

Triarylmethyl cations Encapsulated within Zeolite Supercages

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Abstract: A series of substituted triarylmethyl cations, including malachite green, tris(4-methoxyphenyl)methyl cation, and bis(4-methoxyphenyl)phenylmethyl cations, has been prepared adsorbed on tridirectional large pore zeolites Y and β in their H^+ or La^{3+} form, as well as within the novel mesoporous aluminosilicate MCM-41, by ship-in-a-bottle synthesis from the corresponding benzaldehyde and *N,N*-dimethylaniline or anisole. The resulting composites exhibit diffuse reflectance and IR spectra characteristic of these trityl dyes. The cation content was determined by thermogravimetry–differential scanning calorimetry. Preparation of these triarylmethyl cations exclusively on the external surface of ZSM-5, a medium pore zeolite whose internal voids are too small to accommodate these cations, is also possible. Therefore, the methodology based in the diffusion of smaller precursors does not guarantee itself the intrazeolite location of the synthesized guests. In this work, we have experimentally determined that the dyes are blocked in the interior of the faujasite pores. Thus, direct evidence showing the location of the organic material inside the zeolite supercages was obtained using X-ray diffraction and X-ray photoelectron spectroscopy. These dyes incorporated within microporous solids can act as heterogeneous photosensitizers to promote the sensitized dimerization of 1,3-cyclohexadiene.

Introduction

We are currently developing a series of organic cations incorporated within zeolite media.^{1–8} The physical and photochemical properties of these cations appear to be greatly influenced by the confinement effect provided by the crystalline lattice. Zeolites are microporous aluminosilicates whose crystalline structure, formed by corner-sharing SiO_4^{4-} and AlO_4^{5-} tetrahedra, determines a well-defined array of channels and cavities of molecular dimensions.^{9–11} The negative charge borne by the framework requires the presence of charge-compensating cations, either organic or inorganic, within the internal voids. Therefore, it can be anticipated that these materials are especially appropriate as hosts of cationic sensitizers.

Ship-in-a-bottle synthesis to encapsulate bulky guests entrapped inside the supercages of faujasite (X and Y) zeolites

relies on the easy diffusion of appropriate precursors and has been applied successfully many times before.^{12–16} However, these strategies have been exclusively limited to the formation of metal complexes with either inorganic or organic ligands. In the vast majority of the cases, complexation is the only process occurring and no new covalent bonds are formed during the synthesis since the ligands are already present from the beginning of the process. More related to our work is the obtention of metal–salen^{17,18} and metal–phthalocyanine^{12,19} complexes within zeolites. In these cases, organic ligands are synthesized from less bulky precursors through reactions that involved new C=N and C–C bonds. The importance of these advanced materials in catalysis explains the increasing interest for these systems.^{14,20–42}

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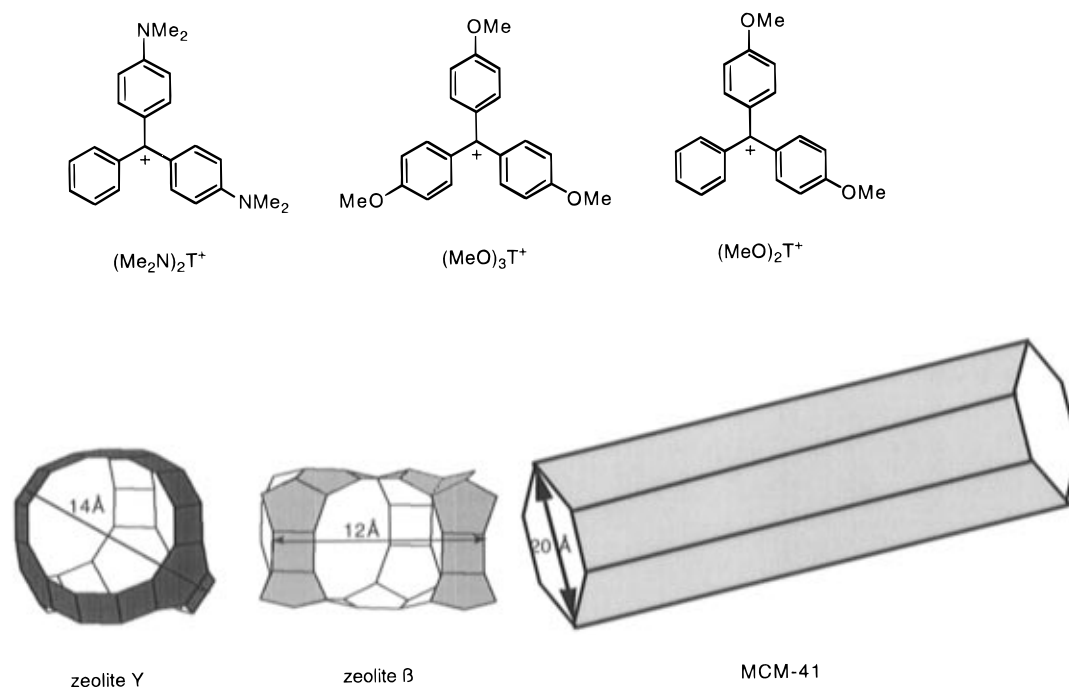
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Chart 1



