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Several functional hybrid materials have been reported as immobilized porphyrin derivatives in various organic and inorganic host materials (polymers, mineral clays, silica, etc.), with potential applications in various fields, such as photochemistry, electrochemistry and heterogeneous catalysis. Layered double hydroxides (LDHs), commonly known as hydrotalcite-like materials, have also been analyzed for use as supports for metalocomplexes. Recently, nanocomposite materials with core-shell structure produced by combining two kinds of nanometer-size materials have received considerable attention, since the use of these materials is a promising strategy to prevent aggregation and self-oxidation of molecules, reducing the catalytic activity. In this study, monodispersed hierarchical layered double hydroxide on silica spheres (LDH@SiO2) with core-shell structures were developed for metalloporphyrin immobilization and the materials were used as oxidant catalysts of different substrates.

# Introduction

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Porphyrins are macrocyclic compounds with a large extended conjugated  $\pi$ -system. They play an important role in many biological systems.<sup>1</sup> These compounds and their metalated complexes exhibit unique properties,<sup>2</sup> which makes them very interesting molecules for application in various fields.<sup>3</sup> Metalloporphyrins (MPs) are present in many important enzymes for oxidation reactions, such as cytochromes P450, peroxidases and catalases.<sup>4-6</sup> Synthetic metalloporphyrins, especially those containing Fe(III) and Mn(III) ions, have been extensively used as catalysts in oxidation reactions of a range of organic compounds using different oxidants.7-10 The combination of metalloporphyrins and host materials with appropriate structure can produce excellent functional solids for different uses. The preparation has been reported of several functional hybrid materials by the immobilization of MP in various organic and inorganic host materials (polymers, clays, silica), with potential applications in different fields, such as photochemistry, electrochemistry and heterogeneous catalysis.11,12

Layered double hydroxides (LDHs), commonly known as hydrotalcite-like materials, are a family of layered nanomaterials having anionic exchange capacity (Fig. 1 left side). Recently, nanocomposite materials with core-shell structure produced by combining two kinds of nanomaterials have received great attention for use as supports to prevent the aggregation and self-oxidation of molecules, reducing the catalytic activity.13

In this work, monodispersed hierarchical layered double hydroxide on silica spheres (LDH@SiO<sub>2</sub>) with core-shell structures.<sup>14</sup> were synthesized for use as supports for MP immobilization. The influence of the support morphology (sphere or platelet) on the catalytic performance of the solid in oxidation reactions of different substrates is reported.

# Experimental

## Characterization and apparatuses

For the X-ray diffraction measurements, the powdered samples were deposited on glass sample holders. The measurements were obtained in the reflection mode using a Shimadzu XRD- 6000 diffractometer operating at 40 kV and 30 mA, using CuK $\alpha$  radiation ( $\lambda$ = 1.5418 Å) and a dwell time of 2°.min<sup>-1</sup>, and the data were collected between 2 and 70° (in 20).

FTIR spectra were recorded with a Biorad 3500 GX spectrophotometer in the 400-4000 cm<sup>-1</sup> range, using KBr pellets. KBr was crushed with a small amount of the solid samples, and the spectra were collected with a resolution of 4 cm<sup>-1</sup> and accumulation of 32 scans.

UV-Vis spectra were recorded in the 200-800 nm range with a Varian Cary 100 spectrophotometer, using cells with path lengths of 1.0 cm or 0.5 cm. Qualitative spectra of the solid samples were also recorded by diffuse reflectance.

Scanning electron microscopic images (SEM) and Energy dispersive spectra (EDS) were obtained with a Tescan VEGA3 LMU device, using tension of 10 KV. The samples were deposited on aluminum stubs and the EDS spectra were collected with an SDD detected with 80 mm<sup>2</sup> and in the range of 0 to 10 KeV. In sequence, the samples were gold sputtered and the SEM images were then obtained.



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Transmission electron microscopic (TEM) images were obtained with a JEOL-JEM 1200 microscope operating at 120 kV. The samples were prepared by dispersion in ethanol at room temperature and a diluted dispersion drop was deposited on a carbon film supported by a 3 mm copper grid.

