

# Porphyrin – zeolite materials synthesis and their use in the photocatalytic oxidation of aromatic compounds

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The photodegradation of organic compounds in aqueous solutions using environment-friendly materials, methods and processes is a topic of growing interest. A great interest regarding this subject has been devoted to photocatalysts for the oxidative photodegradation of various organic pollutants. In this context, some natural and synthetic zeolites impregnated with metalloporphyrins and metallophthalocyanines were studied in this paper. The metalloporphyrins and metallophthalocyanines used for impregnation were prepared in agreement with the scientific reports. After impregnation, the porphyrin – zeolite systems were investigated for their photocatalytic activity in the oxidation reaction of aromatic compounds. A comparison of the photoreactivity of the newly obtained photocatalytic materials was discussed.

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## 1. Introduction

Organic porphyrinic and phthalocyaninic nanomaterials and their metallic complexes (fig. 1, 2) have a special place in material science, having the role of reaction catalysts, oxygen transporters, chemical sensors, anticancer drugs, molecular electronic devices etc.<sup>1-4</sup>.

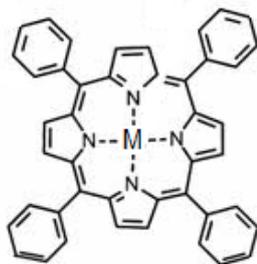


Fig. 1. General structure of metallo-tetraphenylporphyrins (MP).

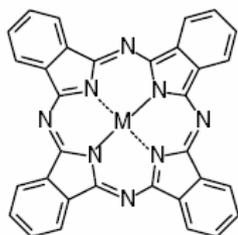


Fig. 2. General structure of metallophthalocyanine (MPc).

Porphyrinic/phthalocyaninic catalysts impregnated on various supports are used on a wide scale in various processes<sup>5-7</sup>. Research concerning systems based on porphyrinic/phthalocyaninic catalysts that mimic natural enzymatic systems can be done to obtain catalysts that can

be used in degradation reactions under mild conditions. Various supports can be used for the impregnation of, especially zeolitic matrices and polymers.

Zeolitic matrices, natural or synthetic, are widely used in a large variety of processes, like additives for cement, household wastewaters purification etc.<sup>8,9</sup> Porphyrinic/phthalocyaninic materials can be encapsulated or deposited in/on the zeolitic matrices, depending on their pore size, which varies from case to case<sup>10</sup>.

In this paper the synthesis of some hybrid materials is presented, obtained by the process of impregnation of porphyrinic/phthalocyaninic materials in natural zeolitic matrices. These new compounds were then used in the process of photocatalytic oxidation of 4 – nitrophenol, their photocatalytic activity being compared with the one of the initial zeolitic matrices.

## 2. Experimental details

The following reagents and materials were used for the synthesis of the new hybrid materials and for the photocatalytic oxidation of 4 – nitrophenol:

- 5,10,15,20-tetraphenyl porphyrin (TPP), 5,10,15,20-tetratolyl porphyrin (TTP), tin 5,10, 15,20-tetraphenyl porphyrin (SnCl<sub>2</sub>-TPP), iron 5,10,15,20- tetratolyl porphyrin (FeCl-TTP), iron 5,10,15,20-tetra-p-sulphonato-phenyl porphyrin (Fe-TSPP), nickel 5,10,15,20-tetra-p-nitrophenyl porphyrin (Ni-TNP), copper phthalocyanine (CuPc).
- Toluene.
- 2x10<sup>-3</sup> M 4 p-nitro phenol solution.
- Clinoptilolite (originated from the Maramures County, Romania).

For the total organic carbon (TOC) analyses, a Multi N/C 2100 Analytik Jena analyzer. The basic principle of this apparatus is oxidation of organic compounds in water at 950°C. The catalyst used in this process is process for a complete oxidation is Pt/Al<sub>2</sub>O<sub>3</sub>. The CO<sub>2</sub> that is produced by the oxidation reaction is transported to the measuring device by a gas current.

For the physico – chemical analyses, the following instruments were used:

- For the FT-IR analyses a Spectrum GX Perkin Elmer spectrometer with a 4000 – 400 cm<sup>-1</sup> range, a DTGS detector, a beam splitter (quartz, KBr, CsI, CaF<sub>2</sub>, Mylar) and DRIFT (Diffuse Reflectance Infrared Fourier Transform) and ATR (Attenuated Total Reflectance) devices.

