched that shown in Fig. 4 for the diffuse reflectance of MCM-41 used as a catalyst of the pyrrole condensation. Unfortunately, this UV/VIS spectrum slowly changed with time towards that of TPP, thus making its further characterization uncertain. In addition, GC-MS analysis of the organic solutions revealed the presence of other condensation byproducts, containing one or two pyrrole and benzyl moieties, and known to be intermediates in the synthesis of porphyrins.[29] Their structures are presented in Scheme 1. Finally, after dissolving the MCM-41 aluminosilicate with HF, TPP was detected in the resulting solution. Our findings are consistent with the recent report that mesoporous FSM-16 can be a convenient catalyst to prepare TPP.[34] Although no indication of the nature of the organic material retained in the mesoporous FSM-16 support after the reaction was given, it was mentioned that FSM-16 becomes dark purple in color after this synthesis.[34]

Taking into account the accepted reaction mechanism for the formation of TPP in solution by condensation of pyrrole and benzaldehyde (Scheme 2),[29] a likely explanation to account for the observations using MCM-41 would be that the material present in MCM-41 is a cyclic intermediate with a porphomethene or porphodimethene structure (see Scheme 2). The characteristic UV/VIS spectra of these compounds show a single broad band at 500 nm, consistent with the diffuse reflectance spectrum of MCM-41 presented in Fig. 4.[35–37] The final steps of the homogeneous TPP synthesis are oxidations of the tetrapyrrole macrocycle to the porphyrin through porphomethene and porphodimethene intermediates. Apparently these oxidations could not readily occur inside the MCM-41 mesopores. Interestingly, in the FSM-16-catalyzed preparation of TPP, an oxidizing reagent such as *p*-chloranil is required in the organic solution to effect the transformation of porphyrinogens into porphyrin.[34] Analogously, the same authors reported the *p*-chloranil oxidation of the porphyrinogen intermediates generated in the K-10 clay-catalyzed synthesis of *meso*-tetraarylporphyrins.[38,39]

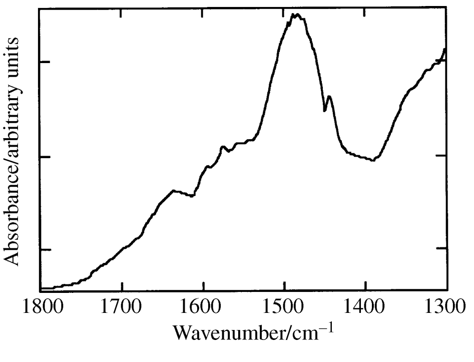
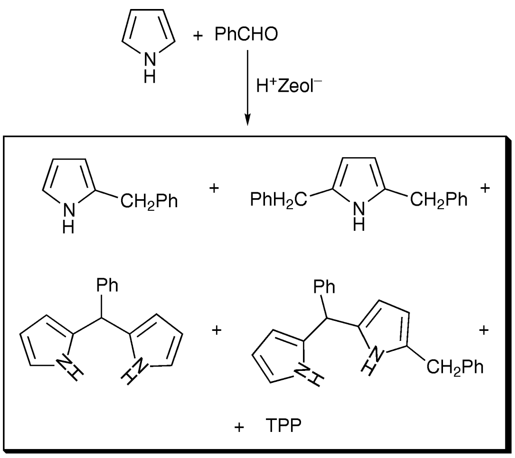
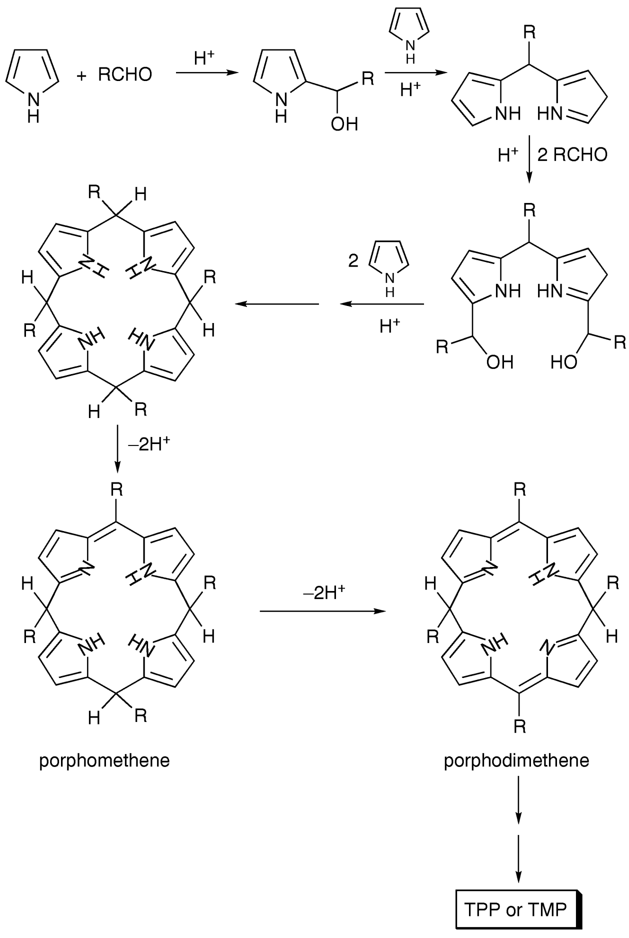


