Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 101 (2005) 383–388

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Synthesis, loading control and preliminary tests of 2,4,6-triphenylpyrylium supported onto Y-zeolite as solar photocatalyst

Ana M. Amat [a,*], Antonio Arques [a], Stefan H. Bossmann [b,1], André M. Braun [b,1], Miguel A. Miranda [c], Rosa F. Vercher [a]

[a] *Departamento de Ingeniería Textil y Papelera, Escuela Politécnica Superior de Alcoy, Universidad Politécnica de Valencia, Paseo Viaducto 1, 03801 Alcoy, Spain*

[b] *Lehrstuhl für Umweltmesstechnik, Engler-Bunte-Institut, Universität Karlsruhe, 76128 Karlsruhe, Germany*

[c] *Departamento de Química, Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, 46071 Valencia, Spain*

Abstract

A heterogeneous photocatalyst has been obtained by hosting the 2,4,6-triphenylpyrylium cation inside the supercages of Y-zeolite. Preparation of the new material has been achieved by means of a formal ion exchange in aqueous medium. Nevertheless, the mechanism is more complex, as bulky 2,4,6-triphenylpyrylium cation is unable to diffuse through the channels of Y-zeolite. The following steps are involved: (a) hydrolytic opening of the pyrylium ion to give a linear diketone; (b) diffusion of the diketone through the channels to reach the supercages; and (c) thermal recyclization under dehydrating conditions. Elemental analysis of the new material was consistent with the pyrylium cation located inside the zeolite. No sulfur was found in the loaded zeolite, indicating that hydrogensulfate is no longer the counter-ion of pyrylium. Accordingly, the stoichiometric amount of Na^+ was found in the filtered waters recovered after the synthesis. Besides, the IR spectrum of the dry material was coincident with that of 2,4,6-triphenylpyrylium, while the spectrum of a less thoroughly dried sample showed, together with the absorption bands corresponding to pyrylium, other bands assignable to the diketone. Zeolite loading can be controlled in the range of 3–15% of organic carbon. The performance of the new material as a solar photocatalyst for oxidative pollutant degradation was checked using four cinnamic acid derivatives as target compounds. Aqueous solutions (250 mL) of these model pollutants (0.001 M) were irradiated by solar light in the presence of different amounts of solid photocatalyst. Oxidation was efficiently achieved as analysed by HPLC and followed in all cases a pseudo first order kinetics. The most satisfactory results were obtained using 1 g/L of Y-zeolite containing 6% of 2,4,6-triphenylpyrylium cation.

Keywords: Pyrylium salts; Photocalysis; Phenolic pollutants; Heterogeneous catalysis; Zeolites; Synthetic methods; Solar irradiation

1. Introduction

In recent years, new methods have been developed to deal with the problem of industrial pollutants that are difficult to treat by classical technologies [1–5]. Solar photocatalysis has been successfully used for industrial wastewater treatment, as it has the ecological and economical advantage of using sunlight as energy source [6,7]. In this context, the use of pyrylium salts (that absorb UV–vis radiation up to 450 nm) seems to be specially advantageous, as the secondary oxidizing agent is atmospheric oxygen. 2,4,6-Triphenylpyrylium hydrogensulfate has been successfully employed as homogeneous photocatalyst to achieve the abatement of several phenolic pollutants [8,9]. Nevertheless, this method is not free from disadvantages, such as the limited stability of the pyrylium cation in aqueous solution and the difficulty to recover the catalyst for further utilization.

A possible strategy to overcome these problems is supporting the catalyst onto inorganic solids. Preliminary

---

* Corresponding author. Fax: +34 966528471.
E-mail addresses: aamat@txp.upv.es (A.M. Amat), andre.braun@ciw.uni-karlsruhe.de (A.M. Braun), mmiranda@qim.upv.es (M.A. Miranda).

[1] Fax: +49 721 6086240.

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.03.020

experiments have been performed using silica gel plates [10]; however, this does not appear to be an adequate solution for technical applications. Zeolites could be more appropriate for this purpose [11–14]. They are microporous aluminosilicates having well-defined structures [15,16]. Among the wide range of zeolites with different characteristics, Y-zeolites have been chosen for the present work. They have a network of 0.74 nm diameter channels, that form wide cavities (supercages) at their crossings, of 1.3 nm diameter. Their chemical formula is $Na_{54}Al_{54}Si_{139}O_{386}\cdot 223H_2O$; the sodium cations can be removed by ion exchange.