The present work broadens the scope of the ship-in-a-bottle methodology, since the key step for the preparation of our organic guests is the formation of C–C bonds that is the central process in any organic synthesis. Note that no organometallic complex is formed in our case. Thus, we have prepared and characterized a series of triarylmethylium cations entrapped within the tridirectional channel system of large pore zeolites (Y and β) as well as the novel extra large pore aluminosilicate MCM-41^{43–46} (Chart 1). The synthetic strategy used here can

also form triarylmethylium cations exclusively on the external surface of ZSM-5, a medium-pore-sized zeolite whose channel system is not large enough to entrap these bulky cations. To prove the internal location of these tritylium cations inside the supercages of tridirectional Y zeolite, an X-ray Rietveld analysis and XPS were undertaken. In a series of exploratory experiments, we have found that these zeolite-bound dyes are able to promote the photosensitized dimerization of 1,3-cyclohexadiene (CHD) to give a dimer distribution characteristic of a combination of electron plus energy transfer mechanisms.

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Our group has previously reported on the ship-in-a-bottle preparation of 2,4,6-triphenylpyrylium ion (TP^+) encapsulated within zeolite Y,^{2,47} based on a different synthetic route. However, in that case proof of the internal location of TP^+ was indirectly obtained by IR spectroscopy. Herein, besides the preparation of a new class of guest, the main objective is to provide enough evidence to firmly support that triarylmethylium ions are included inside the faujasite micropores.

Results and Discussion

Preparation and Characterization of Triarylmethylium Photosensitizers Encapsulated within Zeolites. Molecular modeling calculations show that triarylmethylium cations or their obvious triarylcarbinol precursors can be accommodated inside the cavities of large pore zeolites but that they cannot enter through the 12-oxygen ring openings (7.4 Å diameter⁴⁸) of these zeolites. Notably, the typical propeller conformation found for these cations in solution is preserved inside the faujasite supercages. As an example, visualization of $(\text{MeO})_3\text{T}^+$ inside the faujasite supercages is presented in Figure 1.

As a matter of fact, adsorption of triphenylcarbinol (TOH) onto acid HY faujasite was unsuccessful. Thermogravimetric

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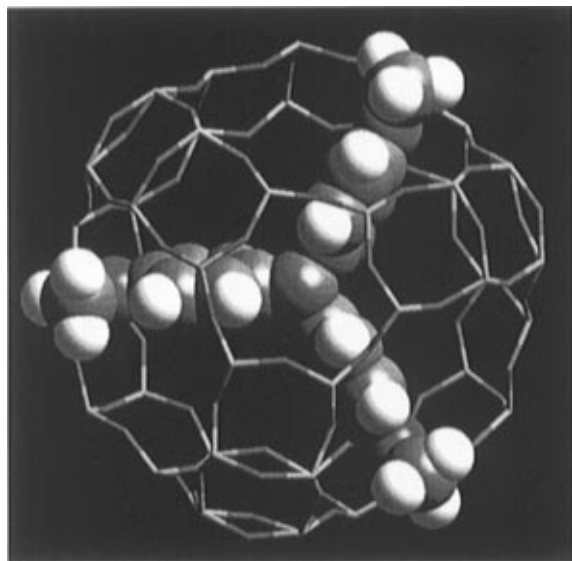


Figure 1. Molecular modeling visualization of a tris(4-methoxyphenyl)methyl cation (CPK view) encapsulated within the supercage of zeolite Y (model 3, see text). The organic cation lies on the 3-fold axis in front of a 6-ring, opposite of one of the four 12-ring windows of the supercage. The methoxy substituents partially penetrate the other three openings.

analysis shows that no significant amount of organic material was retained on this solid after exhaustive Soxhlet extraction. Accordingly, HY developed a very weak yellow coloration when treated with a CH_2Cl_2 solution of TOH. These results are also in agreement with recent reports of incorporation of TOH on HY⁴⁹ as well as with the lack of adsorption of similarly shaped triarylamines on Y faujasites.⁵⁰

In contrast, preparation of substituted trityl cations was successfully achieved by condensation of benzaldehydes with electron-rich aromatic compounds, catalyzed by the acid sites of large pore zeolites (Scheme 1). It is well known⁵¹ that hydroxyalkylation of arenes with aldehydes affords initially benzylic alcohols which are much more reactive than the starting carbonyl compound and hence undergo further alkylation to α,α -diaryllkanes under the reaction conditions. Conventional acid catalysts like AlCl_3 are generally very inefficient for the hydroxyalkylation process and lead to complex mixtures of the expected α,α -diaryllkanes along with high molecular weight oligomers and highly condensed polycyclic aromatic compounds.