Fig. 5 Aromatic region of the FT-IR spectrum of a MCM-41 solid, used as the catalyst for the condensation of pyrrole and benzaldehyde, after exhaustive solid/liquid extraction



Scheme 1

In an attempt to force these oxidations inside the pores of the solid, we progressively heated, in an oven under an air stream, the MCM-41 loaded with the pyrrole condensation products, but a diffuse reflectance spectrum corresponding to TPP could not be obtained. Eventually the aluminosilicate became dark brown, indicating that degradation of the organics has begun.



Scheme 2

According to the molecular modelling TPP cannot be accommodated inside the faujasite cavitites. We were interested in discovering if this fact is reflected in a different behavior of Y zeolites compared to the MCM-41 aluminosilicate, whose channel dimensions are large enough to allow the internal location of TPP. For this purpose, we carried out the pyrrole–benzaldehyde condensation in the presence of HY (Si/Al 15). Notably, the diffuse reflectance spectrum of the HY zeolite after the reaction and solid/liquid extraction shows a remarkable resemblance to that recorded for MCM-41 after the same treatment (Fig. 6). Interestingly, TPP could again be unambiguously observed in the organic phase and its amount steadily increased with reaction time (Fig. 7). We also performed the pyrrole–benzaldehyde condensation in the presence of a CoY (Si/Al 2.6) zeolite, in which TPP was also formed. The amount, after condensation, of organic material adsorbed on HY (17 wt%, C/N 8.9) and CoY (15 wt%, C/N 9.1), as measured by thermogravimetry, is too high to correspond exclusively to products located on the external surface of the particles. The C/N ratio corresponding to pure porphyrins is 9.4, which is not too different from that determined experimentally in our samples. On the other hand, assuming that after the reaction, HY and CoY contain porphodimethenes (MW 614), the loading measured would correspond roughly to one molecule for every three cages. The IR spectra of both solids after the condensation reaction is very similar to that recorded for MCM-41 under the same conditions.

Therefore, in contrast to what it could be anticipated based on the micropore dimensions, both aluminosilicates (faujasites and MCM-41) exhibit essentially similar behavior for the condensation of pyrrole and benzaldehyde. In this regard, it has to be noted that the porphodimethenes are not planar but have a roof-type geometry,[37] and their molecular diameter is thus largely reduced with respect to that calculated for planar TPP. We have estimated that the size of a porphodimethene with a dihedral angle from planarity of 30° would be less than 14 Å, allowing them to fit into the faujasite supercages. Alternatively, some other nonmacrocyclic intermediates with similar spectroscopic properties to those of porphomethenes, while still being immediate precursors of TPP, may also be present in the voids of HY. Incidentally, the larger size of planar porphyrins compared to bent porphyrinogens could be responsible for the reluctance of the latter to undergo oxidation inside the restricted confined spaces of MCM-41 owing to the remarkable increase in steric strain that would result after the oxidation (less than 14 Å for tetraphenyl porphydimethenes to 18.44 for TPP).

As we have previously mentioned, the less bulky TMP has been considered more appropriate for incorporation into the cavities of faujasites.[19] In fact, molecular modelling indicates that TMP could fit within the big α-cages of faujasites (Fig. 1).

