

Photodegradation of organic compounds using TiO₂-based impregnated photocatalysts

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The photodegradation of organic compounds in water solutions using environment-friendly materials, methods and processes is a topic of growing interest. A great interest regarding this subject has been devoted to TiO₂-based photocatalysts for the oxidative photodegradation of various organic pollutants. In this context, some photocatalytic polycrystalline TiO₂ systems impregnated with metalloporphyrins were prepared. The metalloporphyrins used for impregnation were prepared in agreement with the scientific literature. After impregnation, the TiO₂-based photocatalysts were investigated for their photoactivity in the oxidation reaction of organic compounds. A comparison of the photoreactivity of the newly obtained catalytic materials was made.

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1. Introduction

Photocatalysis using catalysts that are impregnated on various supports had a widespread use in the last period of time [1]. The increasing demand for catalysts in oxidation reactions under mild conditions has provided the necessary impulse for research into new efficient systems based on metalloporphyrin catalysts that mimic natural enzymatic systems [2]. For example, for the degradation of aromatic compounds from water [3,4], a greater attention is given to the study of TiO₂ – based photocatalysts. One of the important goals for studying these types of catalysts is the obtaining of photocatalysts with enhanced activity compared to TiO₂. A growing interest is given to studying new hybrid materials that can be obtained by impregnating TiO₂ with various dyes. Dye-impregnated TiO₂ can also have other applications, like in photography or solar energy conversion [5-12]. In this study, the impregnation of some metalloporphyrins, which are heteroatomic macrocyclic compounds, on TiO₂, and the photocatalytic action in the oxidation of 4-nitrophenol of the newly formed hybrid materials were studied. The metalloporphyrins that were used are complexes of 5,10,15,20 tetraphenyl porphyrin (TPP) with Fe(III), Cu(II) and Sn(IV) (Fig. 1).

The efficiency of the new materials depends most of the times on the properties of the sensitizing dye, in this case, the metalloporphyrins. These can be changed in many ways [13].

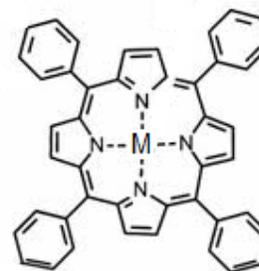


Fig. 1. General structure of the metalotetraphenylporphyrins that were used ($M = \text{Cu}, \text{FeCl}, \text{SnCl}_2$).

Because of their important role during the photosynthesis process, metalloporphyrins are better photosensitizers for extending the light absorption of TiO₂ into the visible region than many other dyes because of their high quantum yield for intersystem crossing, long triplet state lifetime and good chemical stability [1, 6-9].

2. Experimental part

For the preparation of the hybrid materials, the following reagents and materials were used:

- Copper tetraphenylporphyrin (TPP – Cu), iron(II) tetraphenylporphyrin (TPP – FeCl), tin tetraphenylporphyrin (TPP – SnCl₂), which were previously synthesized in our laboratory after methods mentioned in the scientific literature.
- Toluene.
- Titanium dioxide.
- p – nitrophenol.

For analyzing the newly obtained hybrid materials, the following equipment was used:

- Fourier transformed IR spectroscopy (FT-IR) standard spectra were collected using a Perkin Elmer Spectrum GX spectrometer. Scans in the range of 400–4000 were accumulated for each spectrum at a spectral resolution of 4 cm^{-1} . It was possible to use the drift accessory with the powdered pure substance, thereby allowing for a better and easier analysis.
- SPECORD M 400 Carl Zeiss Jena UV-VIS spectrophotometer with microprocessor and double beam.
- The thermogravimetric (TG) curves of the samples were performed on a thermogravimetric analyzer Mettler Toledo system TGA/SDTA 851° under a nitrogen atmosphere (99.999%), from 25 to 1300°C , in Al_2O_3 crucibles ($70\ \mu\text{L}$). The heating rate was $10^{\circ}\text{C}/\text{min}$ and the flow rate of nitrogen was 80 ml/min. The TG equipment was calibrated by indium and aluminum pills.
- Multi N/C 2100 Analytik Jena analyzer

