



Unusual catalytic activity after simultaneous immobilization of two metalloporphyrins on hydrozincite/nanocrystalline anatase



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ABSTRACT

The preparation of hydrozincite in the presence of titanium, followed by the immobilization of two different metalloporphyrins, a positively charged iron porphyrin and a negatively charged manganese porphyrin, is reported. Both metalloporphyrins were immobilized separately and then simultaneously in the same solid support. The resulting solids were used as catalysts for a cyclohexane oxidation reaction in the dark and assisted by light. An unusual increase in the alcohol yield was observed when both complexes were immobilized simultaneously and the catalytic experiments were conducted in the presence of light, suggesting a synergistic effect of the complexes/support/light.

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1. Introduction

In the last three decades, synthetic metalloporphyrins (MP) have been extensively studied as catalysts for homogeneous processes involving a wide variety of alkenes, alkanes [1–5] and other organic molecules [1–8]. These reactions, performed in the presence of different oxidants such as iodosylbenzene or hydrogen peroxide, have revealed promising future applications of MP as catalysts in different technological fields [9]. In these studies, MPs frequently present efficiency and selectivity in the oxidation of organic substrates. To improve their catalytic efficiency, they are often immobilized on different supports with the objective of achieving catalyst recovery and recyclability [10–14]. With this goal, the immobilization MP on different inorganic supports (heterogenization process), such as porous silicas, layered compounds, or even organic supports such as sugars and polymers, have been reported by different research groups worldwide [10,15–17].

Nakagaki et al. [18] reported investigation of the catalytic activity of a manganese porphyrin immobilized on several layered double hydroxides (LDH) in relation to cyclooctene oxidation. Different

catalytic performances were observed under the same reaction conditions, depending on the chemical composition of the LDH used as solid support. The authors concluded that this may be related to the way the manganese porphyrin is attached to the support and the synergic effect of the support/porphyrin.

The use of layered hydroxide salt (LHS) as support for the immobilization of MP aiming to produce heterogeneous phase catalysts for oxidation reactions was first reported by our research group [19]. An anionic iron porphyrin ([Fe(TDCSPP)]) was immobilized on zinc hydroxide nitrate (ZHN) and investigated as catalyst for oxidation reaction of several substrate molecules. This solid catalyst showed excellent yields for cyclohexane oxidation (70% cyclohexanone and 2% cyclohexanol) after one hour of reaction. This result diverges from those predicted by the classic mechanism of oxidation catalyzed by MP in solution (homogeneous catalysis), where often high selectivity for the cyclohexanol product is observed [9,11,20,21], indicating there is some kind of influence of the support properties on the catalytic behavior of MP.

Machado et al. [11] reported the synergistic effect of two MP (one positively charged and the other negatively charged) simultaneously immobilized on nanoscrolls of halloysite clay on the catalytic activity of the synthesized catalyst. Halloysite nanoscrolls occur in mines, as the result of the delamination of kaolinite crystals and wrapping of multiple packed layers [20]. The edges of

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these structures contain positive and negative residual charges, while their surface exhibits negative residual charges. Due to this characteristic, it was possible to immobilize porphyrins with different charges in their structure.

Beside their uses as support for catalytic species immobilized on the surface, synthetic layered materials have proven to be interesting materials for the intercalation of different catalytic species in the interlayer spaces, allowing the modulation of some properties of these materials [22–24]. Layered compounds can also be used after exfoliation [20,25–27] as well as intercalation, cationic exchange [19,28–30] and surface functionalization reactions [12,24,31–33]. Among the compounds whose layers are positively charged, LHS and LDH are the classes that have been most widely studied in the past decade [23–25,34], especially the use of these layered compounds as inorganic supports for species with well-known catalytic activity, such as metalloporphyrins [19,28].

Photosensitive processes, such as photosynthesis, are examples of the effect of light in initiating and regulating molecular and biochemical processes [35]. Titanium dioxide (anatase polymorph) is one of the most suitable semiconductors for practical applications, but the highly oxidizing conditions generated on the oxide surface impose some limitations on its use for oxidation processes, since the desired products can suffer oxidation, and in extreme cases even undergo total degradation [36]. Taking advantage of those possible synergistic effects, Amadelli et al. developed a catalyst that combines properties of TiO_2 with the catalytic activity of MP [37,38]. After 6 hours of reaction, a total yield of 26% of products formation (cyclohexanol + cyclohexanone) was observed for the TiO_2 , when the TiO_2 solid containing MP immobilized was used, the total yield almost doubled (44%) under the same reaction conditions.

Despite this, the nanoparticles of TiO_2 generate a narrow range of absorption in the UV spectrum. Thus, Lee et al. [39] proposed the synthesis of LDH with adsorbed Ti for photocatalysis under visible light radiation. In this way, the formation of the solids (LDH Ni/Ti and LDH Cu/Ti) showed absorption bands in the visible region and the photocatalytic activities of water oxidation were increased compared to the pure TiO_2 .

