

Novel photocatalysts containing 2,4,6-triphenylthiapyrylium encapsulated within zeolites. Enhanced photocatalytic activity as compared to the pyrylium analogues

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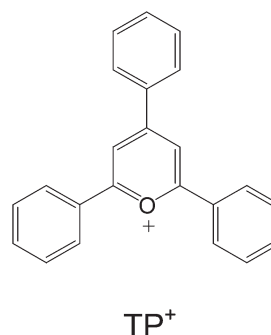
A series of solid photocatalysts containing either 2,4,6-triphenylpyrylium (TP⁺) or 2,4,6-triphenylthiapyrylium (TTP⁺) encapsulated within zeolite Y or Beta, or deposited on amorphous silica or MCM-41, have been prepared. These photocatalysts have been tested for the degradation of aqueous solutions of phenol (40 ppm) or aniline (40 or 80 ppm, initial pH 3) as model reactions. TTP⁺ photocatalysts were found to be more active and stable than those containing TP⁺, the initial efficiency order being: TTP/MCM-41 \approx TTP/SiO₂ > TTP@Beta > TTP@Y > TiO₂. In the case of TTP/SiO₂ and TTP/MCM-41 the photocatalysts are largely decomposed during the photocatalytic reaction, as compared to TTP⁺ encapsulated within zeolites Y and Beta; in the latter, although the initial activity is considerably lower the dye persists after the irradiation and can be reused. In this way the final productivity of TTP@Beta is at least four times higher than when the dye is supported on SiO₂ or MCM-41. Addition of an initial concentration of H₂O₂ (10⁻³ M) accelerates the photodegradation of phenol by a factor of 6 but it does not have much influence in the case of aniline.

Introduction

One of the major applications of photocatalysis is the degradation of organic pollutants in aqueous solutions under aerobic conditions.¹⁻⁴ The two most important requirements of a photocatalyst are to exhibit a high efficiency in the photocatalytic degradation and to be robust enough to survive a considerable number of photocatalytic cycles without undergoing self-degradation or losing photocatalytic activity. Their considerable photochemical stability and robustness is the main reason why most photocatalysts are inorganic semiconductor oxides such as TiO₂, ZnO or SnO₂, the use of organic photosensitizers being very rare.¹⁻⁴ As the objective of photocatalysis is the degradation of any organic compound present in the medium, it seems contradictory to use an organic photosensitizer as photocatalyst. The paucity of organic-based photocatalysts contrasts with the ample use of organic compounds as photosensitizers in organic photochemistry.^{5,6} On the other hand, organic photocatalysts are generally low-surface-area solids and heterogeneous photocatalysis requires solids with a large surface area to favour the interfacial contact between excited photocatalyst molecules and substrates. Nevertheless, phthalocyanines and other metallic complexes having organic ligands have occasionally been used as organic photocatalysts.⁷⁻¹⁷

On the positive side, the use of organic photosensitizers as photocatalysts would have advantages compared to inorganic solids arising from the ease of their synthesis, easier spectroscopic characterization, and the possibility to introduce substituents to produce bathochromic shifts and hyperchromic effects. In fact, λ_{max} in the absorption spectrum of organic compounds can be tuned by introduction of appropriated substituents on the chromophoric structure. A desirable property of a photocatalysts is to exhibit activity upon illumination with solar and/or visible light and this has been much more easily accomplished with organic compounds than with semiconductor oxides.

Some time ago, we reported an original strategy to prepare a photocatalyst in which an organic electron transfer photosensitizer such as 2,4,6-triphenylpyrylium (TP⁺) was encapsulated inside the cavities of tridirectional large pore zeolites or adsorbed in mesoporous MCM-41.^{18,19} In a series of studies we have been showing that the resulting TP⁺ sensitizer encapsulated inside zeolites is indefinitely persistent in aqueous medium at room temperature and upon irradiation it generates hydroxyl radicals.²⁰ TP@Y^{21,22} can effectuate the degradation of various organic pesticides with the same or in some cases even higher photocatalytic activity than TiO₂ with solar light.²³⁻²⁶ Miranda and co-workers have also used TP⁺ supported on silica as a photocatalyst for the degradation of olive oil carboxylic acids.²⁷⁻³² Based on the same strategy, but using different photosensitizers, Bössman, Braun and their co-workers have developed zeolite Y encapsulated metal bipyridyl complexes as photocatalysts for the degradation of 2,4-xylidine in acidic solutions, with or without addition of external H₂O₂.³³⁻³⁷



The search for more efficient photocatalytic systems is an ongoing task in photocatalysis that could eventually lead to the implementation of photocatalytic techniques in real water treatment plants. The key points are activity towards a wide range of organic pollutants, durability and an efficient use of

the electrical energy used to power lamps. In this context, it is known³⁸ from solution studies that sulfur analogues of pyrylium heterocycles are more robust than the corresponding oxygenated heterocycles towards hydrolysis and nucleophilic attack. The higher stability of thiapyrylium compared to pyrylium rings derives from the increased aromaticity of the former due to the similar electronegativity of the sulfur and carbon as compared with the larger electronegativity difference between carbon and oxygen.^{39–41} On the other hand, 2,4,6-triphenylthiapyrylium (TPTP⁺) and TP⁺ have in common several photochemical properties such as similar ground state absorption spectra, similar emission spectra, the corresponding triplet states have similar lifetimes and both TPTP⁺ and TP⁺ are strong oxidizing photosensitizers.^{42–46} Therefore, not surprisingly the photosensitizing properties of thiapyrylium and pyrylium ions are very close, although it is expected based on solution studies that TPTP@zeolite would have a higher photostability than TP@zeolite photocatalyst.

Aiming at increasing the photocatalytic efficiency of zeolite-encapsulated photosensitizers analogous to the TP@Y type, herein we report a detailed photocatalytic study comparing the activity of TP⁺ and TPTP⁺ photosensitizers encapsulated in large-pore zeolites Y and Beta. We have also included in our study photocatalysts in which TP⁺ and TPTP⁺ have been supported on silica and mesoporous MCM-41 as well as Degussa P-25 TiO₂ as a standard. Comparison of the photocatalytic activity of TP⁺ or TPTP⁺ supported on SiO₂ or MCM-41 with that of TP⁺ or TPTP⁺ encapsulated in zeolites allows us to determine the influence of the microporosity of the support on the stability and performance of the hosted photosensitizer. For the present study we have used the photodegradation of aqueous solutions of phenol and aniline, two model reactions that have been used frequently to rank the photocatalytic activity of different solids.^{47–50}

Results and discussion

Preparation and characterization of the photocatalyst

The list of photocatalysts and their relevant analytical and textural data are collected in Table 1. The series includes two sets of photocatalysts containing TP⁺ and TPTP⁺ encapsulated inside the cages of two tridirectional, large-pore zeolites (Y and Beta zeolites) or supported on amorphous silica or mesoporous MCM-41. In the latter two cases, the photocatalysts were prepared by adsorbing pre-formed TP⁺BF₄[−] or TPTP⁺ClO₄[−] from dichloromethane solutions onto thermally dehydrated silica or MCM-41 supports at the desired final loading. The large pore dimensions of the sample of MCM-41 used (32 Å) allows easy diffusion of the organic dyes (13 Å kinetic diameter) inside the mesopores of structured MCM-41 silicate.⁵¹ In these adsorption experiments at the

photosensitizer:support ratio used virtually all the TP⁺ or TPTP⁺ in the CH₂Cl₂ solution is adsorbed onto the solids. TP⁺BF₄[−] and TPTP⁺ClO₄[−] are completely soluble in CH₂Cl₂.