Nitrogen adsorption-desorption isotherms were obtained in a Quantachrome gas sorption analyzer, model NOVA 2000e. The samples were degassed at 110 °C under vacuum for 2 h and the analyses were carried out in liquid nitrogen (–196 °C) and adsorption/desorption isotherms for N<sub>2</sub> were obtained over the relative pressure range of 0.05-0.99. The samples' specific surface areas were calculated using the multi-point Brunauer-Emmet-Teller (BET) method by the adsorption isotherm in the range of relative pressures from 0.05-0.30. Pore diameter and the pore volume were calculated using the desorption isotherm or Barrett–Joyner–Halenda method (BJH), also from the desorption isotherm.

Electron paramagnetic resonance (EPR) measurements of the powdered materials were accomplished with a Bruker EMX microX EPR spectrometer (frequency X, band 9.5 GHz) at room temperature and -196 °C (using liquid  $N_2$ ), and perpendicular microwave polarization X-band.

All the products from the oxidation reactions were quantified with an Agilent 6850 gas chromatograph (flame ionization detector) equipped with a 30 m long DB-WAX capillary column with 0.25 mm internal diameter (J&W Scientific).

#### Materials

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All chemicals used in this study were purchased from Sigma-Aldrich, Merck or Fluka and were of analytical grade. Iodosylbenzene (PhIO) was synthesized according to the literature.<sup>15</sup> The solid was carefully dried under reduced pressure and kept at 5 °C and the purity was assessed by iodometric titration.<sup>16</sup>

The anionic free-base porphyrin Na<sub>4</sub>[H<sub>2</sub>(TDFSPP)] and the corresponding manganese(III) porphyrin (MnP) complex ([Mn(TDFSPP)Na<sub>4</sub>]<sup>+</sup> = [tetrasodium-5,10,15,20-tetrakis (2,6-difluoro-3-sulfonatophenyl) porphyrinate manganese(III)]) (Fig. 1 right) were synthesized, purified, and characterized following a previously described method.<sup>17,18</sup>



Fig. 1 Schematic representation of the LDH structure (left) and the structure of the manganese(III) porphyrin (MnP) complex, [Mn(TDFSPP)Na<sub>4</sub>]<sup>+</sup> (right).

## Synthesis and characterization Preparation of the SiO<sub>2</sub> spheres

In a 50 mL Erlenmeyer flask, 50 mL of ethanol, 30 mL of water and 10 mL of aqueous ammonia solution were added and submitted to magnetic stirring. To the mixture, 9.2 mL of tetraethyl orthosilicate (TEOS) was added, resulting in the formation of a white solid dispersion (silica spheres). The reaction medium was stirred for 17 hours and the resulting solid was separated by centrifugation and washing with ethanol/water (1:1 v/v) solution and dried an analysis of the second sec

#### Preparation of LDH@SiO<sub>2</sub>

The silica spheres (100 mg) and 20 mL of distilled water were added to a beaker and the mixture was submitted to an ultrasound bath until formation of a homogeneous dispersion (around five minutes) and 0.80 mL of aqueous ammonia solution (28%) was then added. A solution containing  $Mg(NO_3)_2$  (0.96 mmol) and  $Al(NO_3)_3$  (0.48 mmol) was dripped onto this dispersion (20 mL) (Mg:Al molar ratio of 2:1)<sup>14</sup>. After that, the dispersion was kept in the ultrasound bath for 1 hour and thereafter the resulting solid was centrifuged and washed with distilled water and oven dried at 60 °C. Considering the step of precipitation and various washing/dispersion steps, only around 105mg of the solid was recovered as dried matter. No leaching of the LDH layers was observed after exhaustive washing of the LDH@SiO<sub>2</sub> solid with distilled water.