However, we have previously shown that acid zeolites can be convenient catalysts for the reaction of aldehydes with arenes,^{52–54} and herein we have applied this reaction for the ship-in-a-bottle synthesis of trityl cations. Thus, when a solution of benzaldehyde or *p*-methoxybenzaldehyde and anisole or *N,N*-dimethylaniline in isooctane was heated at reflux temperature for 12 h in the presence of the H^+ form of Y, β , and MCM-41 silicoaluminates, the solids developed the characteristic green or orange color of the corresponding substituted trityl dye. Moreover, LaY zeolite was also found to be effective for the in situ synthesis of these cations. Acidity and catalytic properties

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of rare earth-exchanged Y faujasites have long been recognized,^{55–57} and our finding constitutes another application of these zeolites as acid solids.

It is worth mentioning that we failed to characterize a sample of the unsubstituted parent T^+ incorporated inside zeolite Y or β by treating benzaldehyde with benzene under analogous experimental conditions. It has been reported recently that this benzene hydroxyalkylation requires superacid media in order to succeed.^{58,59} Furthermore, when TOH was adsorbed onto mesoporous MCM-41, where diffusion of this bulky molecule through the 20 Å channels must be possible, a yellow sample exhibiting a diffuse reflectance compatible with the formation of T^+ through dehydration of TOH_2^+ was obtained. However, this T^+ -MCM-41 faded rapidly and became colorless within minutes, making its characterization uncertain. These observations are again in good agreement with reported behavior of T^+ adsorbed on HY zeolite.⁴⁹

It has to be remarked that the other samples containing substituted trityl cations were found to be stable under usual laboratory conditions, and no appreciable changes in their properties were observed within months. Since zeolites always contain significant amounts of coadsorbed water, these observations can be related to the reported relative stability of trityl cations with water⁶⁰ and other nucleophiles.⁶¹

In order to get samples as free from adventitious organic material as possible, the composites containing the triaryl-methyl cations were submitted to exhaustive solid-liquid extraction. It was assumed that the ionic nature as well as the molecular size would immobilize the organic cations inside the cages and channels of the solid hosts, while other possible neutral byproducts formed during the synthesis could be extracted. In fact, analysis of the organic phases after extraction of the composites revealed the presence of appreciable amounts of triaryl- and diarylmethanes which are known^{52,62} to be the intermediates and the degradation products of trityl cations, respectively (Scheme 2). Identification of these neutral compounds also gives an indirect support to the presence of trityl cations incorporated within the solids.

One question may arise as to whether solid-liquid extraction using CH_2Cl_2 is able to remove triarylmethyl cations from the external surface of the particles. It has to be noted that although some trityl salts are slightly soluble in CH_2Cl_2 , if the zeolite negative framework is acting as a counteranion no solubilization can take place unless an ion exchange would compensate the charge balance. In fact, CH_2Cl_2 extracts were colorless, and samples containing trityl cations exclusively in the external surface (*vide infra* the case of $(\text{Me}_2\text{N})_2\text{T}^+ - \text{HZSM}-5$) did not lose their color.

After the solid-liquid extraction, the resulting solid composites were submitted to characterization by thermogravimetric analysis-differential scanning calorimetry (TG-DSC), UV-vis diffuse reflectance (DR), and IR spectroscopy. Table 1

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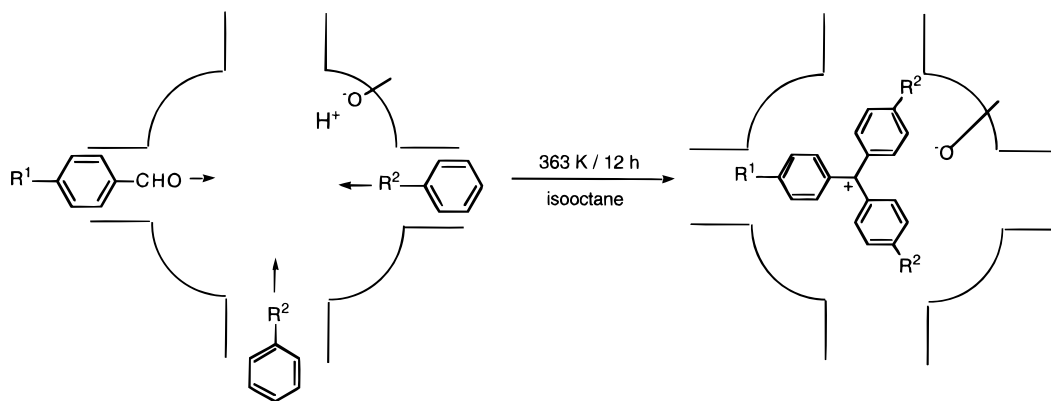
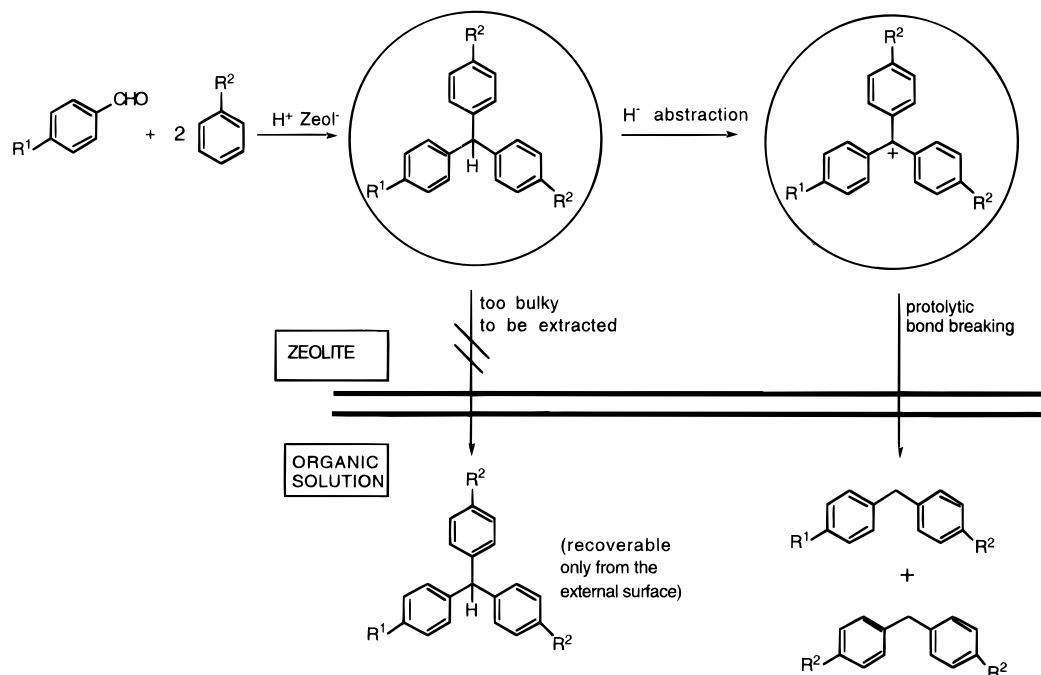
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Scheme 1. Ship-in-a-Bottle Synthesis of Triarylmethylium Cations by Acid-Catalyzed Condensation of Benzaldehydes and Activated Arenes**Scheme 2.** Products Observed in the Organic Phase after Ship-in-a-Bottle Synthesis of Triarylmethylium Cations^a