- For the UV-VIS analyses a SPECORD M400 Carl Zeiss Jena spectrophotometer with a double beam, a Ebert monochromator with a 1400 lines/mm diffraction net, a premonochromator for the 185 – 270 nm domain to reduce the parasitic light, a 11 steps photomultiplier and a microprocessor. The wavelength domain is 185 – 900 nm with a delay that is smaller than 0.3 nm and a 0.1 nm reproductibility. The experiments were made by using 1 cm or 0.1 cm quartz tubs.

- For the TGA/DSC studies, a Mettler Toledo thermogravimeter was used, having the following characteristics: 70 µl (for TGA) and 40 µl (for DSC) alumina crucibles, 25-1600°C (for TGA) and 65-700°C (for DSC) heating intervals, 20°C/min heating speed, air atmosphere with a 70 l/min debit.

### 2.1. Metalloporphyrins' encapsulation into clinoptilolite

The encapsulation that was used has two steps (fig. 3):

a) The metallic complex was mixed and stirred along with the zeolite in toluene at 323K (50°C) for 24 hours.

b) The zeolite was then filtered and dried at 390K (117°C). The process was repeated 2-3 times for a better metallic exchange.

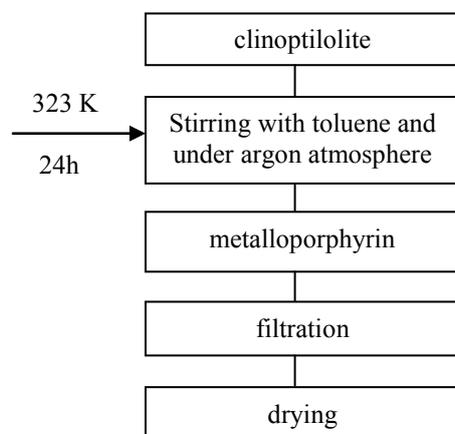


Fig. 3. Technological flux for the encapsulation of porphyrins/metalloporphyrins by diffusion in the zeolites' pores.

### 2.2. Photocatalytic oxidation of 4-nitro phenol in an aqueous solution in the presence of the porphyrinic materials adsorbed/encapsulated in clinoptilolite

A  $2 \times 10^{-3}$  M 4 p-nitro phenol solution was prepared. For 184 ml of solution (the reaction vessel's capacity), 0.2 g from each of the above mentioned products were used as photocatalysts. The 4-nitrophenol solution, along with the photocatalyst, were introduced in a cylindrical photocatalytic minireactor (fig. 4). The air was introduced in the reaction medium using an air generator, with a 50 – 60 l/h debit. In each case, the oxidation took place under the action of visible light using a 375W low pressure mercury lamp. In each case the reaction time was about 6 hours. From hour to hour 5 ml samples were collected to measure the 4-nitrophenol degradation degree by analyzing the total organic carbon (TOC) content in the reaction medium. The first sample was the one where the initial TOC value was determined from the 4-nitrophenol solution.



Fig. 4. Photooxidation lab installation.

### 3. Results and discussions

After the adsorption/encapsulation of the porphyrinic materials into the clinoptilolite matrix, several physico – chemical analyses were performed on the newly obtained materials, among which FTIR (Fourier Transformed IR), UV – VIS and thermogravimetric analyses (TGA/DSC) were the most explanatory. Also, CuPc was also used in this study to see if there is a notable difference between the use of porphyrins and the use of phthalocyanines when associated with clinoptilolite.

Clinoptilolite's structure was verified, among others, by X-ray diffraction (XRD). The resulting diagram is present below:

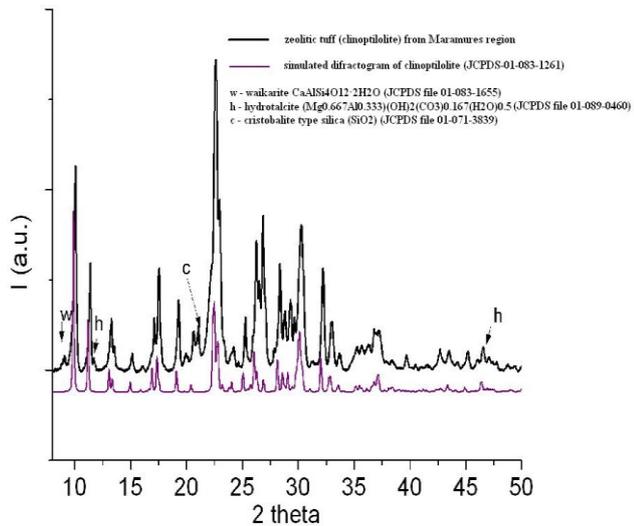


Fig. 5. XRD of clinoptilolite.