For the incorporation of TP⁺ and TPTP⁺ inside the cavities of Y and Beta zeolites, a ship-in-a-bottle methodology, as illustrated in Scheme 1, is necessary given that the large molecular size of TP⁺ and TPTP⁺ does not allow their encapsulation by adsorption of pre-formed heterocycles inside the cavities through the smaller pores (7.4 Å diameter). Basically this methodology consists in the adsorption of 2,4,6-triphenyl-2-penten-1,5-dione in cyclohexane as solvent onto thermally dehydrated zeolites in their H⁺ form at 60 °C, the solution and the solid being saturated or not with hydrogen sulfide (H₂S) depending on whether TP⁺ or TPTP⁺ is to be formed.^{52–54} This simple adsorption procedure is followed by thermal treatment to effectuate the cyclization of the included diketone. Compared to the ship-in-a-bottle synthesis of TP⁺ previously reported,¹⁸ the above experimental procedure has the advantage of forming the encapsulated guest in much higher purity and higher reproducibility, in addition to much shorter preparation times. The term “camel through the eye of a needle” has recently been coined for a similar process starting from a pyrylium ring that becomes included inside the zeolite cages.⁵⁵

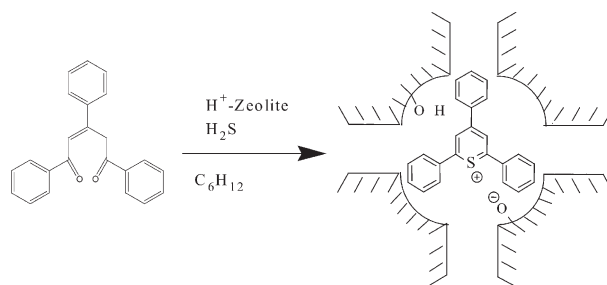
To give an idea of the quality of the samples, Figs. 1 and 2 show selected optical and IR spectra of zeolite-encapsulated or adsorbed dyes compared to the spectra recorded for the pure BF₄[−] or ClO₄[−] salts of pyrylium or thiapyrylium samples. Due to the inherent experimental sample preparation when working with solid opaque powders such as dye-containing zeolites, the spectral resolution of the diffuse reflectance or transmission mode is somewhat lower than when working with transparent solutions of non-encapsulated dyes.

Assessment of the purity and quality of the zeolite-bound photosensitizers is an important issue that has to be properly addressed in order to have reproducible and relevant photocatalytic data. Not only that, the optimum performance of a zeolite-encapsulated photocatalyst may require the complete absence of adventitious material blocking the pores and impeding the accessibility to the photocatalysts. After many successful preparations, it has become clear that properly prepared TP@zeolite or TPTP@zeolite samples are characterized by having an absorption minimum at 310 nm in the UV-visible spectrum (instead of a maximum for unpurified samples) and by lacking C=O vibration bands at 1670 cm^{−1} in the infrared spectrum. All the samples employed in the present work have been spectroscopically characterized and have the hallmarks of well-prepared zeolite-bound TP⁺ or TPTP⁺ photosensitizers.

To study the photocatalytic activity of the solids prepared, two test reactions in aqueous solution, namely the degradation of phenol at initially neutral pH and the degradation of aniline at an initial pH value of 3 units, were selected.

Photocatalytic degradation of phenol

Preliminary screenings varying the substrate-to-photocatalyst weight ratio were carried out in order to determine the most



Scheme 1 Synthesis of the encapsulated TPTP⁺ photocatalysts.

Table 1 Analytical and textural data of the photocatalysts

Photocatalyst	Support surface area/m ² g ^{−1}	Analysis		Loading
		% C	% S	
TP@Y	430	3.91	—	1:4 ^a
TP@Beta	370	3.31	—	1:8 ^a
TPTP@Y	430	5.85	0.44	1:3 ^a
TPTP@Beta	370	3.19	0.21	1:8 ^a
TP/SiO ₂	210	3.41	—	1.2 × 10 ^{−4b}
TP/MCM41	910	3.35	—	30 ^c
TPTP/SiO ₂	210	2.13	0.25	0.65 × 10 ^{−4b}
TPTP/MCM41	910	3.01	0.31	26 ^c

^a Dye:supercage ratio. ^b Moles of dye per g of SiO₂. ^c Molecules per channel

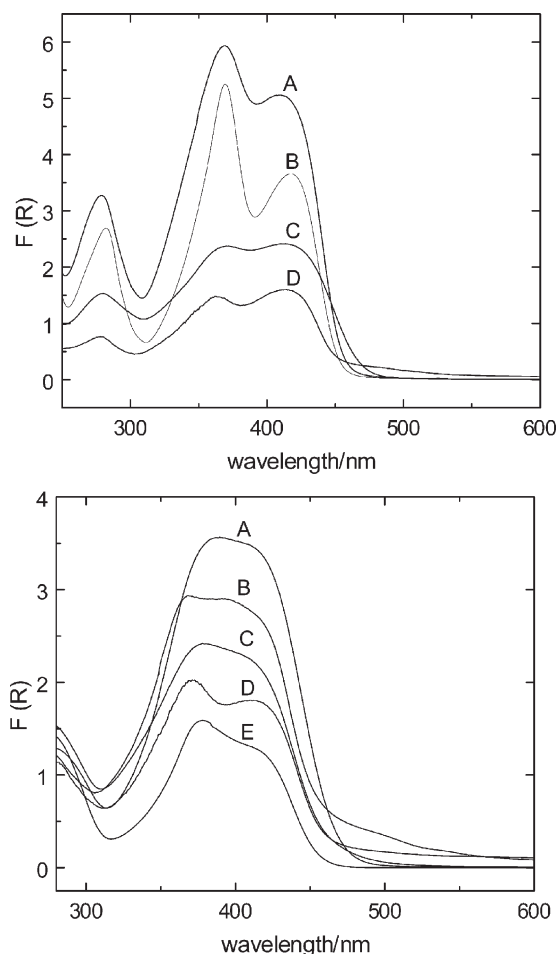


Fig. 1 Diffuse reflectance UV-vis spectra of (top) TP⁺ series: (A) TP@Y; (B) TP⁺BF₄⁻; (C) TP/SiO₂; (D) TP@Beta and (bottom) TPTP⁺ series: (A) TPTP/SiO₂; (B) TPTP@Beta; (C) TPTP/MCM-41; (D) TPTP@Y; (E) TPTP⁺ClO₄⁻.