2,4,6-Triphenylpyrylium (TPP^+) cations can fit inside the supercages of the Y-zeolites; however they are too bulky to diffuse through the channels. Hence, the "ship in a bottle" approach has been used to achieve the synthesis of TPP^+ cations inside the supercages [17]. Although this process is genuine and elegant, it is also rather slow and the control of zeolite loading is difficult.

In a preliminary communication, we reported on a new method to place triphenylpyrylium cation inside the supercages of the zeolites [18]. It consists of a formal ion exchange (Na^+/TPP^+) despite the steric hindrance. In this paper, the method is explained in more detail and the control of zeolite loading is achieved by changing the adsorbate to zeolite ratio using both, pyrylium hydrogensulfate and tetrafluoroborate as sources of the organic matter.

Finally, as a test for the possible environmental applications of the material (TPP-Y), solar photo-oxidation of four different phenolic pollutants, namely cinnamic acid, *p*-coumaric acid, caffeic acid and ferulic acid, has been achieved.

2. Experimental

2.1. Reagents

2,4,6-Triphenylpyrylium hydrogensulfate and 2,4,6-triphenylpyrylium tetrafluoroborate were used as starting reagents for the synthesis of the photocatalyst, and sodium Y-zeolite was employed as supporting material. Cinnamic acid, *p*-coumaric acid (*p*-hydroxycinnamic acid), caffeic acid (3,4-dihydroxycinnamic acid) and ferulic acid (3-hydroxy-4-methoxycinnamic acid) were the substrates employed to check the solar photocatalytic activity of the new material. All these chemicals were supplied by Aldrich and used without further purification. Water employed in the experiments was Milli Q grade.

2.2. Preparation and analysis of the catalyst

The catalyst was prepared according to the following procedure: 2.5 g of Y-zeolite were suspended in an aqueous solution of 2,4,6-triphenylpyrylium hydrogensulfate (0.412 g in 10 mL of water). The mixture was acidified to pH 3 (using HCl) and stirred during one day. Then, the suspension was filtered through cellulose and the solid phase was dried in an oven (105 °C) during one day. At the end of the process, a yellow powder was obtained. The product (TPP-Y) was submitted to elemental analysis to detect the presence of carbon and sulfur and to determine the zeolite loading. X-ray diffraction, IR and diffuse reflectance UV spectrophotometry were employed for the characterization of the catalyst. The same material TPP-Y can also be obtained using the cheaper, although less soluble, 2,4,6-triphenylpyrylium tetrafluoroborate.

2.3. Photocatalytic reactions

In a first stage, ferulic acid was used to test the performance of the photocatalyst. 0.001 M solutions of the compound with different amounts of suspended TPP-Y (0.2–2 g/L) were irradiated in glass open vessels by means of a solar simulator (Oriel Instruments 68811), equipped with a xenon lamp (300 W) whose emission spectrum closely matches the solar one. Periodically, water was added to the solution in order to compensate for evaporation losses. In parallel, experiments were also performed using real sunlight. For acceptable reproducibility, reactions were started at 10:00 on entirely sunny days.

Samples were taken from the solution, filtered through cellulose (0.45 μm) and analyzed by means of HPLC (Perkin-Elmer Autosystem XL) equipped with a diode-array detector and a loop injector. A Lichrosorb 100 RP-18 column was employed and the eluents were a 0.01 M aqueous solution of sulfuric acid (A) and methanol (B) in the following proportion: 100% of A from 0 to 5 min; then a linear gradient to reach 80% of B in 20 min.

3. Results and discussion

3.1. Preparation of the catalyst

The catalyst was prepared according to the procedure described in Section 2. A confirmation of the presence of TPP^+ comes from the comparison of the infrared spectra of the hydrogensulfate salt and the loaded zeolite. Fig. 1 shows that both spectra are almost coincident; the minor residual bands between 1650 and 1700 cm^{-1} correspond to the diketone intermediate (see below).

The new material was submitted to elemental analysis to determine its loading. Being TPP^+ the only species containing carbon, the amount of this element present in the solid is a good indication of the pyrylium ion hosted in the Y-zeolite and thus, of the yield of the process. Percentage of carbon was around 9%, indicating that nearly all the pyrylium initially present in aqueous solution was incorporated to the zeolite.