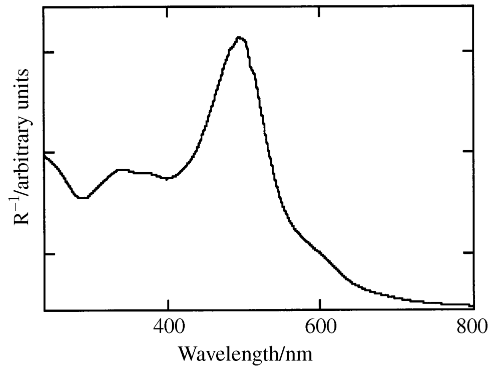


Fig. 6 Diffuse reflectance spectrum (inverse of reflectance, R^{-1}) of the HY (Si/Al 15) zeolite, used as the catalyst for the condensation of pyrrole and benzaldehyde, after solid/liquid extraction

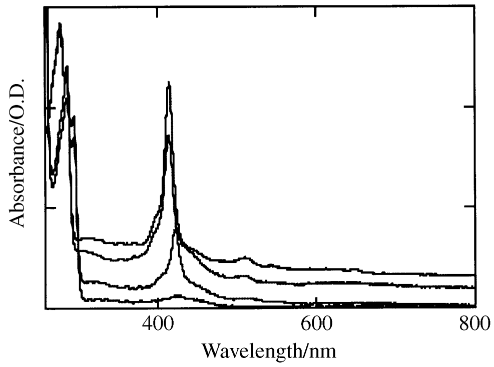


Fig. 7 UV/VIS spectra of the organic phase during the condensation of pyrrole and benzaldehyde in the presence of HY (Si/Al 15). The diffuse reflectance spectrum of the corresponding solid is shown in the Fig. 6. The spectra were taken at 6, 30, 50 and 100 h reaction time (from the bottom to the top). For the sake of clarity, spectra at 50 and 100 h have been shifted along the vertical absorbance axis

Therefore, in this case the ship-in-a-bottle synthesis of TMP adsorbed on Y zeolite should be more favorable. We have carried out the condensation of pyrrole and acetaldehyde in the presence of HY, CoY, ZnY (Si/Al 2.6) and ZnX (Si/Al 1.4). In all cases, the presence of variable amounts of TMP could be observed in the organic phase. The organic content measured by thermogravimetry of the solids after exhaustive solid/liquid extraction varied from 10 to 15 wt%. The diffuse reflectance spectra of these samples showed a broad absorption at 500 nm, similar to those obtained after the attempted synthesis of TPP and coincident with that previously reported for a closely related MnY sample, resulting from the condensation of pyrrole and acetaldehyde.[19] Fig. 8 shows a representative diffuse reflectance spectrum. The broadness of the 500 nm band precluded the observation of small differences in the wavelength maximum depending on the nature of the charge-balancing cation (H^+, Co^{2+}, Zn^{2+} or Al^{3+}) acting as a template for the synthesis. As it can be seen, this spectrum is totally different from that corresponding to TMP in solution, while it shows again a close resemblance to those of porphomethenes and porphodimethenes. The IR spectra of these zeolites after exhaustive solid/liquid extraction again showed remarkable differences with that of pure TMP or its complexes.

Conclusions

Preparation of *meso*-substituted porphyrins adsorbed on faujasites have been reported in the literature.[19–22,40–45] However, we have shown that none of the reported procedures for the encapsulation, either ion-exchange of pre-

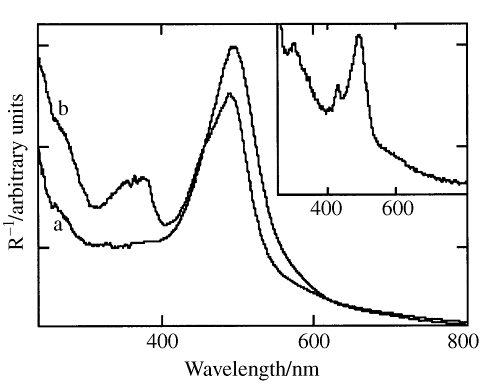


Fig. 8 Diffuse reflectance spectra (inverse of reflectance, R^{-1}) of HY (Si/Al 15) (trace a) and ZnY zeolites (trace b) after the pyrrole–acetaldehyde condensation and solid/liquid extraction. The insert corresponds to the UV/VIS absorption spectrum of one of the fractions isolated by thin layer chromatography from the organic solution extract