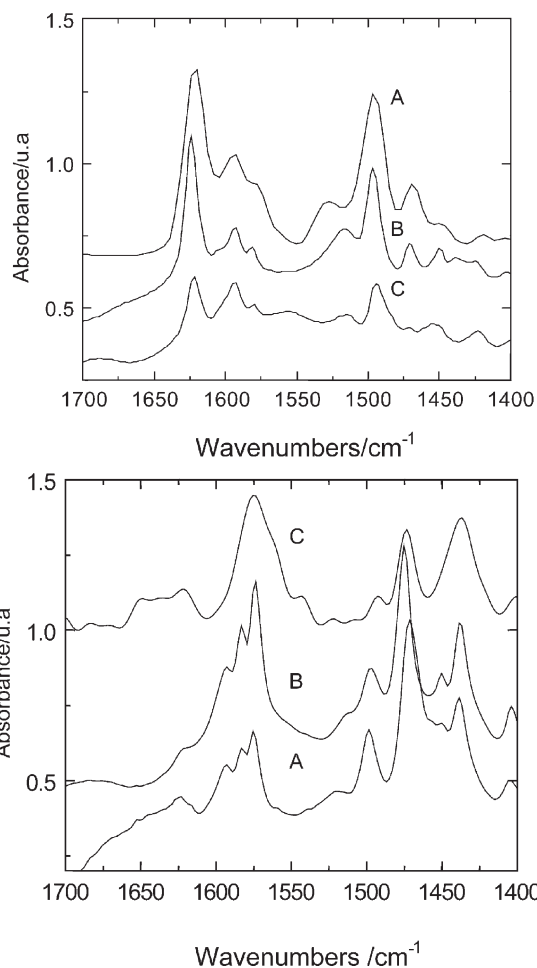


Fig. 2 IR of (top) TP⁺ series: (A) TP⁺BF₄⁻; (B) TP@Beta; (C) TP@Y and (bottom) TPTP⁺ series: (A) TPTP⁺ClO₄⁻; (B) TPTP@Beta; (C) TPTP@Y.

convenient experimental conditions in which large differences in initial activity between photocatalysts can be observed. The course of the photodegradation was followed by plotting phenol disappearance over time. Although hydroquinone and benzoquinone were detected as degradation products, no attempts were made to determine the presence of other known degradation products such as unsaturated or hydroxy acids that are not detectable with our UV-vis detector.

The general behaviour observed when the amount of photocatalyst is increased while keeping constant the concentration of the substrate to be degraded is that the initial degradation rate (r_0) increases along with the weight of the photocatalyst until a plateau is reached beyond which r_0 remains constant upon subsequent additions of photocatalysts. Since all the experiments are made at the same initial phenol concentration, r_0 corresponds to the slope at zero time of the percentage of degradation *versus* the irradiation time. r_0 was, therefore, determined by fitting the experimental points at short irradiation times to a straight line. As an example Fig. 3 shows the plot of the initial photocatalytic activity *versus* the amount of photocatalyst for TP/SiO₂. r_0 measures the initial photocatalytic activity of the fresh photocatalyst. The influence of the substrate-to-photocatalyst ratio on the initial photoactivity can be rationalized considering that as the amount of photocatalyst increases, a more efficient conversion of light into chemical energy occurs until the system becomes “saturated” and absorption of the maximum photon flux impinging the dispersion is achieved. Subsequent increases in the weight of the photocatalyst have no effect either because it does not lead to more light absorption or all the substrate is already all

adsorbed on the catalyst surface. Obviously the photocatalyst weight, for which this plateau is reached, can be somewhat different for the series of photocatalysts studied. However, for the ranking of the photocatalytic activity of various photocatalysts to be meaningful it is necessary to compare r_0 at substrate-to-catalyst ratios for which the plateau has not been reached for any of the photocatalysts studied. Under our experimental irradiation conditions a suitable photocatalyst weight for the

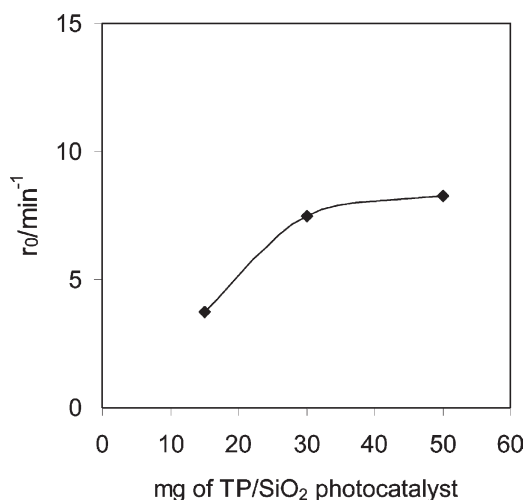


Fig. 3 Photocatalytic activity of TP/SiO₂ for the degradation of phenol (40 ppm) in water (20 ml) *versus* amount of photocatalyst.

experiments was 30 mg, since TPTP/SiO₂ and TPTP/MCM-41 just reach their maximum activity above this value and the plateau for the rest of the photocatalysts is beyond 100 mg. This 30 mg of photocatalyst for the degradation of 40 ppm of phenol corresponds approximately to 4 times more moles of phenol than that of dye present in the photocatalyst. Obviously, the selection of 30 mg of photocatalyst to effectuate the photocatalytic degradation of 40 ppm of phenol is arbitrarily chosen and other photocatalyst weights would lead to different r_0 , but this catalyst weight is presumed to give the largest differences in activity between the samples.

Once the most suitable substrate-to-photocatalyst ratio was selected, the photocatalytic degradation was performed under these conditions. When discussing the photocatalytic activity of different materials the two most important parameters are the initial activity (r_0) as defined before and the percent degradation at final irradiation time. The first parameter r_0 indicates the intrinsic activity of the fresh material, while the degradation percentage at final time is also related with the deactivation of the photocatalyst as the reaction progresses. The final reaction time is arbitrarily selected in order to meet a compromise between the achievement of a significant degree of degradation (extended irradiation periods) and economy (short irradiation times). Fig. 4 shows the course of selected photocatalytic irradiations of phenol in the presence of some of the tested photocatalysts. These plots illustrate the time-conversion profiles of the series of photocatalysts prepared. Analogous temporal profiles have been obtained using other substrate-to-photocatalyst weight ratios.

The most salient features from these photocatalytic experiments comparing the initial activity of the series of photocatalysts are the following: (i) the inherent photocatalytic activities

of TP/SiO₂ and TPTP/SiO₂ are similar to those of TP/MCM-41 and TPTP/MCM-41, and considerably higher than that of any photocatalyst containing the TP⁺ or TPTP⁺ dyes encapsulated in zeolites; (ii) zeolitic photocatalysts containing TPTP⁺ are more active than those containing the TP⁺ analogues; (iii) the activity of the P-25 TiO₂ standard is lower than some of the TP⁺ and considerably smaller than the TPTP⁺ photocatalysts; (iv) the activity of most of these materials follows the same order through out the reaction except for TPTP@Beta, which becomes the most efficient photocatalyst at longer times.

When comparing the activity of the series of photocatalyst containing TP⁺ or TPTP⁺ it has to be noted that the total light absorption is considered to be constant for all these photocatalysts. This assumption is based on the fact that the absorption spectra are very similar in terms of wavelength and molar absorptivity for all the samples according to the diffuse reflectance UV-vis spectra. However, it is obvious that the total absorption intensity of P-25 TiO₂ could be less than that of the organic dyes and, on the other hand, P-25 TiO₂ has much smaller surface area than that of zeolites. Whatever the combination of reasons to justify the differences in photocatalytic activity between the zeolites containing organic dyes and P-25 TiO₂, it is obvious that other irradiation conditions in terms of lamp emission could lead to a different efficiency order, particularly if the excitation light matches more closely the P-25 TiO₂ absorption spectrum. Assuming this similarity in the integrated absorption of all TP⁺ and TPTP⁺ samples, the results of photocatalytic activity shown in Fig. 4 clearly indicate that the maximum intrinsic activity exhibited by the TP⁺ and TPTP⁺ photosensitizers adsorbed onto SiO₂ or MCM-41 is reduced upon encapsulation inside the zeolite micropores.