^a The circles represent the supercages of zeolites.

Table 1. Main Physicochemical Parameters of the Samples Prepared in This Work

composite	zeolite Si/Al ratio	amount of organic cation (mg/g of zeolite)	loading level		UV-vis absorption bands (nm)
			guest/supercage	guest/acid site	
(Me ₂ N) ₂ T ⁺ -HY	2.4	36.5	0.15		415, 607
(Me ₂ N) ₂ T ⁺ -LaY	2.4	82.8	0.40		417, 609
(Me ₂ N) ₂ T ⁺ -MCM-41	11.3	61.5		0.13	428, 617
(Me ₂ N) ₂ T ⁺ -HZSM-5	20	31.2		0.12	414, 605
(MeO) ₃ T ⁺ -HY	2.4	20.6	0.09		486, 510
(MeO) ₃ T ⁺ -LaY	2.4	22.6	0.10		483, 534
(MeO) ₃ T ⁺ -Hβ	13	21.5	0.12		478, 538
(MeO) ₃ T ⁺ -MCM-41	11.3	34.4		0.07	484, 571
(MeO) ₂ T ⁺ -HY	2.4	46.8	0.23		407, 502
(MeO) ₂ T ⁺ -Hβ	13	18.4	0.12		411, 495

collects the main physicochemical and spectroscopic properties of the composites prepared in this work.

Thus, an estimate of the amount of trityl cations encapsulated inside each solid was obtained by the weight loss measured in the TG profile from 300 to 700 °C. As an example, the TG curve of (MeO)₃T⁺-HY is presented in Figure 2. In this context, it is interesting to note that thermal decomposition of the incorporated trityl cations takes place in the same temperature range (about 525 °C measured as the minimum in the DSC

curve) as other composites containing organic cations that we have characterized earlier.^{1,2} This high desorption temperature has been associated with a strong interaction between the positively charged organic guest and the negative framework of the host.

UV-vis spectra of these dyes showed the two characteristic bands assigned to the independent chromophoric substructures defined by one aryl group and the trivalent carbon center (Ar¹-C⁺) and the other two aryl groups plus the central carbon (Ar²-

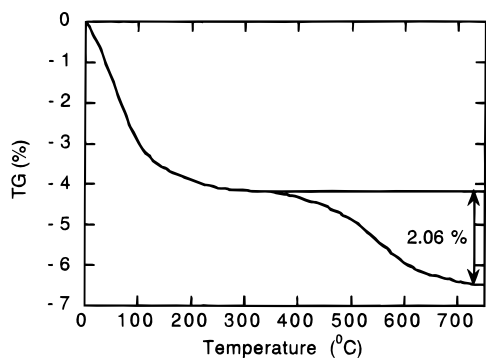


Figure 2. Thermogravimetric profile of the $(\text{MeO})_3\text{T}^+-\text{HY}$ sample. The initial loss of weight ($T < 150\text{ }^\circ\text{C}$) corresponds to coadsorbed water. The jump from 350 to 700 $^\circ\text{C}$ is associated with decomposition of $(\text{MeO})_3\text{T}^+$.