## Preparation of MnP/LDH@SiO<sub>2</sub>

A methanol solution of MnP (10 mL; 4.92x10<sup>-5</sup> mol·L<sup>-1</sup>) was added to a methanol dispersion of the support LDH@SiO<sub>2</sub> (50 mg/10 mL) under magnetic stirring at room temperature. After 3 hours under stirring, the supernatant was removed by centrifugation and collected in a volumetric flask. The solid was washed five times with methanol and all liquids resulting from the washing process were collected in the respective volumetric flasks mentioned above. The final volume was completed with methanol and the solution was quantitatively analyzed by UV-Vis spectroscopy in order to determine of the MnP amount that leached out from the support after the reaction and the washing process. The loading value was determined indirectly by the difference between the initial metalloporphyrin content and the leached metalloporphyrin. The resulting pale yellow MnP/LDH@SiO<sub>2</sub> solid was dried for 24 h at 60 °C.

The purity of the MnP/LDH@SiO<sub>2</sub> solid is intrinsically dependent on the purity of the metalloporphyrin and LDH@SiO<sub>2</sub> support which had their purity proven by various analytical techniques before carrying out this reaction. Thus, the final material obtained, MnP/LDH@SiO<sub>2</sub>, was considered absent of impurities.

#### **Catalytic oxidation reactions**

The synthesized MnP/LDH@SiO<sub>2</sub> was investigated as catalyst for oxidation of different substrates (*cis*-cyclooctene and cyclohexane) using iodosylbenzene (PhIO) as oxidant. The following general procedure was used: in a 2.0 mL vial the catalyst and PhIO (MnP/oxidant molar ratio 1:50) were degassed with argon for about 10 minutes to eliminate molecular oxygen. After that, the mixture of degassed solvents (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub>-1:1 v/v) was added to a reaction flask followed by the substrate (MnP/substrate molar ratio of 1:5000). The reaction was kept under magnetic stirring and argon atmosphere at 25 °C for 1 h in a dark chamber. After an appropriate reaction time, a saturated acetonitrile solution of Published on 23 November 2017. Downloaded by Gazi Universitesi on 28/11/2017 08:46:15.

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sodium sulfite was added to the reaction mixture, to eliminate excess PhIO and to quench the reactions. Then methanol was added to the reaction vial to solubilize the remaining insoluble PhIO. Next, the solid catalyst was separated from the reaction solution by centrifuging and the reaction supernatant was then quantitatively transferred to a volumetric flask. The catalyst was washed many times with small amounts of the solvent mixture (CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> 1:1, v/v), to extract any remaining reaction product. All extracts were combined in the same volumetric flask, which was analyzed in duplicate or triplicate by gas chromatography to quantify the reaction products, using bromobenzene as the internal standard. The reaction yields were calculated based on starting PhIO and all catalytic reactions were also performed in duplicate or triplicate.

All substrates were checked prior to use by gas chromatography, to ensure they were free of oxidation products. Control reactions were carried out with a  $CH_3CN/CH_2Cl_2$  mixture (1:1 v/v) using the same procedure as that of the catalytic runs, but in the presence of (a) substrate + PhIO and (b) substrate + PhIO + LDH@SiO<sub>2</sub> (with no MnP).

The solid catalysts recovered at the end of the oxidation reaction were exhaustively washed, dried, and reused in further reactions, adopting the same procedure described before, using cyclohexane as substrate.

The corresponding non-immobilized MnP was also tested as catalyst (in homogeneous medium) in an experimental procedure similar to that used for the heterogeneous medium. The amount of MnP used was about  $2.0 \times 10^{-4}$  to  $3.3 \times 10^{-4}$  mmol in order to keep a MnP/PhIO/substrate molar ratio of 1:50:5000. The washing solvents and the reaction media were monitored by UV-Vis, to verify whether any MnP was leached from the MnP/LDH@SiO<sub>2</sub> material during either the reactions or the catalyst washing procedures.

# **Results and discussion**

# Characterization of the silica, LDH@SiO\_2 and MnP/LDH@SiO\_2 solids

All the prepared materials were characterized by XRD, UV-Vis, FTIR, TEM, SEM, EDS and nitrogen adsorption. Figure 2 shows the powder X-ray diffraction pattern of the silica spheres and the solid obtained by the preparation of LDH covering the silica spheres (LDH@SiO<sub>2</sub>) in a core shell process.