In the figures showed below (fig. 5 – 10), the FT – IR analyses results are presented:

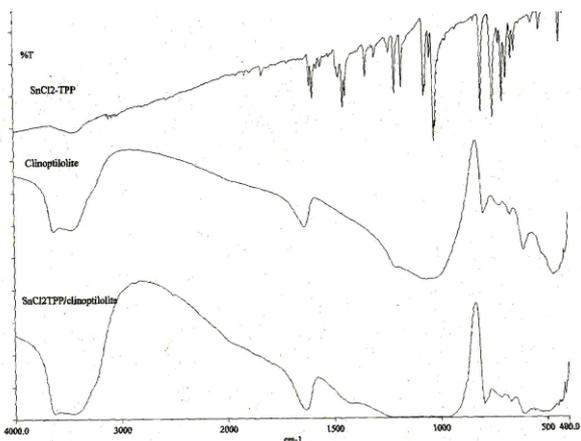


Fig. 6. FTIR spectra of  $\text{SnCl}_2\text{TPP}$ , clinoptilolite and  $\text{SnCl}_2\text{TPP}/\text{c}$  clinoptilolite.

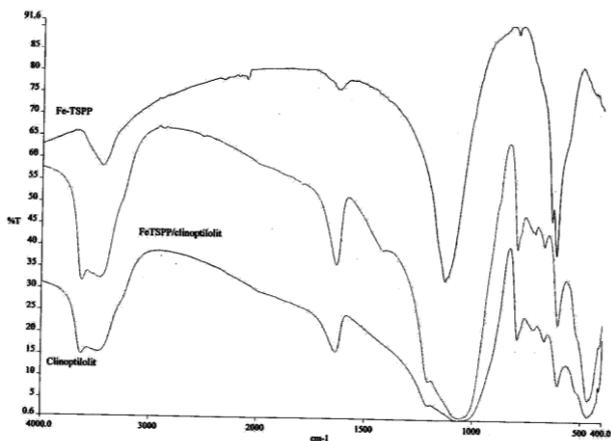


Fig. 7. FTIR spectra of FeTSPP, FeTSPP/c clinoptilolite, clinoptilolite.

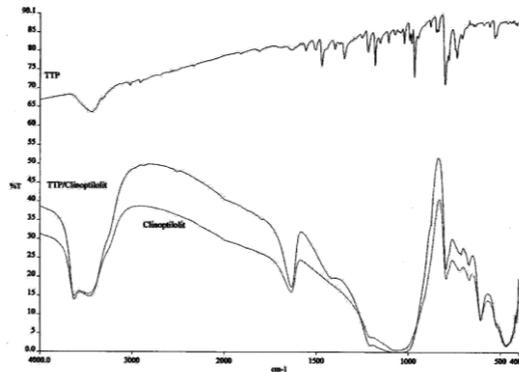


Fig. 8. FTIR spectra of TTP, TTP/c clinoptilolite, clinoptilolite.

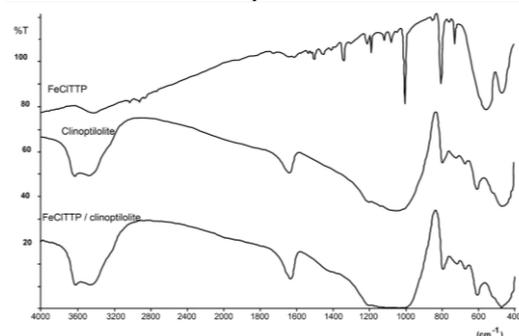


Fig. 9. FTIR spectra of FeClTPP, clinoptilolite, FeClTPP/c clinoptilolite.