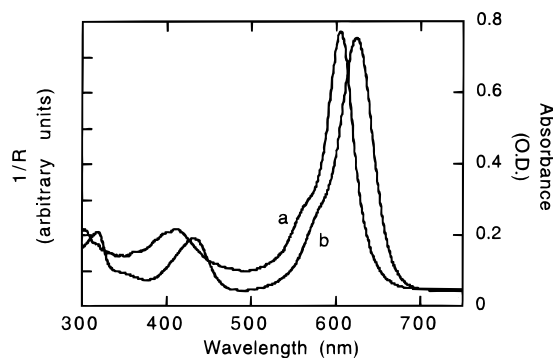


Figure 3. Diffuse reflectance ($1/R$, arbitrary units) and UV-vis absorption (OD) spectra of the $(\text{Me}_2\text{N})_2\text{T}^+$ cation incorporated inside zeolite Y (a) and in CH_2Cl_2 ($\approx 10^{-4}\text{ M}$) solution (b), respectively. The shift of the wavelengths of the maxima reflects the different characteristics of the media.

C^+-Ar^3), respectively.⁶³ It is well established that the relative intensities of these two absorption bands are very sensitive to distortion and changes in the molecular rigidity experienced by the triarylmethyl cation. Although we do observe minor shifts in the λ_{max} of the bands and also in their apparent extinction coefficients (see Table 1), these variations are not significant with regard to the structural assignment of the chromophores and may probably reflect differences in the polarity of the media or small conformational changes experienced by the trityl cations. Solvatochromic λ_{max} shifts of dyes depending on the polarity of the medium are well known in solution.⁶⁴ This would suggest that trityl cations are easily accommodated in the supercages of both β and Y zeolites, in good agreement with the predictions of molecular modeling. Figure 3 compares the DR of the $(\text{Me}_2\text{N})_2\text{T}^+-\text{HY}$ sample to the UV-vis absorption spectrum of a CH_2Cl_2 solution of malachite green oxalate.

IR spectroscopy also confirmed the formation of trityl cations. IR spectra of the parent triphenylmethyl cation adsorbed on amorphous silica-aluminas had been subjected to intensive studies in the past,⁶⁵ and specific vibration bands for the trityl cation were found which are not present in related neutral compounds such as triphenylmethane or triphenylcarbinol. In the region where the zeolite framework does not absorb (3100–1350 cm^{-1}), the intense band at 1360 cm^{-1} has been proposed for identification purposes as specifically characteristic of these cations. As can be seen in Figure 4 for the $(\text{Me}_2\text{N})_2\text{T}^+-\text{HY}$

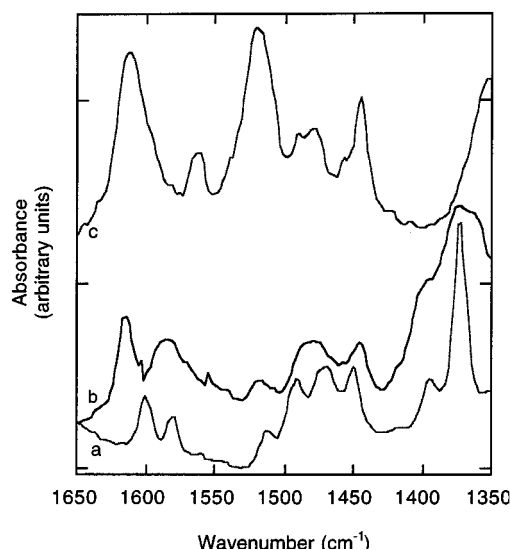


Figure 4. Aromatic region (1650–1350 cm^{-1}) of the FT-IR spectrum of the $(\text{Me}_2\text{N})_2\text{T}^+-\text{HY}$ sample (curve a) after outgassing for 1 h at 100 $^\circ\text{C}$. The intense band at 1372 cm^{-1} has been assigned as typical of trityl cations (ref 65). The spectra b and c correspond to $(\text{Me}_2\text{N})_2\text{T}^+\text{Cl}^-$ and $(\text{Me}_2\text{N})_2\text{TOH}$, respectively.

sample, such a band is also present in the FT-IR spectrum. In contrast, this band is totally absent in the spectrum of the corresponding alcohol $(\text{Me}_2\text{N})_2\text{TOH}$ (see Figure 4). Moreover, comparison of the spectrum of malachite green oxalate or chloride with those of the $(\text{Me}_2\text{N})_2\text{T}^+$ cation incorporated in zeolite Y and MCM-41 showed remarkable coincidences, with the exception of those bands attributable to the corresponding counteranion. The good match of the UV-vis and IR spectra of the organic material present on the zeolite after the benzaldehyde-arene treatment and those corresponding to authentic trityl cations constitutes the main piece of evidence to establish the chemical identity of the guests formed. Noteworthy, if adventitious byproducts were also present, they should not absorb in the UV or IR spectra. This makes the presence of coadsorbed byproducts very unlikely taking into account that the aromatic nature of the reagents and intermediates involved in the process would certainly originate some absorption bands in these spectra.