The insertion of Ti^{4+} into the LDH structure has been previously discussed by other authors [40–43]. This insertion appears to be effective based on the information obtained by X-ray diffraction. However, Leroux et al. do not agree with this hypothesis, and based on X-ray absorption spectroscopy results concluded that titanium was not inserted in the layered structure, but somehow was segregated homogeneously as an amorphous phase on the LHS surface [44].

The combination of properties of materials such as MP, MP immobilized on layered solids and titanium-based supports generates great interest. Thus, the present work describes the preparation of new solids based on layered solids containing titanium and their use to support the immobilization of one or more MP (Fig. 1) in order to investigate the possible application of the resulting solids in catalysis and catalytic oxidation reactions assisted by light.

2. Materials and methods

2.1. Instrumental

For the X-ray diffraction (XRD) analysis, the solids were placed on glass sample holders and the measurements were performed in reflection mode using a Shimadzu XRD-6000 diffractometer operating at 40 kV and 40 mA (Cu $K\alpha$ radiation $\lambda = 1.5418 \text{ \AA}$) in a Bragg-Brentano (θ – 2θ) geometry with a scan rate of $2^\circ \cdot \text{min}^{-1}$ using values of 2θ from 3 to 70° .

The electronic spectra (UV–Vis) of the solutions were obtained with an HP 8452A Diode Array UV–Vis spectrophotometer, in the 200–800 nm range. The UV–Vis spectra of the solid samples were obtained using a Varian Cary 100 BIO by placing the samples in a Teflon sample holder and measuring the absorbance in the 200–800 nm range.

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Thermo Scientific ESCALAB 250Xi spectrometer with a base pressure $<1 \cdot 10^{-9}$ mbar. A monochromatic Al $K\alpha$ ($h\nu = 1486.6 \text{ eV}$) excitation energy source was employed, and the overall energy resolution of the collected spectra was approximately 0.6 eV. A flood gun emitting low-energy electrons and Ar^+ ions was used to prevent surface charging. The electron energy analyzer was operated at constant pass energy of 25 eV and 40 eV for high resolution core level and survey spectra, respectively. The Thermo Scientific Advantage XPS software package (version 5.95) was used to acquire and process the XPS spectra. A linear combination of Gaussian and Lorentzian line shapes was selected for the spectral fitting, while the Shirley function was used for background correction. For all spectra, the binding energy calibration was performed using the Au ($4f_{5/2}$) line at 84.0 eV.

The thermogravimetric analysis (TGA) and the derivative curves were obtained using a STA 449 F3 Jupiter (Netzsch) and a heating rate of $10^\circ \text{C} \cdot \text{min}^{-1}$ within the range of 20–1000 $^\circ \text{C}$ and under a flow of synthetic air atmosphere ($50 \text{ mL} \cdot \text{min}^{-1}$).

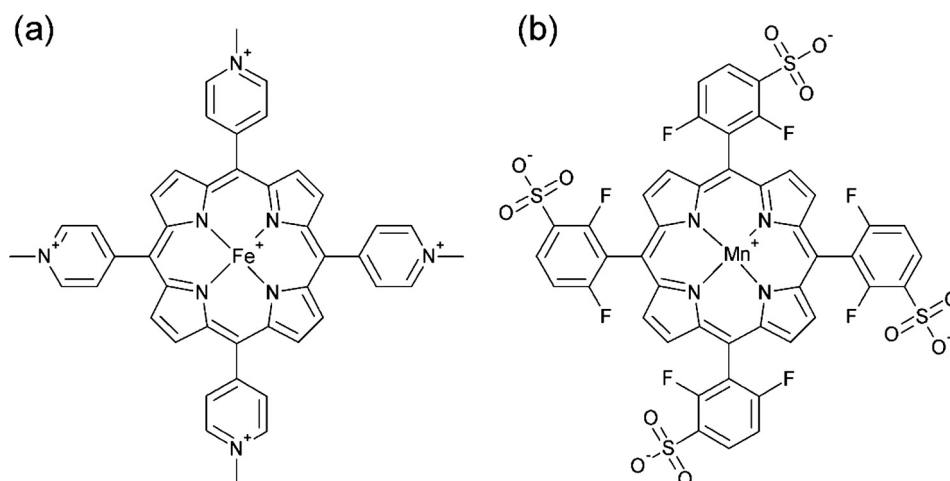


Fig. 1. Structures of the MPs used in this work. (a) cationic MP, iron(III)tetrakis-4-methylpyridilporphyrin ([Fe(T4MPyP)] – **FeP**) and (b) anionic manganese(III)tetrakis-2,6-difluor-3-sulfonatophenylporphyrinate ([Mn(TDFSP)] – **MnP**).

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