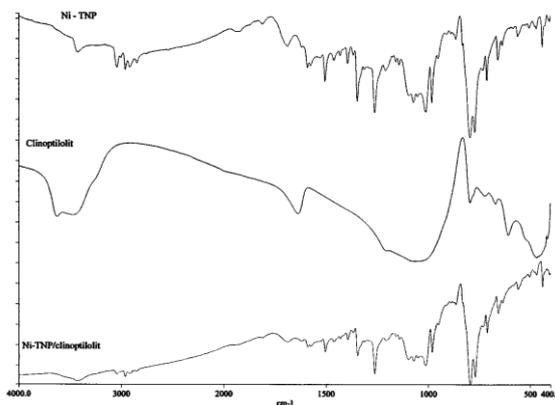


Fig. 10. FTIR spectra of Ni-TNP, clinoptilolite, Ni-TNP/c clinoptilolite.

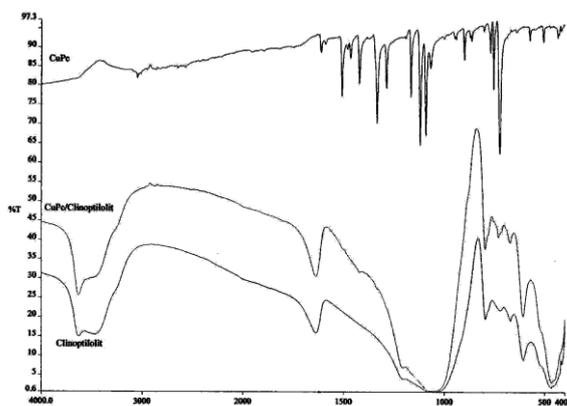


Fig. 11. FTIR spectra of CuPc, CuPc/c clinoptilolite, clinoptilolite.

Because of the complexity of the porphyrinic structure some difficulties were met. Between the characteristic frequencies of the porphyrinic – zeolite materials, the following were more intense than the others: 3400-3600  $\text{cm}^{-1}$  (the N – H pyrrolic, porphyrinic and phthalocyaninic bonds), 1635-1640  $\text{cm}^{-1}$  and 975 – 1065  $\text{cm}^{-1}$  (associated with the zeolitic matrix), 1075 – 1080  $\text{cm}^{-1}$  (associated with pyrrole), 400 - 800  $\text{cm}^{-1}$  (the Me – N and Me – Cl links).

From the UV – VIS spectra the adsorption degrees of the porphyrinic materials on the clinoptilolite matrix were calculated, the most representative result, in this case, being obtained for  $\text{SnCl}_2$  – TPP/c clinoptilolite ( $\Delta=80.9\%$ ). (fig. 11)

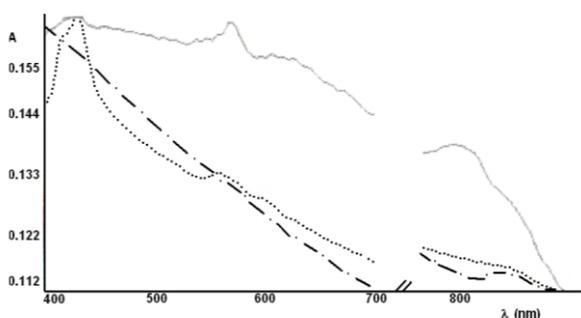


Fig. 12. UV – VIS spectra of  $\text{SnCl}_2\text{TPP}$  (---),  $\text{SnCl}_2\text{TPP}/\text{clinoptilolite}$  (•••) and clinoptilolite (—•—).

By the thermogravimetric analyses (TGA/DSC), the resistance to thermal degradation of the porphyrin – zeolite materials was researched. The differential thermogravimetric analyses showed that the maximum desorption rate occurred at 100 – 200 $^{\circ}\text{C}$ , showing that synthesized materials had an approx. 11% (m/m) water content. At 200 – 300 $^{\circ}\text{C}$ , CO and  $\text{CO}_2$  were left the systems, while in the 400- 450 $^{\circ}\text{C}$  interval was attributed to a recrystallization effect of  $\text{SiO}_2$  without a weight loss. Around 750 $^{\circ}\text{C}$  all the analyzed porphyrinic materials melted, all the metallic oxides that were formed being recuperated after 850 $^{\circ}\text{C}$ .