Finally, in order to discuss if this type of synthesis can occur exclusively on the external surface, we used the same procedure to prepare $(\text{Me}_2\text{N})_2\text{T}^+$ on a HZSM-5 sample of very small particle size (0.1 μm). The small particle size provides a large external surface area, making this sample more appropriate to support higher amounts of the “guest” molecule.

As a matter of fact, we were able to obtain a $(\text{Me}_2\text{N})_2\text{T}^+-\text{HZSM-5}$ composite with the same spectroscopic properties as those observed for the same cation in Y zeolites. ZSM-5 has a channel system consisting of straight and sinusoidal channels with pore openings of 5.2×5.7 and 5.3×5.6 Å.^{48,66–68} It is known that only simple monosubstituted or *para*-disubstituted benzene derivatives can diffuse through their internal voids.^{66,69} Therefore, there is no doubt that the bulky organic cations of the $(\text{Me}_2\text{N})_2\text{T}^+-\text{HZSM-5}$ composite can only be located on the external surface of the crystals.

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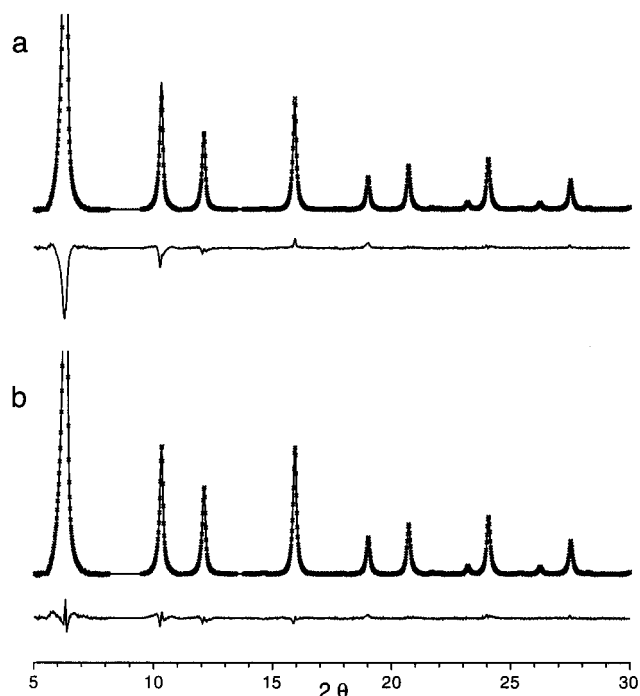


Figure 5. Observed (x), calculated (solid line), and difference (bottom) pattern for the Rietveld refinement (a) of framework only and (b) with the $(\text{MeO})_3\text{T}^+$ ion included (model 3).

The above experiment clearly establishes that the ship-in-a-bottle synthesis per se does not guarantee that the cations are located inside the zeolite and also that the solid-liquid extraction procedure does not remove trityl cations from the external surface of the particles. In cases where the dimensions of the internal voids of a zeolite allow it, it is reasonable to assume that the synthesized species would be distributed on external and internal sites. Direct experimental evidence is, therefore, needed to prove the hypothesis of the internal location for these dyes. Although solid-state MAS ^{13}C -NMR is a powerful technique to assess the chemical structure of ^{13}C -labeled trityl ions,⁴⁹ it has been found that the chemical shifts are rather insensitive to the location of these cations. Indirect reactivity tests were provided to disclose this point.⁴⁹ Herein, we have undertaken a direct approach to assess the intrazeolite location of the organic chromophores by carrying out a high-resolution X-ray diffraction study and XPS analysis of these samples.

X-ray Structure Refinement and XPS Analysis of $(\text{MeO})_3\text{T}^+ - \text{HY}$. The refinement of the XRD using the XRS-82 system of programs⁷⁰ was initiated with geometrically idealized coordinates for the framework atoms. Using only the data with $2\theta > 36^\circ$, the framework atoms were refined using distance and angle restraints. The temperature factors of the oxygens were constrained to be equal. This refinement converged well and gave an almost perfect fit for this 2θ range. Only the 2θ region below 30° showed significant intensity differences (Figure 5a). A difference Fourier map calculated at this stage revealed no peaks in the sodalite cages or the double 6-ring and only diffuse electron density in the supercage. Although attempts to interpret this electron density peak directly without any assumption of the structure of the guest failed, XRD positively establishes that some supercages are filled.

From the TGA analysis, it was expected that only about every fifth supercage would be occupied by a $(\text{MeO})_3\text{T}^+$ ion, so the maximum electron density would be $1.2 \text{ e}/\text{\AA}^3$ for a C atom.

Furthermore, the ions were likely to be disordered within the supercages. It is therefore not surprising that only the low-angle peaks showed any remaining intensity differences. It was also clear that a complete "traditional" refinement of the molecule (i.e., direct location by Fourier synthesis and refinement of the individual 46 atoms) was not possible on the basis of so little information.