formed metal–porphyrin complexes[2] or condensation of pyrrole with acetaldehyde,[19] leads to a sample of porphyrin embedded within zeolite whose spectroscopic properties match those of the corresponding porphyrin, either in solution or adsorbed on mesoporous MCM-41. Furthermore, these properties would be in better agreement for porphyrinogen compounds. This hypothesis is supported by the fact that the corresponding porphyrin, although not characterized in the zeolite matrix, is indeed observed for all the zeolites studied in the liquid phase during the condensation reaction of pyrrole with benzaldehyde or acetaldehyde. The concentration of porphyrin in the solution increased along with the reaction time. Moreover, prophyrin was also detected by dissolving the aluminosilicates with HF, thus indicating that the species inside the solid has to have a structure very close to that of porphyrin. These conclusions are parallel to those previously reached by Cady and Pinnavaia for the condensation of pyrrole and benzaldehyde in the presence of ion-exchanged layered clays.[46]

Experimental

TPP, benzaldehyde and pyrrole were commercial samples (Aldrich) and used as received. For acetaldehyde condensations, the corresponding trimer paraldehyde was used as the reagent. HY (Si/Al 15) was a commercial sample (P. Q. Industries). CoY, ZnY and ZnX were prepared starting from commercial NaY (Union Carbide, SK-40, Si/Al 2.6) or NaX (Aldrich, 13X, Si/Al 1.3) samples by treating at room temperature with aqueous solutions of the corresponding nitrates. MCM-41 was obtained by hydrothermal crystallization of amorphous silica (Degussa) and alumina (Basf) in a 25% aqueous solution of hexadecyltrimethylammonium bromide and tetramethylammonium hydroxide according to the procedure reported in the literature.[47] The Si/Al ratio measured by chemical analysis was 13. UV/VIS spectra were recorded on a Shimadzu UV-2401 PC scanning spectrophotometer. For the diffuse reflectance mode an integrating sphere was attached and $BaSO_4$ was used as the reference. IR spectra of self-supported wafers (10 mg) were prepared by compressing the aluminosilicate powder at 10 Ton cm^{-2}. The disks were placed in a greaseless quartz cell fitted with CaF_2 windows. The samples were outgassed at 10^{-2} Pa at 200 °C for 1 h before recording the IR spectra at room temperature on a Nicolet 710 FT-IR spectrophotometer. The IR spectrum of pure TPP was recorded in a KBr disc with the same instrument. Thermogravimetry–differential scanning calorimetry profiles were obtained on a Netsch-STA 409 EP thermobalance under air stream and using kaolin as the standard. Combustion chemical analyses (C and N) were carried out in a Perkin-Elmer analyzer.

Adsorption of TPP (10 mg) on MCM-41 (500 mg) was carried out by stirring a cyclohexane solution (30 ml) at 60 °C in the presence of dehydrated (500 °C, air, overnight) aluminosilicate for 2 h.

Condensation of pyrrole (100 mg) and benzaldehyde (150 mg) or acetaldehyde (150 mg) was carried out by stirring a suspension in CH_2Cl_2 or isooctane (50 ml) at 40–100 °C in the presence of dehydrated zeolite (500 °C, air, overnight). The course of the reaction was periodically followed by recording UV/VIS spectra of the organic phase. After 8 days, the solids were submitted to continuous solid/liquid extraction in a micro Soxhlet apparatus using CH_2Cl_2 as the solvent. The extracts were analyzed by GC-MS (Hewlett Packard 5988A, 25 m capillary column of 5% phenylmethylsilicone) and tlc (Merck, silica gel 60 F_{254}). Byproducts shown in Scheme 1 were identified based on their mass spectra, coincident with those reported in the literature.[29]

Molecular mechanics calculations were carried out using the Discover 3.1 program package running on a Silicon Graphics computer. The molecular size of TPP and TMP was estimated as the distance between the two furthest hydrogen nucleii plus two covalent hydrogen atom radii.

Acknowledgements

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32 A referee suggested to use all-silica MCM-41 as a control. Experiments using aluminum-free MCM-41 have shown that even this solid is able to catalyze the reaction in spite of the absence of "conventional" acid sites. We believe that the acid requirements to

catalyze this reaction are low enough to allow silanol groups (pK_a 7.4) to intervene in the reaction as active sites. Recognition that $\equiv$Si—OH groups can be active sites for organic reactions is currently attracting considerable interest (see ref. 33). Work is in progress to fully establish this possibility.

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