2.1. Deposition of the metalloporphyrins on titanium dioxide

The same method was used for all the metalloporphyrins that were used in this research. First, the appropriate amount of metalloporphyrins (TPP – Cu, TPP – FeCl, TPP – SnCl_2), so that the concentration is 10^{-3}M , were dissolved in 10 ml of toluene. After they were dissolved, 2 g of titanium dioxide were added. The mixture was then magnetically stirred for 3 – 4 hours. After this time elapsed, the mixtures were vacuum filtered. The newly obtained materials had a pale coloration, depending on each metalloporphyrin that was used. After filtration, the products were left to dry in the air.

2.2. Photodegradation of p-nitrophenol

For the photooxidation reaction, a $2 \times 10^{-3}\text{M}$ solution of p-nitrophenol was prepared. For 250 ml of this solution, 0.2 g of each newly obtained material mentioned above. The solution was added, along with the photocatalyst, into a laboratory scale photooxidation reactor. Air was then bubbled into the reaction medium with a 3 l/h debit, with an air flow meter (ITM Romania). The oxidation reaction took place, in each of the three cases, under the action of light, by using a medium-pressure 375 W Hg-lamp. In each case, the reaction time was around 3.5 hours.

For the analysis of the newly obtained photocatalysts, some analytical methods were used, like UV-VIS spectroscopy, FT-IR spectroscopy and thermogravimetric analysis (TGA).

For the preparation of the samples for the FT-IR analysis, approximately 1,5 mg of the $<63\ \mu\text{m}$ fraction was carefully mixed with 100 mg of powdered anhydrous KBr in an agate mortar. A pressure of 10 tons was applied to this mixture for 5 minutes in order to obtain transparent pellets. KBr pellets of the powdered binder fraction of the

samples were examined in the $4000\text{--}400\text{cm}^{-1}$ region at a resolution of 4cm^{-1} .

For the TOC analysis, the basic principle of thermal oxidation method is the oxidation of the organic constituents of water using oxygen at temperature 950°C . The catalysts used for complete oxidation is $\text{Pt}/\text{Al}_2\text{O}_3$. The carbon dioxide produced from thermal oxidation is transported into the CO_2 measurement system with a carrier gas stream.

3. Results

Fig. 2 depicts the UV – VIS spectrum recorded for TPP – FeCl deposited on titanium dioxide.

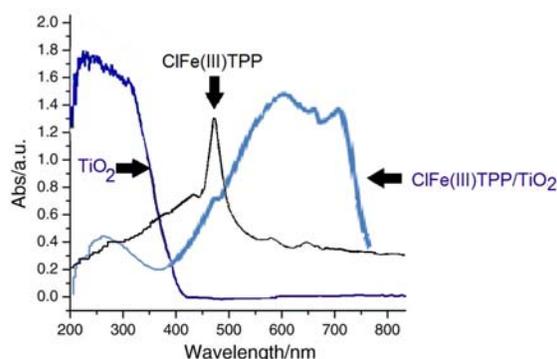


Fig. 2. UV - VIS spectra of TPP – FeCl.

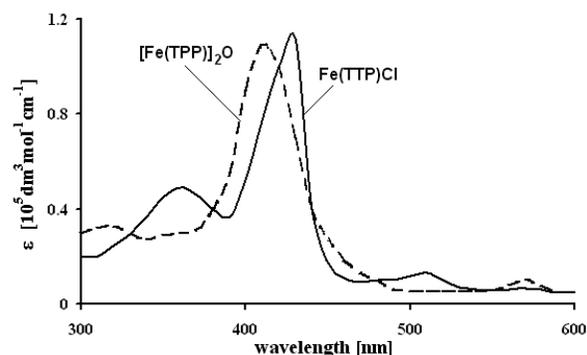


Fig. 3. The absorption spectrum of TPP-FeCl and its oxo-dimer.

In Fig. 4, the representation of the thermogravimetric curve of TPP – Cu supported on titanium dioxide is presented.