We checked if the high activity of TP⁺ and TPTP⁺ on SiO₂ or MCM-41 was totally or in part due to some photosensitizer dissolved in the water upon contacting the solid with the phenol solution. To address this point and to rule out the presence of photoactive dye in the solution two controls were performed. In one of them, the solid was stirred in distilled water and the solution checked periodically by UV-vis spectroscopy. No evidence of the presence of the dyes in the water was obtained. In a different type of control, photodegradation of phenol in the presence of TP/SiO₂ was conducted under the normal conditions up to 40% conversion. At this time, the solid was filtered and the resulting clear solution submitted to photolysis for additional periods. No further conversion was observed in the absence of the solid, thus confirming that the photodegradation is due to the presence of solid photocatalyst. The above results on the heterogeneity of the process for TP⁺ and TPTP⁺ supported on SiO₂ or MCM-41 are not unexpected given that these dyes are insoluble in water.

Most probably the higher photodegradation r_0 observed for TP⁺ and TPTP⁺ dyes supported on SiO₂ or MCM-41 is due to diffusion restrictions on the mobility of the substrate through the zeolite micropores as compared to the more favourable situation in which the dyes are located on the external surface (in the case of silica) or incorporated on mesoporous MCM-41. In the latter case the very large channel diameter (32 Å) as compared to the phenol kinetic diameter (~5.4 Å) does not cause any restriction. In addition, the very high surface of MCM-41 as a support (910 m² g⁻¹) also favours photodegradation as compared to zeolites Y and Beta (see Table 1). However this initial advantage in terms of photosensitizer accessibility is also the reason for a much faster deactivation of the photocatalyst, caused by the photochemical and thermal instability of TP⁺ and TPTP⁺ under the irradiation conditions. In addition, powder XRD shows that MCM-41 exhibits poor stability in water and a remarkable decrease in the periodic structure was observed after the photocatalytic reactions.^{56–58} Thus, the initial benefits having an organic photosensitizer

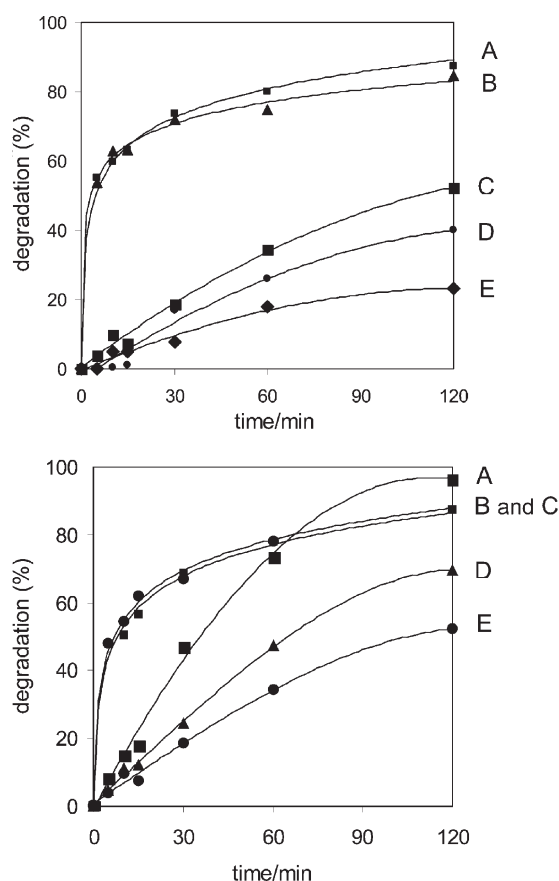


Fig. 4 Percentage degradation of phenol in the presence of different photocatalysts of (top) the TP⁺ series: (A) TP/MCM-41; (B) TP/SiO₂; (C) TiO₂; (D) TP@Beta; (E) TP@Y and (bottom) the TPTP⁺ series: (A) TPTP@Beta; (B) TPTP/MCM-41; (C) TPTP/SiO₂; (D) TPTP@Y; (E) TiO₂.

deposited on a very high surface area MCM-41 are lost during the use of the photocatalyst.

On the other hand, it is interesting to comment the poor performance of TP@Y shown in Fig. 4. TP@Beta exhibits somewhat higher photocatalytic activity but still it is lower than that of P-25 TiO₂ standard. We think that this low photocatalytic activity is a consequence of the encapsulation of the photocatalytic dye inside the micropores of the zeolite. This encapsulation makes the photoactive TP⁺ molecules less accessible to phenol. The same trend is also observed for the TPTP⁺ series. Even though the initial activity of TPTP@Beta is not as high as that of TPTP/SiO₂ or TPTP/MCM41, the final degradation percentage is significantly higher, most probably due to the role of the zeolite host in protecting the dye and impeding its degradation and by the strong adsorption of phenol in the zeolite pores. Such a cooperative effect derives from the adsorption ability of the zeolite, thus concentrating the substrate inside the pores in close contact with the photosensitizer, and has been already claimed for related photocatalytic degradations.²³

Influence of photocatalyst loading

Given the importance of diffusion in the case of the zeolite-encapsulated photosensitizers, a series of samples was prepared to obtain data about the optimum loading of photosensitizer inside zeolite for the maximum activity. Thus, four TP@Y photocatalysts were prepared under exactly the same conditions, but the TP⁺ content was varied between 1 and 6 wt %. Diffuse reflectance UV-vis spectra and IR spectra of these TP@Y samples were in the four cases coincident and correspond to well-prepared samples (Fig. 5).

It was anticipated that high loadings of TP⁺ might have a negative effect, decreasing the catalytic activity due to restrictions on the intracrystalline diffusion, while low loadings may also be disadvantageous since this will reduce the light-harvesting ability of the photocatalyst. Thus, the turnover frequency measured as the number of phenol molecules degraded per number of TP⁺ and per unit of time should be constant up to a certain loading beyond which it would decrease. Fig. 6 shows the percentage-time plot of the photocatalytic irradiations using the series of TP@Y at various loadings. From this figure, it can be clearly seen that the optimum loading corresponds to a carbon content around 2 wt %, which is

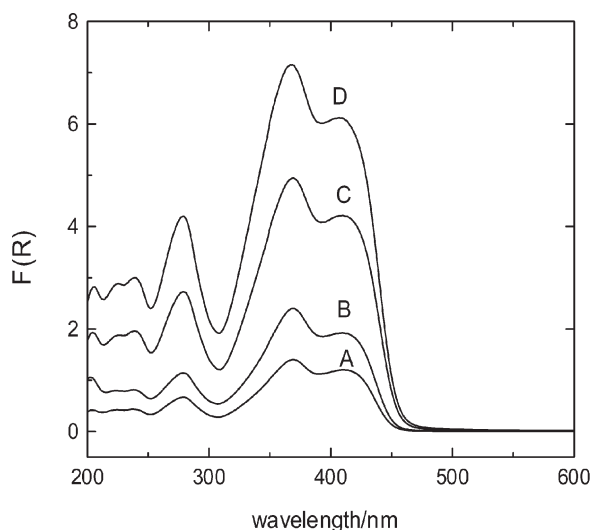


Fig. 5 Diffuse reflectance UV-vis spectra of TP@Y photocatalysts having different TP⁺ loadings (given in carbon content): (A) 1, (B) 2, (C) 4, (D) 6 wt % C.