A different approach was needed. Molecular modeling (performed with the Cerius² package⁷¹ using the Burchart 1.01–Dreiding 2.11 force field) of the $(\text{MeO})_3\text{T}^+$ cation inside the supercage was used to generate plausible models which were then tested with the X-ray powder data. Because of the stereochemical restrictions of the cation itself and the space available inside the supercage, only three slightly different conformations/orientations of the organic guest species proved to be feasible. In each case the 3-fold axis of the cation (on the central C atom) coincides with that of the supercage. The three models can be briefly characterized as follows: model 1, central atom of cation near center of supercage (distance to center 0.8 Å), orientation of benzene ring perpendicular to plane of cation (benzene ring parallel to the 3-fold axis); model 2, same as model 1, but the cation is shifted by 1.8 Å from the center of the supercage along the 3-fold axis of the framework toward the 6-ring of the sodalite cage (toward position SII); and model 3, same as model 2, but the planes of the benzene rings are tilted 10° from the perpendicular orientation of models 1 and 2.

All three models (with H positions included) were tested, and only the occupancy factor of the complete cation was refined (i.e., the population factors of all atoms were constrained to be equal). The temperature factors for all atoms of the models were kept fixed at $B = 5 \text{ \AA}^2$. All three models yielded similar *R*-values and a good fit to the X-ray data, but the best agreement was obtained with model 3 which gave also the highest occupancy factor. This model is shown in Figure 1 and the corresponding Rietveld plot in Figure 5b.

This refinement shows that (1) the supercage is not empty and (2) the electron density found in this cage can be explained with a very plausible model of the $(\text{MeO})_3\text{T}^+$ ion located in this cage. Together with the other spectroscopic data (which identify the molecule), this is strong direct evidence that $(\text{MeO})_3\text{T}^+$ ions have been formed inside the supercage.

The average (Si,Al)–O distance is 1.61 Å, which is close to the expected distance of 1.62 Å for a Si/Al ratio of 13. Also, the number of $(\text{MeO})_3\text{T}^+$ ions (1.35/unit cell or 0.17 cations/supercage) is in reasonable agreement with the value of 1.7/unit cell found by TGA. The results of the X-ray refinement can, therefore, be considered convincing evidence that the $(\text{MeO})_3\text{T}^+$ ions are indeed located inside the zeolite HY.

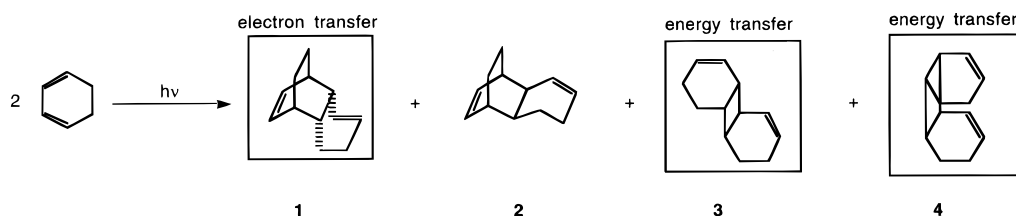
Direct evidence of the external versus internal location of the organic material has been additionally obtained by carrying out XPS analysis of the C-to-Si atomic ratio of the exposed external surface of the particle.⁷² Herein, we have combined this technique with progressive sputtering with a fast Ar^+ beam that produces increasing decapping of the external layers of the zeolite crystals.⁷² In this way it is possible to map out the C-to-Si atomic ratio from the exterior to the interior of the solid particle up to a depth of several hundred angstroms.

The results obtained for the $(\text{MeO})_3\text{T}^+ - \text{HY}$ sample are presented in Figure 6. Each point corresponds to the average of three independent measurements, and the area of the peaks due to C and Si have been calibrated to account for the different

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Scheme 3. Photosensitized 1,3-Cyclohexadiene Dimerization^a

^a The characteristic dimers of the electron and energy transfer mechanisms are indicated.

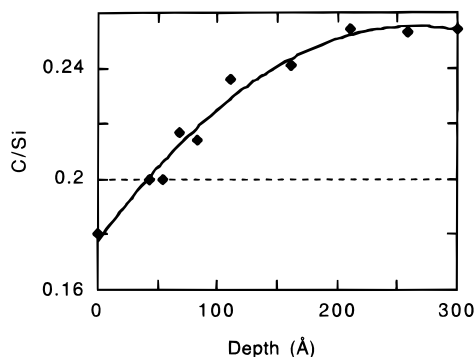


Figure 6. Plot of the C-to-Si atomic ratio measured by XPS analysis of $(\text{MeO})_3\text{T}^+-\text{HY}$ versus the depth of the particle. Each point is the average of three measurements. Sputtering has been achieved using an Ar^+ beam. The dashed line corresponds to the average C-to-Si atomic ratio calculated from TG data.

response of C and Si atoms. From these data, it can be clearly stated that carbon atoms are spread out through the whole particle.

Note that the last experimental point has been obtained at 300 Å depth, corresponding to more than 15 supercages depth from the external surface of the particles. The mean C-to-Si atomic ratio of the whole particle calculated from the TG analysis would be 0.20, approximately. From the experimental carbon distribution through the particle obtained by XPS, it is clear that the TG value is a weighted average of different populations. Thus, while the C-to-Si atomic ratio of the external surface is lower than the average, the carbon content progressively increases as we penetrate into the particle, reaching a plateau of 0.25 (well above the mean value) at about 200 Å from the external surface.