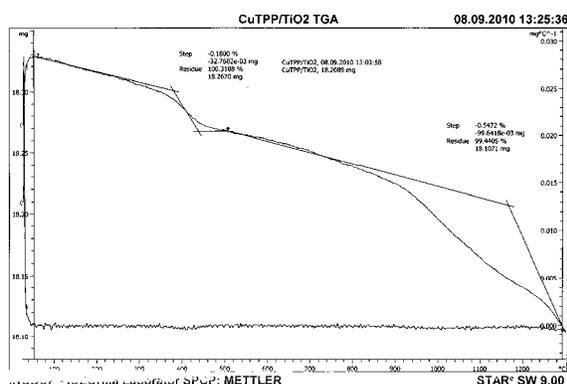


Fig. 4. Thermogravimetric curve of TPP - Cu deposited on titanium dioxide.

In Fig. 5, a FT - IR spectrum of TPP - FeCl deposited on titanium dioxide is represented.

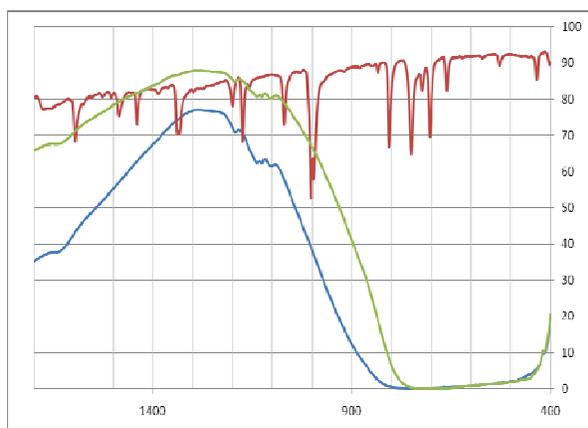


Fig. 5. FT - IR spectrum of TPP - FeCl deposited on titanium dioxide. (red is for TPP - FeCl, green is for TiO₂ and blue is for TPP-FeCl/TiO₂).

After the photooxidation reaction, to see if the degradation of p-nitrophenol took place in some degree, a TOC (total organic carbon) analysis was performed.

4. Discussion

From the UV - VIS spectral analysis some conclusions can be drawn. By deposition on titanium dioxide, the metalloporphyrins show a bathochromic shift of the absorption bands in the visible domain. This observation is based on the molecular interactions between the two semiconductors (porphyrins are well known as p - type semiconductors and titanium dioxide is an n - type semiconductor). Supplementary, broad bands appear in the near-IR region, which are not resolved very good and

which could be assigned to a new aggregated form as m-oxo-dimer of porphyrin [14, 15].

In our opinion, the newly appeared bands in the close IR domain (approx. 750 nm) can be associated with the formation of porphyrinic μ -oxo-dimers (fig. 6).

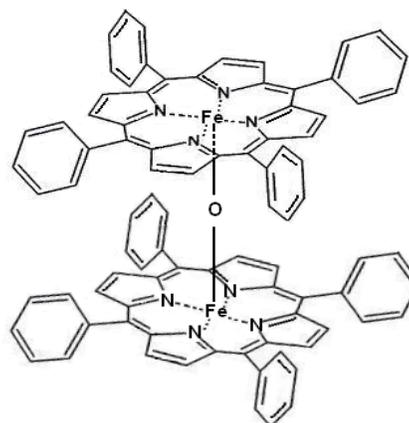


Fig. 6. Example of a μ -oxo-dimer of TPP - FeCl.

After analyzing the thermogravimetric analysis (TGA), it can be concluded that the metalloporphyrins deposited on titanium dioxide preserved their thermal characteristics. The decomposition (melting) temperature remains around the value of 450°C, in agreement with the already existent literature data (see fig. 3 above).

In order to identify the specific FTIR bands for porphyrins after deposition on TiO₂, a special program of second derivative and spectra difference has been used, all these belonging to the apparatus software. Because in the spectrum are too many similar FT - IR bands, we chose the vibrations of the benzene rings belonging to the porphyrin ring. Except the TiO₂ bands, there are few specific bands for porphyrin which could be identified after deposition on TiO₂. The second derivatives for TiO₂ and for TPP - FeCl/ TiO₂ were recorded. We created a difference spectrum between the first two derivative spectra and tried to identify the specific bands, as a proof for porphyrin deposition on TiO₂ (fig. 7).