As stated in the introductory part of the paper, dimensions of the supercages of the zeolite are big enough to host 2,4,6-triphenylpyrylium cation, but the channels leading to them

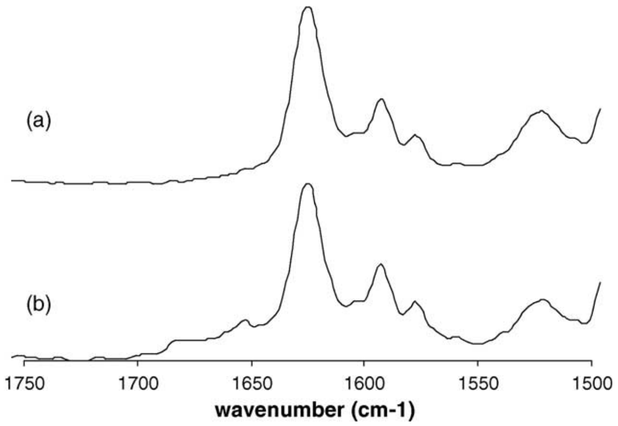

Fig. 1. Infrared spectra of (a) 2,4,6-triphenylpyrylium hydrogensulfate; and (b) pyrylium-loaded zeolite.

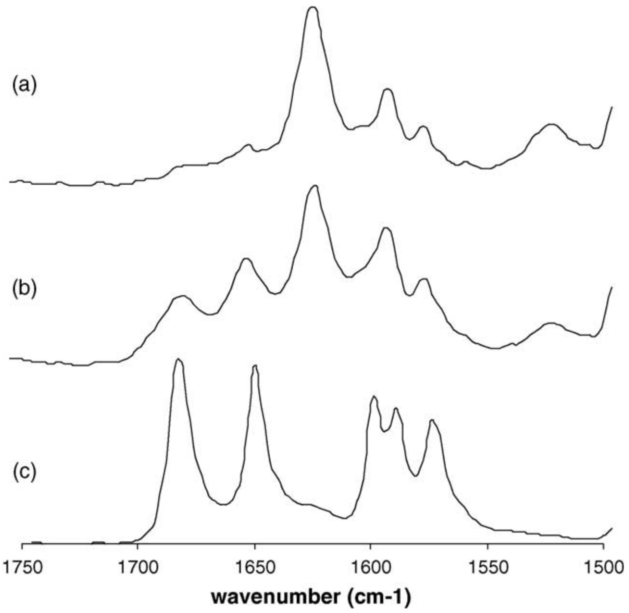

Fig. 3. Infrared spectra of (a) 2,4,6-triphenylpyrylium hydrogensulfate; (b) pyrylium-loaded zeolite (wet batch); and (c) 1,3,5-triphenylpent-2-en-1,5-dione.

are too narrow to allow diffusion. Hence, the mechanism cannot be simply an ion exchange reaction. As a matter of fact, we have found that it involves three steps: (a) in aqueous medium, TPP^+ undergoes hydrolytic ring opening, to give a linear diketone (1,3,5-triphenylpent-2-en-1,5-dione); (b) the diketone is now able to diffuse through the channels to reach the supercages; and (c) when heated at 105 °C, recyclization of the diketone occurs with dehydration. All this process is depicted in Fig. 2. The experimental evidence supporting this mechanism is given below.

Hydrolysis of the pyrylium cation is well established. Actually, when TPP^+ hydrogensulfate was treated with a slightly basic (pH 8) aqueous solution, the known 1,3,5-triphenylpent-2-en-1,5-dione was obtained. After adsorption of the diketone onto Y-zeolite and heating in an oven at 105 °C for 1 day, cyclisation to TPP-Y took place. When heating was performed at lower temperature and for shorter times (2 h, 70 °C) cyclization of the diketone to give the pyrylium ion was only partial. This agrees with the fact that the diketone was also detected after moderate heating of the TPP^+ exchanged zeolite. The IR spectrum of this product (Fig. 3) shows, together with the characteristic bands of 2,4,6-triphenylpyrylium, those typical of the diketone (1650–1700 cm^{-1}).