Below are presented the thermal diagrams of the synthesized materials (fig. 13 – 18)

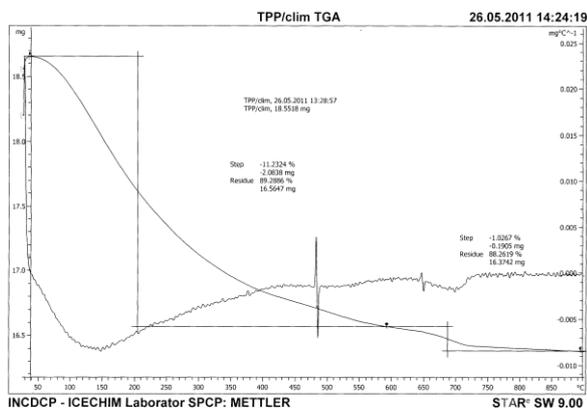


Fig. 13. TGA of TPP/c clinoptilolite.

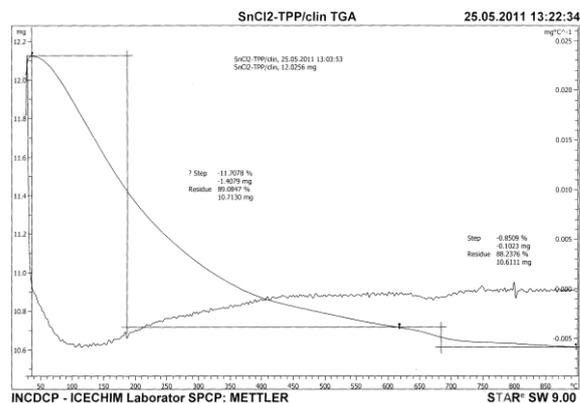


Fig. 14. TGA of  $\text{SnCl}_2\text{TPP}/\text{clinoptilolite}$ .

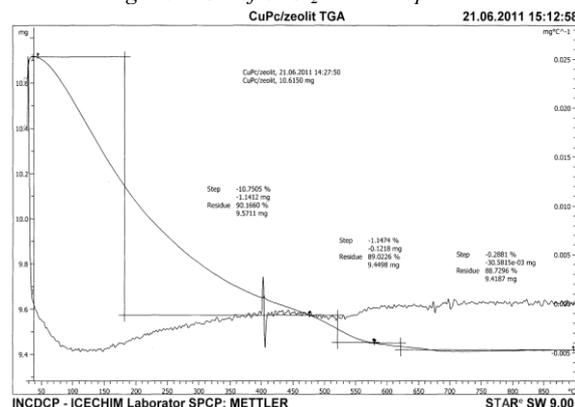


Fig. 15. TGA of CuPC/c clinoptilolite.

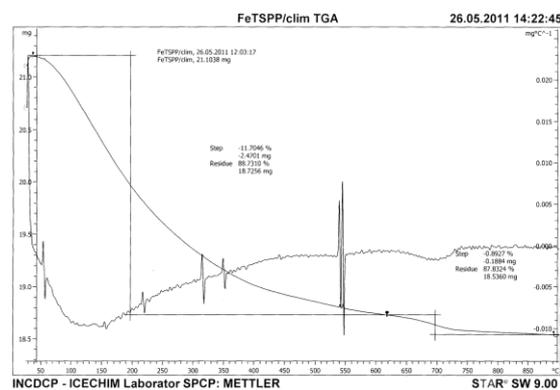


Fig. 16. TGA of FeTSPP/c clinoptilolite.

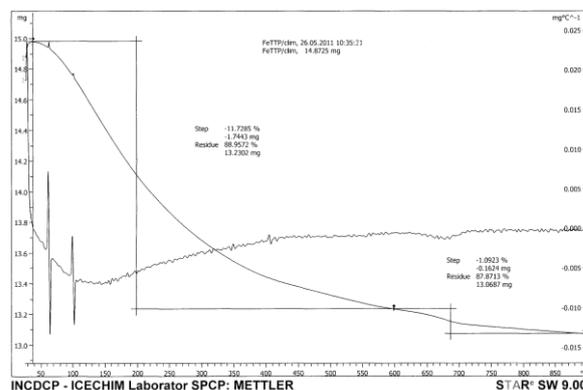


Fig. 17. TGA of FeCl-TTP/c clinoptilolite.