Some modes are indicated in the FT - IR spectrum of TPP - FeCl as three bands in the range 1600-1500 cm⁻¹. An intense peak appears at 1596 cm⁻¹ specific for the C=N bond from the porphyrin ring. The (C β -C α) and other vibrations in the pyrrole rings also occur in this region (1576 cm⁻¹), but the corresponding IR absorption is too weak. A small wing at 1555 cm⁻¹ is attributed to the asymmetric skeleton vibrations of the methyn bridges and pyrrole rings of the porphyrin macrocycle.

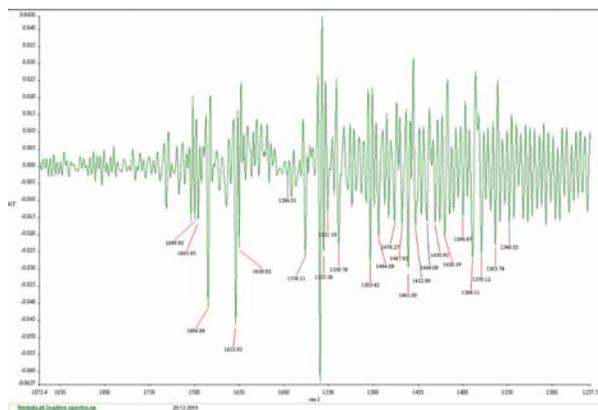


Fig. 7. FT – IR spectrum of TPP - FeCl/TiO₂ after spectral difference.

The left shoulder of this band (1551 cm⁻¹) is assigned to the symmetric C=C stretching. The complicated intense band at 1485 cm⁻¹ also belongs to the benzene rings, but includes overlapping of the C=C stretching and δ(CH) and the late mode belongs to the C α -C β and C β -C β vibrations of the pyrrole rings. Besides the region 1500-1600 cm⁻¹, specific bands appear at 1485 cm⁻¹, attributable to methyn rings, and also 1449 cm⁻¹, assigned to the C=C bond [14].

All these band frequencies in the range 1600–1500 cm⁻¹ are insensitive to the introduction of the iron ion, but their intensities are higher in TPP – FeCl. The behavior of the weak complicated band (1577 cm⁻¹) upon introduction of the Fe³⁺ ion requires special interest, since it includes both the porphin and benzene ring modes. In the TPP – FeCl molecule, they are split strongly. For TPP – FeCl, specific bands appear in the region 550-400 cm⁻¹, as a proof for the iron ion from the ring macrocycle.

After the photocatalytic reaction, the results show that best results of the TOC (total organic carbon) analysis were obtained for TPP – FeCl and TPP – Cu deposited on TiO₂ (Fig. 8).

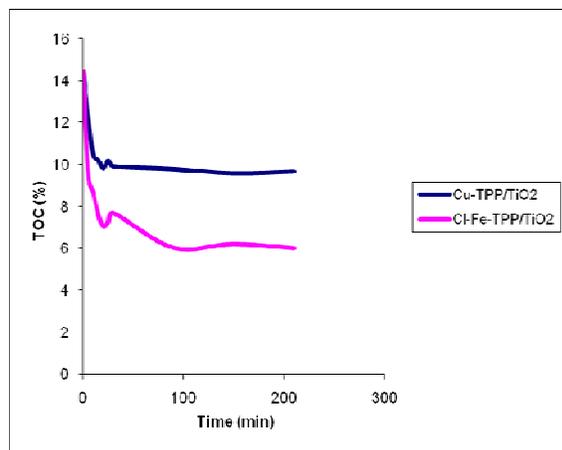


Fig. 8. TOC analysis after the photodegradation of *p* - nitrophenol.

5. Conclusions

The syntheses of the proposed photocatalysts were successful. From the series of the studied photocatalysts, the case of TPP – FeCl was the most relevant. These catalysts were preliminary tested in the photocatalytic degradation of *p*-nitrophenol, TPP - FeCl/TiO₂ having the best photocatalytic activity.

Aknowldegments

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