Thus, the synthesis of the material involves a formal ion exchange process, where the negative charge of the aluminosilicate is equilibrated by the pyrylium cation; consequently, an equivalent amount of sodium should be

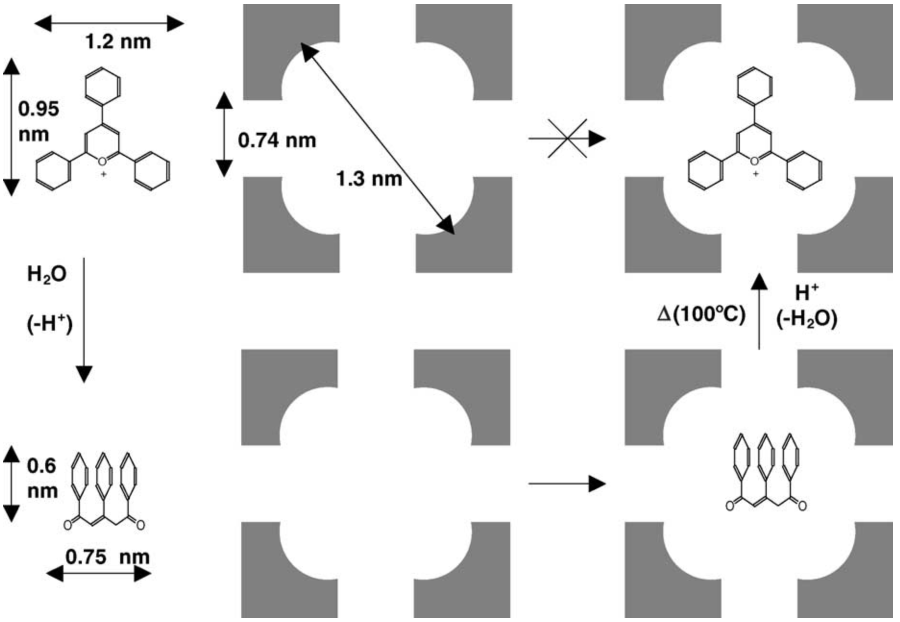

Fig. 2. Scheme of the introduction of 2,4,6-triphenylpyrylium ion inside the supercages of the zeolite.

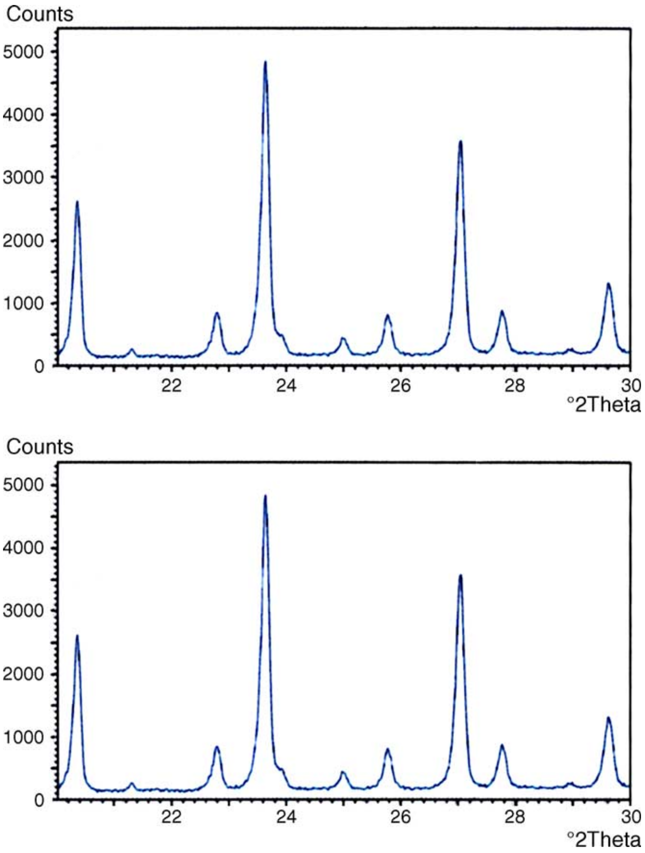

Fig. 4. Interferogrammes of pyrylium-loaded zeolite (above) and Y-zeolite (below) in a selected range for crystallinity.

found in the filtered aqueous phase. As a matter of fact, when this solution was analyzed by means of ionic chromatography, the results matched expectations: 0.98 mmol of pyrylium cation added versus 0.87 mmol of sodium cation in the filtered water. Besides, elemental analysis of the solid did not allow to detect significant amounts of sulfur; indicating that hydrogensulfate is no longer the counter anion of the pyrylium cation.