Fig. 2 X Ray diffraction patterns of the  $SiO_2$  spheres (a) and LDH@SiO<sub>2</sub> (b).

 $SiO_2$  X ray diffraction pattern present, as expected, a broad halo between 15 and 35° (in 20) confirming the amorphous

structure. In LDH@SiO<sub>2</sub>, broad diffraction peaks were observed at around 35, 45 and 62 ° (in 20, indicated 0.03%, 7.00% at 56f (012), (015) and (110) LDH reflections, with low stacking order.<sup>19,20</sup> The absence of an evident basal peak in the region of 10° (in 20) indicated very small number of packed layers.

The FTIR spectra of LDH@SiO<sub>2</sub> and MnP/LDH@SiO2 (data not shown) displayed the typical silica bands at 960 cm<sup>-1</sup> and 1100 cm<sup>-1</sup>, assigned respectively to the Si-OH and Si-O bond stretching and H-O-H angular deformation at 1620 cm<sup>-1</sup>. LDH could not be detected due to the small concentration and superposition of bands at 470 cm<sup>-1</sup>, attributed to M-O bonding (M= Mg, Al, Si).<sup>21,22</sup>

To confirm the presence of the MnP in LDH@SiO<sub>2</sub>, UV-Vis spectra of the solid samples in the solid state were recorded by diffuse reflectance (Fig. 3). Due to the white and pale yellow color respectively, SiO<sub>2</sub> and LDH@SiO<sub>2</sub> showed no spectral signals in the analyzed region (Fig. 3a,b), while the solid MnP/LDH@SiO<sub>2</sub> presented a band at 564 nm, indicating the presence of immobilized MnP (Fig. 3c). The Soret band position observed at 467 nm for MnP/LDH@SiO<sub>2</sub> (Fig. 3d) is slightly red shifted in comparison to the Soret band recorded for the non-immobilized MnP in aqueous solution (459 nm) (Fig. 3e).

This fact can be attributed to steric constraints of the inorganic support over the metalloporphyrin structure, causing macrocycle ring distortions.<sup>12,17,23-25</sup>



Fig. 3 UV-Vis spectra of SiO<sub>2</sub> spheres (a), LDH@SiO<sub>2</sub> (b), MnP/LDH@SiO<sub>2</sub> (c), manganese(III)porphyrin (d) (pellet of MnP diluted in MgSO<sub>4</sub>) and aqueous solution of MnP (e).

The MnP loading on the support, obtained by UV-Vis of all washing solutions, was of 2.43x10<sup>-5</sup> mol of MnP per mass (g) of the support, corresponding to immobilization yield of 72.4%. Anionic MnP is expected to immobilize on LDH@SiO<sub>2</sub> surface thorough strong electrostatic bonding between the positive charges of the LDH layers and the sulfonate negative charges of the MnP structure. No leaching of MnP from the solid, even after exhaustive washing processes, was observed, which indicates a strong electrostatic MnP/LDH@SiO<sub>2</sub> interaction conferring high stability to the solid.

The TEM images of the  $SiO_2$  (Fig. 4) showed spheres with a uniform radius around 240 nm and some sphere coalescence, while the LDH@SiO<sub>2</sub> solid maintained the spherical morphology with some plate-like crystals coating the surface, typical of LDH crystals (Fig. 4 bottom).

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<u>0.5 µm</u>

Fig. 4 Transmission electron microscopic (TEM) images of the  $SiO_2$  spheres (top) and LDH@SiO\_2 spheres (bottom).

The SEM images of LDH@SiO<sub>2</sub> and MnP/LDH@SiO<sub>2</sub> obtained after evaporation of the dispersions indicated raspberry-like particles with an average diameter of 5  $\mu$ m (Fig. 5), which are close to 20 times bigger than the isolated silica spheres and were clearly obtained by the silica spheres aggregations.

Plate-like particles were clearly deposited on the surface of both samples, indicating the presence of LDH, which persisted after the immobilization of the MnP. These images were consistent with the TEM images (Fig. 4).