It is obvious that X-ray diffraction and XPS analysis do not allow to determine the chemical structure of the organic guests, which has to be based on the previous UV and IR spectroscopic identification of the dyes. Nevertheless, it provides the key information of the internal distribution of the carbon through the particle. As no other organic material was detected by IR, the intrazeolite material can be securely assigned as owing to the tritylium ions.

Photosensitized Dimerization of 1,3-Cyclohexadiene. In order to ascertain the ability of these zeolite-bound triarylmethyl cations as photosensitizers, a series of exploratory experiments were undertaken using the well-documented photodimerization of CHD as a test reaction (Scheme 3).^{73,74}

Heterogeneous photolyses were carried out through a Pyrex filter, under inert atmosphere, by stirring a suspension of CHD in CH_2Cl_2 in the presence of the corresponding composite. Parallel control experiments were performed to ensure that previously reported^{75,76} thermal and photochemical (direct,

unsensitized) CHD dimerizations are not taking place to a significant degree.

All the zeolite samples containing triarylmethyl cations promoted the photosensitized dimerization of CHD to give a mixture of dimers 1–4. The possibility that minor amounts of adventitious carbonyl compounds could be responsible, at least in part, for the observed dimer distribution pattern was ruled out in view of the fact that the same product ratio was observed using as excitation source 400–500 nm filtered light, where aromatic ketones rarely absorb.

CHD dimerization has been proposed as a test reaction to discriminate between energy or electron transfer photosensitization just by determining the dimer distribution.⁷³ Under typical energy transfer conditions, [2 + 2] cycloadducts 3 and 4 are predominantly formed, along with a minor proportion of [4 + 2] *exo* adduct. In contrast, under electron transfer conditions, either photochemical, thermal, or electrochemical, the [4 + 2] *endo* dimer 1 is the major reaction product with a high selectivity (>80%).

The dimer distribution upon heterogeneous photosensitization does not correspond to any of the previously reported patterns in homogeneous solution. As a representative example, the photosensitized dimerization of CHD according to the procedure described in the Experimental Section in the presence of $(\text{MeO})_3\text{T}^+-\text{HY}$ at a CHD conversion of 13% affords the dimers with a selectivity of 81% and a distribution 1:2:3:4 of 48:12:23:7. Thus, although a more comprehensive study is required in order to get a deeper insight into the detailed mechanisms of the photosensitization, a combination of electron (predominant) and energy (minor) transfer pathways seems at the moment the most reasonable assumption to account for the observed dimer distribution.

Conclusions

Twelve triarylmethyl cations have been prepared adsorbed on acid zeolites by ship-in-a-bottle synthesis from benzaldehydes and electron-rich arenes. The resulting encapsulated cations show UV–Vis and IR spectra similar to those observed for the same species in solution. No changes in the spectroscopic properties of these samples were observed during months after their synthesis. It is also possible to form these cations exclusively in the external surface of medium pore HZSM-5, where internal voids are too small to accommodate any of these cations. This clearly indicates that synthesis of bulky species from smaller precursors does not guarantee itself the internal location of the guest. Indisputable experimental evidence for the encapsulation of these cations within the Y zeolite supercage has been obtained by X-ray diffraction and XPS analysis of $(\text{MeO})_3\text{T}^+-\text{HY}$. The diffraction data agree with a visualization of $(\text{MeO})_3\text{T}^+$ inside the Y supercages based on molecular modeling, while the C-to-Si atomic ratio increases from the exterior to the interior of the particles. Finally, the ability of these triarylmethyl dyes adsorbed on zeolites to act as heterogeneous photosensitizers has been explored using CHD dimerization as a test reaction.

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Experimental Section

Preparation of the Triarylmethyl cations within Acid Zeolites. Synthesis of the trityl cations was carried out by stirring for 12 h at reflux temperature a solution of the corresponding benzaldehyde (50 mg) and arene (100 mg) in isooctane (25 mL) in the presence of the appropriate zeolite (1.00 g) previously thermally activated (500 °C, overnight). Then, the suspension was filtered, and the solid was submitted to continuous solid-liquid extraction, using micro-Soxhlet equipment and CH₂Cl₂ as solvent. The combined organic solutions were analyzed by GC-MS (Varian Saturn II fitted with a 25 m capillary column of 5% phenylmethylsilicone). A 400 MHz ¹H-NMR (Varian Unity Plus) spectrum of the residue after removal of the solvent was also recorded in CDCl₃. Products of the condensation of benzaldehyde with anisole were compared to those previously reported.⁵²

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Supporting Information Available: Table 2 listing the occupancy factors (converted to number of (MeO)₃T⁺ ions per unit cell) and the final *R*-values obtained for these models and experimental details concerning the zeolites employed, characterization techniques, X-ray data collection, XPS measurements, and irradiation procedure (4 pages). See any current masthead page for ordering and Internet access instructions.

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