Finally, X-ray analysis was performed in order to test whether the structure of the Y-zeolite suffered any change during the ion exchange process. A comparison between the interferogrammes of Y-zeolite before and after the synthetic process (Fig. 4) shows clearly the absence of any important structural change. Quantitatively, integration of the three characteristic major bands results in more than 99% crystalinity in the new material.

3.2. Solar photocatalyzed degradation of ferulic acid, using pyrylium-loaded zeolite

2,4,6-Triphenylpyrylium hydrogensulfate has been found to be a good solar photocatalyst to oxidize and eventually degrade an important number of phenolic pollutants. Its photocatalytic activity remains when supported onto silica gel plates [10]. It was therefore interesting to check the possibility of using 2,4,6-triphenylpyrylium hosted in the cages of Y-zeolite as heterogeneous solar photocatalyst in wastewater treatment. For this purpose, ferulic acid was employed as a target pollutant. This compound was chosen because of its cinnamic acid structure, which is widely found in food industry. In fact, solar photocatalyzed oxidation of ferulic acid in homogeneous solution using pyrylium cation, has already been studied [8]. A solution of this acid (250 mL, 0.001 M) was submitted to solar irradiation in the presence of the pyrylium-loaded zeolite (0.2 g/L). Fig. 5 shows that after a short period of time (2.5 h), more than 20% photodegradation was achieved using solar light. The insert in Fig. 5 (logarithmic plot of the relative concentration of substrate versus time) showed that the reaction follows a pseudo first order kinetics.

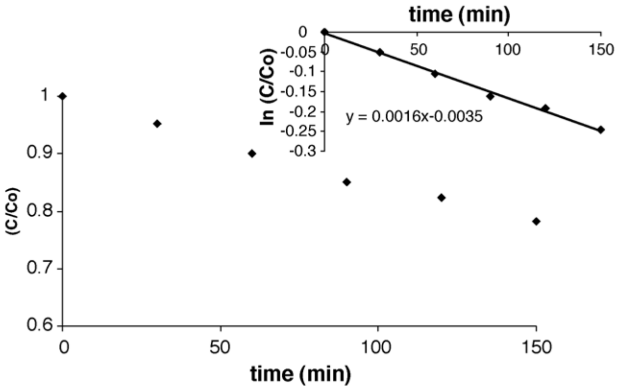

Fig. 5. Solar photodegradation of ferulic acid in the presence of pyrylium-doped zeolite. A logarithmic plot is also shown as an insert.

Dark experiments were carried out in order to rule out the possible disappearance of the substrate by strong adsorption onto the zeolite. Results were negative using both the unloaded zeolite and the pyrylium-loaded one. Other controls consisted of the irradiation of ferulic acid in the presence of unloaded zeolite. Also in this case, degradation of the substrate was negligible. Finally, in a previous paper it was reported that solar photolysis of ferulic acid does not lead to photodegradation, while in the presence of 2,4,6-triphenylpyrylium hydrogensulfate as homogeneous photocatalyst important degradation yields are obtained [8]. All these data indicate that 2,4,6-triphenylpyrylium cation hosted in the supercages of the zeolite is the actual photocatalyst of the degradation of ferulic acid.

As preliminary results were encouraging, more experiments were carried out to check the effect of the concentrations of substrate and catalyst on the efficiency of the process. In order to obtain more reproducible results, irradiations were performed by means of a solar simulator. Solutions of ferulic acid (100 mL, 0.001 M) were irradiated in parallel experiments in the presence of different amounts of catalyst (0.2–2 g/L). Photodegradation of the substrate was found to follow a pseudo first order kinetics; the rate constants are shown in Fig. 6a. The optimum concentration of catalyst was 1 g/L and no further enhancement of the reaction rate was found for higher catalyst concentration. In