The semi-quantitative EDS results (Fig. 6) indicate that in LDH@SiO<sub>2</sub> only the expected elements are present (O, Mg, Al, Si and Cl), while in MnP/LDH@SiO<sub>2</sub>, sulfur was also detected, due to the presence of sulfonate groups in the MnP (Fig. 6 right).



Fig. 5 SEM images of LDH@SiO\_ (top) and MnP/LDH@SiO\_ (bottom). Magnifications: left: 25k, middle: 50 k.

The amount of LDH could be estimated from the EDS Si/Mg Wt% ratios in both samples (LDH@SiO2 = 24.9/3.2= 7.78 and MnP/LDH@SiO2 = 19.8/2.5 = 7.92), which lead to percentages of

around 19% in wt% (considering the anhydrous Zn/A) 2 is  $D_{\rm e}$  and reproducibly the both samples of this amount will not interfere in the catalysis performance, which is defined by the amount of porphyrin in the catalyst.

Figure 7 shows the schematic representation of the proposed process of immobilization of the MnP in LDH@SiO<sub>2</sub>.



Fig. 6 EDS spectra of LDH@SiO<sub>2</sub> (left) and MnP/LDH@SiO<sub>2</sub> (right).



Fig. 7 Schematic representation of the MnP catalyst immobilization on the surface of LDH@SiO2 and catalyst obtaining.

The specific surface areas ( $S_{BET}$ ) found for the silica spheres were 310.2 m<sup>2</sup>g<sup>-1</sup>, while for the neat LDH the value was of 9.0 m<sup>2</sup> g<sup>-1</sup>. When the LDH was prepared in the presence of SiO<sub>2</sub> spheres, the value  $S_{BET}$  was reduced to 39.9 m<sup>2</sup>g<sup>-1</sup>. This reduction of the surface area of the core-shell compound suggests the deposition of the LDH plated-like crystals on the surface of SiO<sub>2</sub> spheres, partially covering the silica solid and blocking the silica spheres and silica interspheres pores. The solid Mn/LDH@SiO<sub>2</sub> was also characterized by EPR, and no signal was detected at -196°C (data not shown), in agreement with the presence of Mn(III) in the porphyrin core.<sup>26</sup>

# Catalytic investigation of Mn/LDH@SiO<sub>2</sub>using (Z)-cyclooctene and cyclohexane as substrates

The efficiency of the MnP/LDH $@SiO_2$  as catalyst in the heterogeneous oxidation reaction process was tested using the substrates (Z)-cyclooctene and cyclohexane, and iodosylbenzene (PhIO) as model oxidant (Table 1).

The (Z)-cyclooctene molecule is a useful diagnostic substrate, since it is easily oxidized in the presence of metalloporphyrins, with (Z)-cycloocteneoxide usually being the sole reaction product.<sup>27-29</sup> The catalytic activity of the MnP using (Z)-cyclooctene as a substrate in homogeneous catalysis resulted in about 89% yields (Table 1). After immobilization on LDH, the yield dropped to 51%, as expected due to the change from homogeneous to heterogeneous process and the immobilization of the catalyst species on a solid support.<sup>30</sup> MnP/LDH showed catalytic results comparable to their

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homogeneous analogues, suggesting that the immobilization did not prevent the access of the reactants to the MnP catalytic center.

 Table 1 Results of the cyclooctene<sup>a</sup> and cyclohexane<sup>b</sup> oxidation using iodosylbenzene as oxidant.

| Solids                 | Product yield (%) <sup>c</sup> |                      |                     |
|------------------------|--------------------------------|----------------------|---------------------|
|                        | Epoxide <sup>a</sup>           | Alcohol <sup>b</sup> | Ketone <sup>b</sup> |
| MnP                    | 89.2 ± 2.37                    | 14.3 ± 0.75          | 2.8 ± 0.13          |
| MnP/LDH <sup>e</sup>   | 51.3 ± 3.20                    | $5.4 \pm 0.01$       | <1                  |
| MnP/LDH@SiO₂           | 99.6 ± 0.40                    | 9.0 ± 0.93           | <1                  |
| First reuse            | *                              | 6.3 ± 0.95           | <1                  |
| LDH <sup>d,e</sup>     | 4.00 ± 3.80                    | <1                   | <1                  |
| LDH@SiO <sub>2</sub> e | 6.7 ± 0.37                     | <1                   | <1                  |
| Control <sup>f</sup>   | $14.0 \pm 1.30$                | <1                   | <1                  |