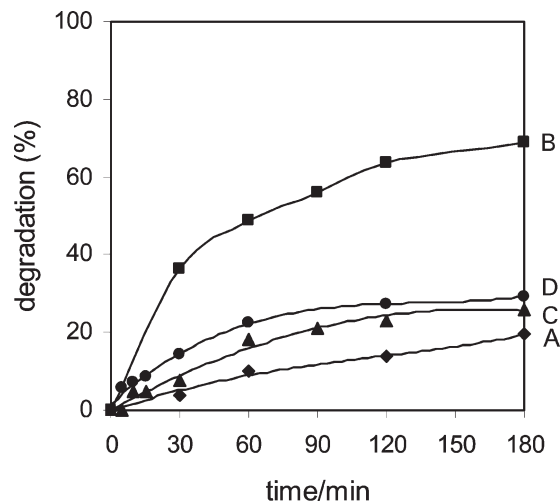
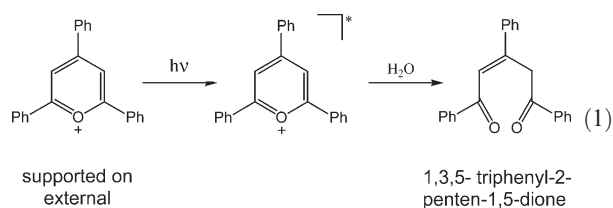


Fig. 6 Percentage of phenol degradation for different TP@Y photocatalysts having different TP⁺ loadings (given in carbon content): (A) 1, (B) 2, (C) 4, (D) 6 wt % C.

equivalent on average to about one TP⁺ molecule per nine zeolite supercages.

Photocatalyst deactivation

In order for a photocatalyst to be usable in real situations, the solid has to retain a large degree of activity after consecutive reuses. Thus, we addressed the problem of the deactivation of the series of TP⁺ and TPTP⁺ photocatalysts upon consecutive reuse. Importantly, even though the activity of TP⁺ and TPTP⁺ supported on SiO₂ and MCM-41 is very large compared to that of photocatalysts in which the dyes are encapsulated within zeolites, these two types of photocatalysts are completely deactivated after very short irradiation times. In this regard, irradiation of TP/SiO₂, TPTP/SiO₂, TP/MCM-41 and TPTP/MCM-41 in distilled water leads to complete self-degradation of the dye in less than 30 min. Diffuse reflectance spectroscopy shows that the reason for this deactivation is the self-degradation of the TP⁺ or TPTP⁺ dyes. Thus, the characteristic absorption spectra of TP⁺ and TPTP⁺ shown in Fig. 1 disappear gradually upon irradiation. Among other possible photoprocesses, we have previously observed that TP⁺ in aqueous SDS micellar solutions undergoes photohydrolysis, giving rise to 1,3,5-triphenyl-2-penten-1,5-dione, which does not act as a photosensitizer.⁵⁹ This photohydrolysis is the result of the reaction of TP⁺ in its excited state with water [eqn. (1)].



In contrast, TP⁺ or TPTP⁺, when encapsulated in zeolites Y or Beta, persist indefinitely when these solids are irradiated in distilled water at room temperature. In view of this, it is not surprising that TP⁺ or TPTP⁺ encapsulated within zeolites survive the photocatalytic irradiation of phenol. However, due to the low initial activity of TP@Y and TP@Beta compared to TPTP@Beta, consecutive reuse was only studied with the latter photocatalyst. The lower activity of TP⁺ based photocatalysts compared to TPTP⁺ based ones parallels the relative photoinduced electron transfer efficiency of these dyes in organic solvents as reported by Saeva and Olin³⁸ and which

was explained by a higher thermodynamic driving force for the photoinduced electron transfer for a given donor molecule (most likely water in our case) using TPTP^+ than TP^+ .

Also, in contrast to the behaviour of TP^+ or TPTP^+ adsorbed on silica or MCM-41, TPTP@Y and TPTP@Beta survived the photocatalytic degradation of phenol and still showed significant activity in successive runs. For instance, Fig. 7 shows time conversion plots for the photocatalytic degradation of phenol upon consecutive reuses of TPTP@Y . DR UV-vis spectroscopy establishes, however, that the deactivation of TPTP^+ photocatalyst is not due, as in the cases of TP/SiO_2 or TP/MCM-41 commented earlier, to the decomposition of TPTP^+ . In fact, the characteristic optical spectrum of TPTP^+ dye remains unaltered through consecutive irradiations and is still present in the deactivated photocatalyst. A reasonable explanation to account for the deactivation observed to TPTP@Y is that the zeolite pores become blocked by the presence of degradation by-products, impeding the intracrystalline diffusion of the substrates to reach the organic photosensitizer. Deactivation was particularly noteworthy from the second to the third use, and this rather abrupt decrease in activity could correspond to the complete filling of the zeolites pores by phenol or photoproducts derived therefrom. After this third use, the decrease in activity is more gradual but still observed. Most probably, the progressive evolution in the product distribution adsorbed in the zeolite upon consecutive photocatalytic cycles is causing these progressive changes. A quantitative estimation of the photocatalyst deactivation can be obtained from the decrease in r_0 or from the percentage of phenol degradation at final time. Thus r_0 from the first to the fifth reuses decreased from 0.93 down to $0.55\% \text{ min}^{-1}$.

Influence of the initial addition of H_2O_2

Photocatalytic degradation of phenol was also carried out in the presence of the series of photocatalysts under the same operational conditions as before but with addition of an initial 10^{-3} M concentration of hydrogen peroxide. It has been reported^{33,34,36} that for those degradations that occur through the intermediacy of OH^\bullet radicals the addition of H_2O_2 remarkably enhances the photodegradation activity by providing a direct source of OH^\bullet radicals. As Fig. 8 shows this turns out to be the case for TP^+ and TPTP^+ photocatalysts. The initial activity in the presence 10^{-3} M H_2O_2 increases by a factor of 6 as compared to those runs in which H_2O_2 was not added.

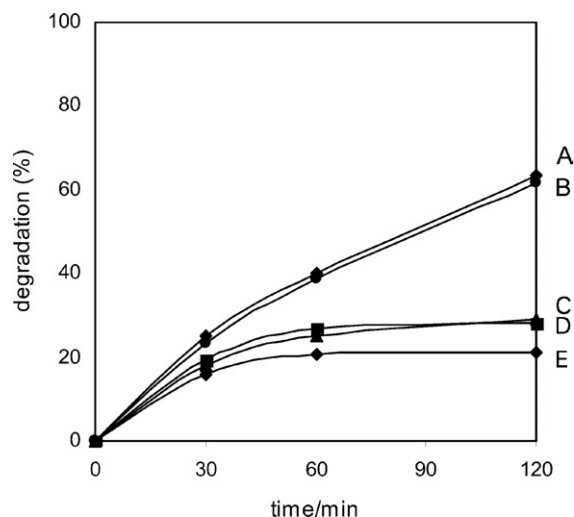


Fig. 7 Photocatalytic activity for the phenol degradation of TPTP@Y upon successive reuses under the same conditions: A, B, C, D, E correspond to the first, second, third, fourth and fifth reuse.