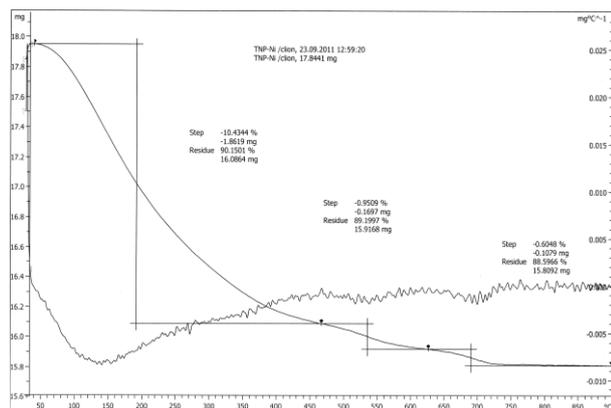


Fig. 18. TGA of Ni – TNP/clinoptilolite.

From these thermal analyses some aspects were observed as follows:

- the water that exists in the structure of clinoptilolite is attributed to a large band, from 50 to 300°C. Usually, zeolites have three types of water in their structures, “external” water, strongly linked/bonded “internal” water and “weakly” linked/bonded water, everyone of them having it’s own band. In our case, all three water types are represented by only one band.

- usually, the encapsulation of the porphyrins, metalloporphyrins and copper phthalocyanine takes place inside the zeolites’ pores, but in the case of clinoptilolite, which has small pore size, most probably it appears a very strong bonding.

- an interesting case is the one of tin porphyrine chloride, where hydrogen bonds are most probably formed between the water molecule inside the zeolite and the chlorine ions that are present in the porphyrin structure.

- on the other hand, tin porphyrin chloride has a larger spatial dimension than tetraphenyl porphyrin (TPP) and because of this fact it is hard to be encapsulated inside the clinoptilolite’s pores.

- the same behavior was observed in the the case of iron-tetrasulphophenyl porphyrin (Fe – TSPP) where supplementary bands appeared in the thermogram up to 300°C.

After all the photocatalytic oxidation reactions were performed as described above, the following results were obtained, which are represented in fig. 19.

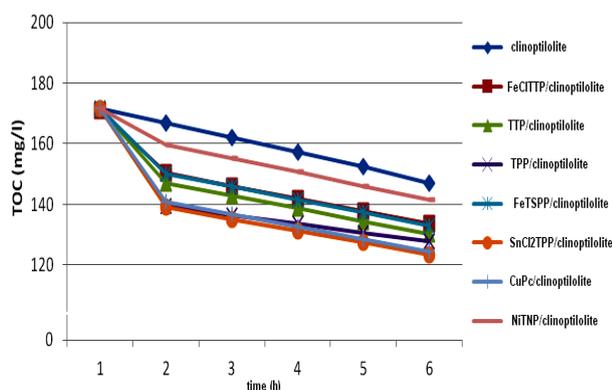


Fig. 19. The catalytic activity of the porphyrin-zeolitic materials, CUPC/clinoptilolite and clinoptilolite in the photocatalytic oxidation of 4-nitro phenol.

As it can be seen from the diagram, all the porphyrin – zeolitic materials and CuPc/clinoptilolite improved the photocatalytic activity of clinoptilolite. From all the materials used in these experiments, the best photocatalytic activity was that of SnCl<sub>2</sub>TPP/clinoptilolite.

#### 4. Conclusions

The porphyrinic/phthalocyaninic materials were successfully synthesized. These materials were as follows: TPP/clinoptilolite, SnCl<sub>2</sub>-TPP / clinoptilolite, Fe-TSPP/clinoptilolite, FeCl-TTP/clinoptilolite, TTP/clinoptilolite, CuPc/clinoptilolite, Ni-TNP/clinoptilolite.

The absorption/deposition process in/on the clinoptilolite went at a relatively high rate.

Using the UV – VIS technique it was possible to calculate the absorption degree of the porphyrinic/phthalocyaninic materials onto clinoptilolite. The best result was recorded in the case of SnCl<sub>2</sub>-TPP/clinoptilolite.

The catalytic photooxidation of 4-nitrophenol in the presence of clinoptilolite and the synthesized porphyrin/phthalocyanin – zeolitic materials gave good results. The best result was obtained in the case of SnCl<sub>2</sub>-TPP/clinoptilolite. All the porphyrinic/phthalocyaninic materials improved the photocatalytic activity of the zeolitic matrix.

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