<sup>a</sup>Epoxide = cyclooctenoxide, <sup>b</sup>alcohol = cyclohexanol and ketone = cyclohexanone. <sup>c</sup>Yields based on the amount of PhIO used in the reaction. <sup>d</sup>Reaction using only LDH (prepared by coprecipitation under the same condition of the prepared solid LDH@SiO<sub>2</sub>) or LDH@SiO<sub>2</sub> as catalyst. <sup>e</sup>Data from reference 12. <sup>f</sup>Reaction with no catalyst using only PhIO+substrate. \* Not investigated.

On the other hand, MnP/LDH@SiO<sub>2</sub> presented nearly 100% epoxide yield. The increase of the yield presented by the solid catalyst MnP/LDH@SiO<sub>2</sub> in comparison to MnP/LDH suggests that the dispersion of the layered compound on the spheres'surfaces leads to a better catalyst support for the MnP immobilization. This is probably due to the higher surface area and low number of stacked layers in the LDH structure, optimized the MnP loading and the access of the substrates to the catalytic sites under the reaction conditions used.

Cyclohexane is a less reactive substrate than (Z)-cyclooctene in oxidation reactions, and when metalloporphyrins are used as catalysts, both cyclohexanol and cyclohexanone are obtained as products, but in homogeneous catalysis, high selectivity for the alcohol product is frequently observed.<sup>27-29,31</sup> The novel MnP/LDH@SiO<sub>2</sub> solid reported here presented alcohol yield (9%) similar to that observed for the homogeneous catalysis (14%) and higher than that observed for the solid resulting from the immobilization of MnP on LDH (5%). Selectivity for alcohol was also observed, which is in agreement with reported results of homogeneous catalysis using this MnP and other metalloporphyrins.<sup>27-29</sup> and suggests that the catalytic mechanism of the hydroxylation reaction can be similar to that observed for the MnP in solution.<sup>32,33</sup>

MnP/LDH@SiO<sub>2</sub> also showed recycling capacity since no leaching of the MnP from the support solid was detected by UV-Vis monitoring during the catalytic reaction or during the recovery and reactivation by washing and dried step. In fact, in the second use of the solid on the cyclohexane oxidation, a small drop in activity was observed, but the materials were still active.

# Conclusions

Monodispersed nanometric size silica spheres were obtained by a hydrolysis method and used as support for the deposition of a 2:1 Mg:Al layered double hydroxide. After observing the LDH plate-like crystals at the silica spheres surface, the resulting solid was used as support to immobilizentine manganese(III) porphyrin (MnP) ପୈନାହାର୍ଥ୍ୟ<sup>039</sup>/ନିମ୍ପିର୍ଦ୍ଦି ଅନିନ୍ଦିନ immobilization loading of 2.43x10<sup>-5</sup> mol of MnP per mass (g) of the support was obtained.

The immobilized MnP on LDH and LDH@SiO<sub>2</sub> were investigated as catalysts for oxidation of different substrates (*Z*)-cyclooctene and cyclohexane) using iodosylbenzene (PhIO) as oxidant, where high yields of products were observed. Although the MnP/LDH@SiO<sub>2</sub> spheres were aggregated in a raspberry-like particles, the material presented the highest catalytic activity, due to the monodispersed hierarchical layered double hydroxide on silica spheres, exposing the catalytic site of the porphyrin. Although the catalyst was only reused in the cyclohexane oxidation, the materials showed potential for recycling, with partial preservation of the catalytic activity.

# **Conflicts of interest**

The authors declare that they have no conflict of interest.

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