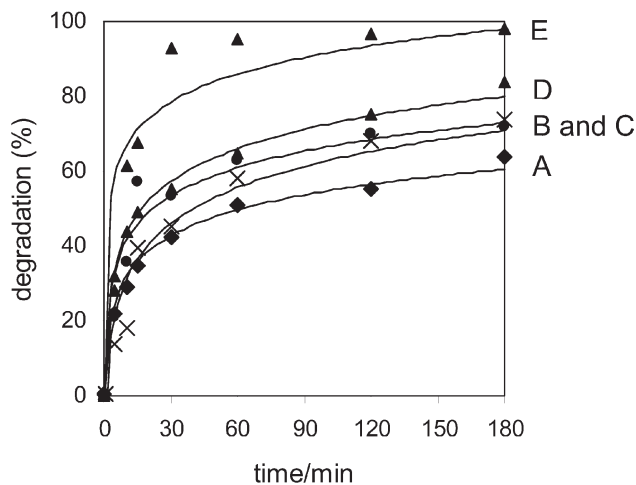


Fig. 8 Photocatalytic degradation of phenol (40 ppm) adding an initial 10^{-3} M concentration of H_2O_2 in the presence of a series of photocatalysts (30 mg): (A) TP@Y ; (B) TiO_2 ; (C) TP@Beta ; (D) TPTP@Y ; (E) TPTP@Beta .

However, addition H_2O_2 shows no advantages in terms of the final degradation percentage, probably indicating that the initial amount of H_2O_2 added only exerts influence at short irradiation times before its complete decomposition. Higher concentrations of H_2O_2 (above 10^{-2} M) leads to a significant bleaching of the photocatalyst and experiments at H_2O_2 concentrations higher than 10^{-3} M were not pursued.

Photocatalytic degradation of aniline

Photocatalytic degradation of aniline has also been proposed as a model reaction to rank the activity of different photocatalysts.^{33,34,36} Herein, we have undertaken a systematic study of the degradation of aniline in water at an initial pH of 3 units. Fig. 9 shows a plot of the degradation percentage versus time for a series of irradiations in the presence of various TP^+ and TPTP^+ containing photocatalysts. In this case a similar order of photocatalytic activity as that observed for phenol was measured except that the activity of TP@Beta is in this case remarkably enhanced and comparable to that of TPTP@Beta . Importantly, the initial degradation rate (r_0) of TPTP@Beta and TP@Beta based photocatalysts is again much higher (by 2.5) than that of the P-25 TiO_2 standard.

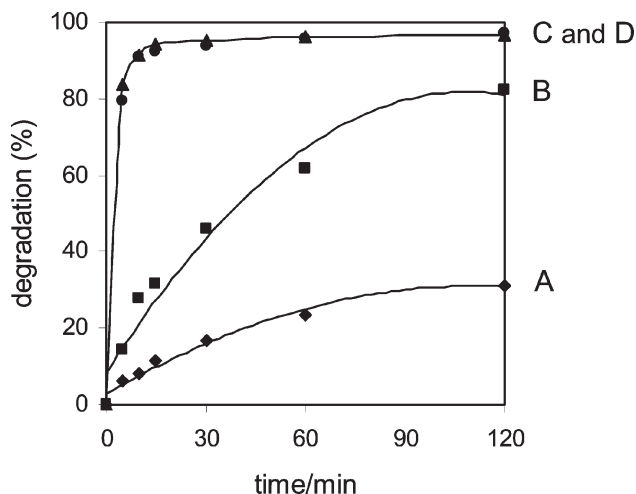


Fig. 9 Degradation of aniline (40 ppm) in the presence of various photocatalysts (30 mg): (A) TP@Y ; (B) TPTP@Y ; (C) TP@Beta ; (D) TPTP@Beta .

Comparing the photocatalytic activity for the degradation of phenol and aniline the most salient fact is that the activity of photocatalysts for aniline is significantly higher than that for phenol. We interpret this as reflecting the stronger adsorption of basic aniline on the zeolite acid sites. In fact, most of the aniline disappearance from the aqueous solution occurs immediately upon contacting the photocatalyst and aniline becomes adsorbed on the zeolite. However, it has to be emphasized that our photodegradation study does not consider at all the adsorbed probe as photodegraded since for each experimental point, the solid is extracted to recover the adsorbed probe and this amount is added to that present in the liquid phase. In fact, solid-liquid extraction allows a large portion of the adsorbed aniline retained on the solid to be recovered, thus indicating that the photocatalytic degradation is much slower compared to the fast adsorption in the solid.

In order to determine more accurately the relative photocatalytic efficiency of the different photocatalysts and considering the readiness of aniline to undergo photocatalytic degradation, a series of experiments was also carried out using higher initial concentrations of aniline (80 ppm). This substrate-to-photocatalyst ratio corresponds approximately to 8 times more moles of aniline than dye contained in the zeolite. The results are indicated in Fig. 10. From these results, it is interesting to note that to achieve 80% aniline degradation using 30 mg of photocatalyst requires twice the time (and, therefore, energy consumption) using P-25 than TPTP@Beta. An interesting point to be commented is that the overall productivity of TPTP@Beta before being deactivated is higher than that of TP/SiO₂ or TPTP/SiO₂. Thus, overall TPTP@Beta is able to degrade more phenol and aniline molecules per molecule of photosensitizer than any other dye-supported photocatalyst.

The effect of the addition of 10⁻³ M H₂O₂ on the degradation of aniline, either at 40 ppm or 80 ppm, was very minor. This lack of influence can be interpreted by considering that the high intrinsic activity of the photocatalyst for the degradation of aniline makes the presence of H₂O₂ irrelevant.

Conclusions

We have prepared a new generation of photocatalysts based on thiapyrylium photosensitizer encapsulated inside large pore zeolites Y and Beta or deposited on silica or mesoporous MCM-41. These systems exhibit much higher activity and stability than the pyrylium analogues and P-25 TiO₂ standard

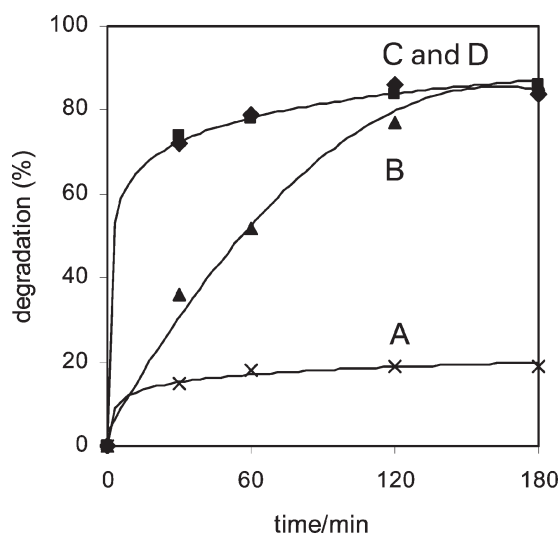


Fig. 10 Degradation of aniline (80 ppm) in the presence of various photocatalysts (30 mg): (A) TPTP/SiO₂; (B) TiO₂; (C) TP@Beta; (D) TPTP@Beta.

in the degradation of phenol and aniline. When the dyes are supported on SiO₂ or MCM-41 the solids exhibit the highest initial photocatalytic activity, but the dye rapidly self-degrades. Encapsulation of the dyes within zeolites instead of supporting them on an external surface makes the systems less active, but increases remarkably the photostability of the dyes, leading to higher productivity. TPTP⁺ and TP⁺ encapsulated within zeolites can be reused in consecutive runs, although with a gradual decrease in the photocatalytic activity. This deactivation is not caused by self-degradation of the photosensitizer but most likely is due to pore blockage by the degradation by-products.