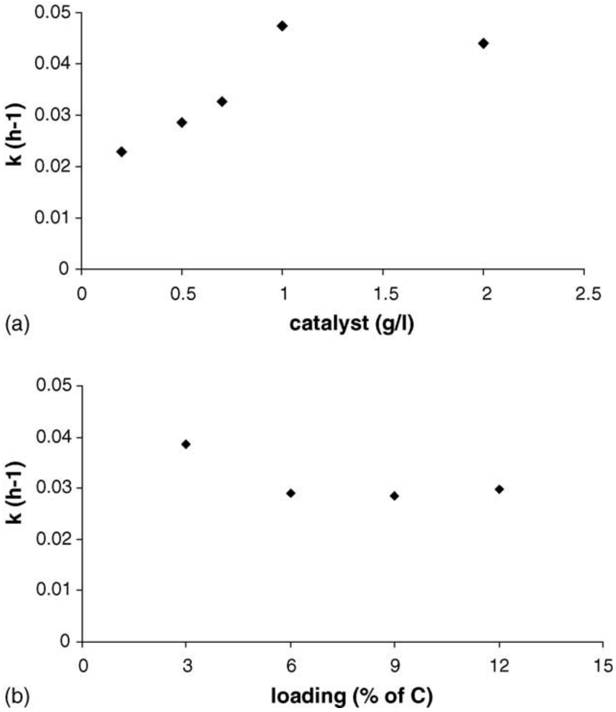

Fig. 6. Plot of the first order rate constants obtained in the photodegradation of ferulic acid (a) in the presence of different amounts of photocatalyst; (b) using differently loaded zeolites.

addition, in the presence of too much catalyst the light penetration inside the reactor is more difficult [19].

The concentration of the substrate is known to play a very important role when pyrylium salts are used as homogeneous photocatalysts, pollutant degradation being faster in more diluted solutions. The same behavior should be found in heterogeneous catalyst, and the results of experiments made with different concentrations of ferulic acid (Table 1) confirm our hypothesis.

3.3. Control of the catalyst loading

It has been shown in Section 3.1, that all the TPP^+ employed in the preparation of TPP-Y is found to be inside the supercages of the zeolites. Thus, using the ‘‘camel through the eye of a needle’’ approach, it could be possible to control the loading of the zeolite. To check this point, six batches of TPP-Y were prepared by changing the amount of pyrylium hydrogensulfate added to the zeolite, so that the percentage of carbon found in the solid was 3, 6, 9, 12, 15 and 18%, respectively. Table 2 shows the results of the elemental analysis of the obtained products. In most cases (except for the 18% batch), the amount of carbon found in the zeolite was in agreement with expectations, showing that loading control was, indeed, possible. The percentage of sulfur was also determined in the same series. Remarkably, this element was not present in the 3–15% batches indicating that the ion exchange process was completely accomplished and that pyrylium was acting as charge-compensating cation of the zeolite network. On the other hand, in the 18%-loaded batch significant amounts of sulfur were detected (probably due to some of the hydrogensulfate salt impregnating the external surface), and the percentage of carbon was slightly lower than expected. These data indicate that the maximum loading of the zeolite must be close to this level.

Table 1
Photodegradation of ferulic acid at different concentrations, using pyrylium-loaded zeolite (1 g/L) as heterogeneous photocatalyst

Concentration (mM)	k (h^{-1})
0.5	0.114
1	0.055
2	0.027

Table 2
Elemental analysis of different batches of pyrylium-loaded Y-zeolite

Expected carbon (%)	Actual carbon (%)	Sulphur (%)	Nitrogen (%)
3	3.0	0.0	0.0
6	6.8	0.0	0.0
9	9.6	0.0	0.0
12	12.8	0.0	0.0
15	15.0	0.0	0.0
18	16.8	0.8	0.0

Then, experiments were performed to check the influence of zeolite loading on its photocatalytic activity. Solutions of ferulic acid (100 mL, 0.001 M) were irradiated by means of a solar simulator in the presence of 0.5 g/L of photocatalyst. Data in Fig. 6b show that the photocatalytic activity depends of the pyrylium loading up to 15%, and the best results were obtained with the 3% loaded zeolite. This can be attributed to three different factors: (a) only the pyrylium molecules that are close to the surface of the zeolite can act as photocatalysts; (b) as the number of occupied cavities increases, the intrazeolite diffusion of the substrate is slower; and (c) higher loadings produce an increase of the hydrophobicity in the material.