Experimental

Photocatalyst preparation

SiO₂ (BASF, 200 m² g⁻¹) and HY (PQ CBV 720) were commercial samples. HBeta was prepared by hydrothermal crystallization using tetrapropylammonium as template following the reported procedure.⁶⁰ MCM-41 (Si/Al = 13) was synthesized according to the experimental procedure using cetyltrimethylammonium bromide with aerosil and alumina as the silicon and aluminium sources, respectively.^{61,62} To decompose the surfactant MCM-41 was calcined by heating gradually the silicate in a deep bed from room temperature up to 550 °C at a rate of 10 °C min⁻¹ and then maintaining the temperature for 8 h. While heating the MCM-41 was flushed with N₂ the first 5 h and then the flow changed gradually to dry air. Chemical analysis after calcination showed that the MCM-41 sample contained no carbon. The crystallinity of the HBeta and MCM-41 samples was determined by powder X-ray diffraction. The surface area was measured by isothermal N₂ adsorption using a Micromeritics 2000 ASAP apparatus. The tetrafluoroborate salt of pyrylium was supplied by Aldrich and TPTPClO₄ was synthesized by reacting TP⁺ with SH⁻ as reported in the literature.⁶³⁻⁶⁵

TP⁺ on silica, TP⁺ on MCM-41, TPTP⁺ on silica and TPTP⁺ on MCM-41 were prepared by depositing from a dichloromethane solution (10 ml) given amounts of TP⁺ (40 mg) or TPTP⁺ (40 mg) onto thermally dehydrated (120 °C, 2 h) silica or MCM-41 (1 g). TP@Y and TP@Beta were prepared by absorbing 1,3,5-triphenyl-2-penten-1,5-dione (50 mg) onto thermally dehydrated zeolites HY (1 g) and HBeta (1 g) from cyclohexane solutions (10 ml) using at solid:liquid ratio of 1:10. For other loadings, the same volume of solvent and weight of zeolite was used, but the amount of 1,3,5-triphenyl-2-penten-1,5-dione was varied accordingly. After adsorption the light yellow solids were heated in an oven at 150 °C for 2 h, to effectuate dehydration and cyclization of the pentadione. TPTP@Y and TPTP@Beta were prepared by saturating with H₂S a suspension of the zeolite (1 g) in cyclohexane (10 ml) before adding 1,3,5-triphenyl-2-penten-1,5-dione (50 mg) and refluxing the mixture 72 h under H₂S atmosphere.

The photocatalysts were characterized by combustion chemical analysis (Fisons CHNS analyzer), DR UV-visible (Cary 5G adapted with a praying mantis accessory and BaSO₄ as standard) and FTIR (Nicolet 710 spectrophotometer, self-supported wafers recorded at room temperature under vacuum after heating at 200 °C for 1 h) spectroscopy.

Photocatalytic tests

Photocatalytic tests were carried out by stirring in open air at room temperature an air-saturated aqueous suspension (25 ml) of phenol (40 ppm, pH 7) or aniline (40 or 80 ppm, pH 3 by adding H₂SO₄) in the presence of photocatalyst (from 100 to 10 mg). The suspension was stirred for at least 10 min before irradiation. The samples were placed in a series of individual Pyrex test tubes (25 ml capacity) provided with

magnetic stirring bars. The test tubes were placed in a thermostatted water bath around a water-refrigerated Pyrex well containing a 125 W medium pressure Hg lamp. The course of the irradiation was followed by taking one test tube at the required reaction time and analyzing the supernatant aqueous solution as well as the products retained in the solid. The solids were extracted by sonicating the powder redispersed in 3 ml of fresh water (case of phenol) or acetone (case of aniline). The combined extracts (supernatant plus products recovered from the solid) were analyzed by phase-reversed HPLC (suprasil column, diode array detector monitoring at 254 nm) in the case of phenol or by GC (gas chromatograph HP5890; crosslinked 5% Ph Me silicon, 25 m × 0.32 mm × 1.05 µm film thickness) in the case of aniline. Some experiments were carried out by adding the required amount of H₂O₂ (50% in water) to obtain an initial 10⁻³ M concentration of H₂O₂ before starting the irradiation. The Reuse study was carried out by recovering the solid photocatalyst from the irradiation suspension by centrifugation and washing the solid with distilled water (3 ml) by sonication (10 W, 15 min). The solid was reused by centrifuging the washed photocatalyst and simply adding a fresh solution containing the phenol or aniline.