The photocatalytic activity of TPP-Y was also checked using real sunlight. For this purpose 0.001 M solutions of cinnamic acid, *p*-coumaric acid, caffeic acid and ferulic acid were irradiated in the presence of TPP-Y (1 g/L of the 9% carbon-loaded material). All of them were efficiently photodegraded; the pseudo first order rate constants can be seen in Table 3. The same trends were observed as in the case of homogeneous catalysis [8] with TPP^+: the reaction

Table 3
Pseudo first order rate constants obtained for the solar oxidative degradation of four cinnamic acid derivatives in the presence of TPP-Y (1 g/L, 9% carbon batch)

Compound	k (min^{-1})
Cinnamic acid	0.056
p-Coumaric acid	0.063
Caffeic acid	0.115
Ferulic acid	0.118

rate was strongly dependent on the presence of electron-donating groups directly attached to the aromatic ring. Ferulic acid and caffeic acid, with two activating groups, were more easily degraded than *p*-coumaric acid that only has one hydroxyl substituent. As expected, cinnamic acid was even harder to degrade, due to the absence of methoxy and/or hydroxy groups attached to the ring.

4. Conclusions

The 2,4,6-triphenylpyrylium cation fits into the supercavities of zeolite Y and is accessible via formal ion exchange in aqueous medium. Loading of the zeolite can be controlled through the concentration of TPP^+ in solution; the carbon contents of the obtained material TPP-Y can reach values as high as 15–17%. TPP-Y can be advantageous used as photocatalyst in the oxidation of cinnamic acid derivatives by solar light.

Acknowledgement

We wish to thank the financial support of Universidad Politécnica de Valencia and Generalitat Valenciana (Grupo 03/082).

References

[1] P.R. Gogate, A.B. Pandit, Adv. Environ. Res. 8 (2004) 501.
[2] P.R. Gogate, A.B. Pandit, Adv. Environ. Res. 8 (2004) 553.
[3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[4] O. Legrini, E. Oliveros, M.A. Braun, Chem. Rev. 93 (1993) 671.
[5] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Jiménez, S. Esplugas, Appl. Catal. B 47 (2004) 219.
[6] M.A. Blesa, Ed., Eliminación de contaminantes por fotocatalisis heterogénea, CYTED, http://www.cnea.gov.ar/cyted/default.htm, 2001.
[7] D.F. Ollis, Photochemical Conversion and Storage of Solar Energy, Kluwer Academic Publishers, Dordrecht, 1991.
[8] M.A. Miranda, F. Galindo, A.M. Amat, A. Arques, Appl. Catal. B 28 (2000) 127.
[9] A.M. Amat, A. Arques, M.A. Miranda, Appl. Catal. B 35 (2002) 167.
[10] M.A. Miranda, A.M. Amat, A. Arques, Catal. Today 76 (2002) 113.
[11] A. Sanjuan, G. Aguirre, M. Alvaro, H. García, J.C. Scaiano, Appl. Catal. B 25 (2000) 257.
[12] M. Anpo, S.G. Zhang, M. Matsuoka, H. Yamashita, Catal. Today 39 (1997) 159.
[13] M. Alvaro, E. Carbonell, H. García, C. Lamaza, M. Narayana, Photochem. Photobiol. Sci. 3 (2004) 189.
[14] S.H. Bossmann, S. Jockusch, P. Schwarz, B. Baumeister, S. Goeb, C. Schnabel, L. Payawan, M.R. Pokhrel, M. Woerner, A.M. Braun, N.J. Turro, Photochem. Photobiol. Sci. 2 (2004) 477.
[15] D.W. Breck, Zeolite Molecular Sieves: Structure Chemistry and Use, John Wiley & Sons, New York, 1974.
[16] H. Van Bekkum, E.M. Flanigen, J.C. Jansen, Introduction to Zeolite Science and Practice, Elsevier, Amsterdam, 1991.
[17] A. Corma, V. Fornés, H. García, M.A. Miranda, J. Primo, M.J. Sabater, J. Am. Chem. Soc. 116 (1994) 2276.
[18] A.M. Amat, A. Arques, S.H. Bossmann, A.M. Braun, S. Göb, M.A. Miranda, Angew. Chem. Int. Ed. Engl. 42 (2003) 1653.
[19] L. Jakob, E. Oliveros, O. Legrini, A.M. Braun, TiO_2 photocatalytic treatment of water. Reaction design and optimization experiments, in: D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993 , pp. 511–532.