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References

- N. Serpone and E. Pelizzetti, *Photocatalysis. Fundamentals and Applications*, John Wiley & Sons, New York, N.Y., 1989.
- M. Schiavello, *Heterogeneous Photocatalysis*, Wiley, New York, N.Y., 1997.
- D. Robert, *Industrial and Environmental Applications of Photocatalysis-Parts 3 & 4*, Ain Shams University, Photoenergy Center, Cairo, Egypt, 2003.
- D. Robert, *Industrial and Environmental Applications of Photocatalysis-Parts 1 & 2*, Ain Shams University, Photoenergy Center, Cairo, Egypt, 2003.
- A. Gilbert and J. Baggott, *Essentials of Molecular Photochemistry*, Blackwell Scientific Publishers, Oxford, 1991.
- N. J. Turro, *Modern Molecular Photochemistry*, Benjamin Cummings, Menlo Park, California, 1978.
- V. Iliev, A. Mihaylova and L. Bilyarska, *J. Mol. Catal. A: Chem.*, 2002, **184**, 121.
- J. Grodkowski, T. Dhanasekaran, P. Neta, P. Hambright, B. S. Brunshwig, K. Shinozaki and E. Fujita, *J. Phys. Chem. A*, 2000, **104**, 11 332.
- V. Iliev, L. Prahov, L. Bilyarska, H. Fischer, G. Schulz-Ekloff, D. Wöhrle and L. Petrov, *J. Mol. Catal. A: Chem.*, 2000, **151**, 161.
- O. L. Kaliya, E. A. Lukyanets and G. N. Vorozhtsov, *J. Porphyrins Phthalocyanines*, 1999, **3**, 592.
- V. Iliev, A. Ileva and L. Bilyarska, *J. Mol. Catal. A: Chem.*, 1997, **126**, 99.
- J. Premkumar and R. Ramaraj, *J. Photochem. Photobiol., A*, 1997, **110**, 53.
- J. R. Premkumar and R. Ramaraj, *Chem. Commun.*, 1997, 343.
- V. Iliev and A. Ileva, *J. Mol. Catal. A: Chem.*, 1995, **103**, 147.
- R. Gerdes, O. Bartels, G. Schneider, D. Wöhrle and G. Schulz-Ekloff, *Int. J. Photoenergy*, 1999, **1**, 41.
- R. Gerdes, O. Bartels, G. Schneider, D. Wöhrle and G. Schulz-Ekloff, *Polym. Adv. Technol.*, 2001, **12**, 152.
- R. Gerdes, D. Wöhrle, W. Spiller, G. Schneider, G. Schnurpfeil and G. Schulz-Ekloff, *J. Photochem. Photobiol., A*, 1997, **111**, 65.
- A. Corma, V. Fornés, H. García, M. A. Miranda, J. Primo and M. J. Sabater, *J. Am. Chem. Soc.*, 1994, **116**, 2276.
- A. Corma, V. Fornés, H. García, M. A. Miranda and M. J. Sabater, *J. Am. Chem. Soc.*, 1994, **116**, 9767.
- A. Sanjuán, M. Alvaro, G. Aguirre, H. García and J. C. Scaiano, *J. Am. Chem. Soc.*, 1998, **120**, 7351.
- Since TP⁺ has a positive charge and the zeolite framework is negative the sample should be denoted as TPY by analogy with NaCl. The symbol @ has been previously used by Turro and coworkers (see next reference) to indicate that TP⁺ is hosted within the interior of the zeolite cavities.
- N. J. Turro, *Acc. Chem. Res.*, 2000, **33**, 637.
- A. Sanjuán, G. Aguirre, M. Alvaro and H. García, *Appl. Catal., B*, 1998, **15**, 247.
- A. Sanjuán, G. Aguirre, M. Alvaro, H. García and J. C. Scaiano, *Appl. Catal., B*, 2000, **25**, 257.
- A. Sanjuán, A. Guillermo, M. Alvaro and H. García, *Water Res.*, 2000, **34**, 320.
- A. Sanjuan, G. Aguirre, M. Alvaro, H. Garcia, J. C. Scaiano, M. N. Chretien and K.-S. Focsaneanu, *Photochem. Photobiol. Sci.*, 2002, **1**, 955.
- M. A. Miranda, A. M. Amat and A. Arques, *Catal. Today*, 2002, **76**, 113.
- M. A. Miranda, M. L. Marin, A. M. Amat, A. Arques and S. Segui, *Appl. Catal. B*, 2002, **35**, 167.
- M. A. Miranda, A. M. Amat and A. Arques, *Water Sci. Technol.*, 2001, **44**, 325.
- M. A. Miranda, F. Galindo, A. M. Amat and A. Arques, *Appl. Catal. B*, 2001, **30**, 437.
- M. A. Miranda, F. Galindo, A. M. Amat and A. Arques, *Appl. Catal. B*, 2000, **28**, 127.
- A. M. Amat, A. Arques and M. A. Miranda, *Appl. Catal. B*, 1999, **23**, 205.
- S. H. Bossmann, S. Jockusch, P. Schwarz, B. Baumeister, S. Goeb, C. Schnabel, L. Payawan, Jr., M. R. Pokhrel, M. Woerner, A. M. Braun and N. J. Turro, *Photochem. Photobiol. Sci.*, 2003, **2**, 477.
- S. H. Bossmann, N. Shahin, H. Le Thanh, A. Bonfill, M. Worner and A. M. Braun, *ChemPhysChem*, 2002, **3**, 401.
- S. H. Bossmann, C. Turro, C. Schnabel, M. R. Pokhrel, L. M. Payawan, Jr., B. Baumeister and M. Woerner, *J. Phys. Chem. B*, 2001, **105**, 5374.
- S. H. Bossmann, D. Herrmann, A. M. Braun and C. Turro, *J. Inf. Rec.*, 1998, **24**, 271.
- K. T. Ranjit, I. Willner, S. Bossmann and A. Braun, *J. Phys. Chem. B*, 1998, **102**, 9397.
- F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, 1980, **102**, 299.
- F. Morlet-Savary, S. Parret, J. P. Fouassier, K. Inomata and Matsumoto, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 745.
- B. J. Graphakos, A. R. Katritzky, G. Lhomme and K. Reynold, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1345.
- M. H. Palmer, R. H. Findlay, W. Moyes and A. J. Gaskell, *J. Chem. Soc., Perkin Trans. 2*, 1975, 841.
- M. A. Miranda, F. Galindo, A. M. Amat and A. Arques, *Appl. Catal. B*, 2001, **30**, 437.
- F. Galindo and M. A. Miranda, *J. Photochem. Photobiol., A*, 1998, **113**, 155.
- N. Serpone and A. Salinaro, *Pure Appl. Chem.*, 1999, **71**, 303.
- Y. Goto, E. Yamada, M. Nakayama and K. Tokumaru, *J. Polym. Sci.*, 1988, **26**, 1671.
- S. Gob, E. Oliveros, S. H. Bossmann, A. M. Braun, C. A. O. Nascimento and R. Guardani, *Water Sci. Technol.*, 2001, **44**, 339.
- A. Salinaro, E. Aleixei, J. Zhao, H. Hidaka, V. Ryabchuk, K. Vladimir and N. Serpone, *Pure Appl. Chem.*, 1999, **71**, 321.
- A. Salinaro, A. V. Emeline, J. Zhao, H. Hidaka, V. K. Ryabchuk and N. Serpone, *Pure Appl. Chem.*, 1999, **71**, 321.
- S. Gob, E. Oliveros, S. H. Bossmann, A. M. Braun, R. Guardani and C. A. O. Nascimento, *J. Inf. Rec.*, 2000, **25**, 447.
- K. T. Ranjit, H. Cohen, I. Willner, S. Bossmann and A. M. Braun, *J. Mater. Sci.*, 1999, **34**, 5273.
- A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
- Z. Zhenghua and Z. Jinlong, *Dyes Pigm.*, 1994, **26**, 89.
- M. J. S. Dewar and A. J. Holder, *Heterocycles*, 1989, **28**, 1135.
- T. Zimmermann and G. W. Fischer, *J. Prakt. Chem.*, 1986, **328**, 373.
- A. M. Amat, A. Arques, S. H. Bossmann, A. M. Braun, S. Gob and M. A. Miranda, *Angew. Chem., Int. Ed.*, 2003, **42**, 1653.
- A. Sayari, M. Kruk and M. Jaroniec, in *Proceedings of the 12th International Zeolite Conference, Baltimore, July 5–10, 1998*, ed. M. M. J. Treacy, Materials Research Society, Warrendale, PA, 1999, vol. 1, 725–729.
- M. Kruk, M. Jaroniec and A. Sayari, *Microporous Mesoporous Mater.*, 1999, **27**, 217.
- A. Sayari, P. Liu, M. Kruk and M. Jaroniec, *Chem. Mater.*, 1997, **9**, 2499.

- 59 M. Alvaro, B. Ferrer, H. Garcia and M. Narayana, *Chem. Phys. Lett.*, 2002, **362**, 435.
- 60 M. A. Camblor, A. Mifsud and J. Pérez-Pariente, *Zeolites*, 1991, **11**, 792.
- 61 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- 62 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature (London)*, 1992, **359**, 710.
- 63 C. C. Price, J. Follweiler, H. Pirelahi and M. Siskin, *J. Org. Chem.*, 1971, **36**, 791.
- 64 V. G. Kharchenko, S. K. Klimenko, A. M. Plaksina and A. R. Yakoreva, *Zh. Obshch. Khim.*, 1966, **2**, 1122.
- 65 G. Suld and C. C. Price, *J. Am. Chem. Soc.*, 1961, **83**, 1770.