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## Accepted Article

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# Hybrid-Metalloporphyrin Magnetic Nanoparticles as Catalysts for Sequential Transformation of Alkenes and CO<sub>2</sub> into Cyclic Carbonates

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**Abstract:** The synthesis and full characterization of manganese and chromium metalloporphyrins and hybrid magnetic nanocomposites prepared thereof is described. Their application in homogeneous and heterogeneous sequential epoxidation/CO<sub>2</sub> cycloaddition reactions using O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> as oxidant showed high activity and selectivity for the preparation of a variety of cyclic carbonates directly from olefins. The combination of manganese and chromium nanocomposites allowed to set the keystone for the development of a reusable dual catalytic system to transform olefins into cyclic carbonates.

## Introduction

The demand for renewable raw materials by the chemical industry is a crucial issue regarding the development of low-carbon economy.<sup>[1,2]</sup> In this context, conversion of carbon dioxide into valuable organic chemicals<sup>[3-9]</sup> has become a topic with increasing awareness, with remarkable economic and environmental impacts. Among numerous possible transformations, the cycloaddition of carbon dioxide to epoxides is an atom-economic approach to prepare cyclic carbonates,<sup>[10-13]</sup> which have a wide range of applications, namely as intermediates for fine chemicals or in plastics industry, in biomedical applications, as electrolytes for lithium batteries, fuel additives or green solvents.<sup>[14-17]</sup> So far, great efforts have been devoted to the development of efficient catalytic systems for this conversion,<sup>[10,18,19]</sup> such as organocatalysts,<sup>[20-22]</sup> ionic liquids<sup>[23,24]</sup> and metal catalysts,<sup>[25,31]</sup> namely those based on metalloporphyrins.<sup>[32-43]</sup> However, the previous synthesis of epoxides often involve the use of toxic and expensive reagents, and require hard separation/purification

procedures.<sup>[44-48]</sup> Alternatively, synthetic metalloporphyrins have been described as excellent cytochrome-P450 biomimetic catalysts to selectively promote olefin epoxidation in a sustainable fashion.<sup>[49-62]</sup> Despite such advances, the design of efficient catalytic systems able to sequentially promote olefin epoxidation followed by CO<sub>2</sub> addition to epoxides is a great challenge<sup>[63,64]</sup> and further studies are still required to overcome several issues related with the instability of homogeneous catalysts and the selection of appropriate oxidants.<sup>[65-70]</sup> Therefore, more robust catalysts such as heterogeneous and/or biphasic systems have been lately developed, namely those based on metal oxides<sup>[71,72]</sup> supported gold catalysts,<sup>[73-75]</sup> sodium phosphotungstate<sup>[76]</sup> and ionic liquids,<sup>[77]</sup> most of them using alkyl hydroperoxides as oxygen donors. Nevertheless, to the best of our knowledge, there are no reports on the application of heterogeneous metalloporphyrin-based recyclable catalysts to promote the sequential transformation of olefins into cyclic carbonates, using green oxidants such as O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>. From the existing literature and our own previous experience, the introduction of halogen atoms at metalloporphyrin's macrocycle structure is known to enhance their catalytic activity and stability in both epoxidation<sup>[78-80]</sup> and CO<sub>2</sub> addition to epoxides.<sup>[82]</sup> Particularly, fluorinated groups are highly advantageous because they also increase the catalyst's solubility in compressed CO<sub>2</sub>, avoiding the use of solvents.<sup>[83,84]</sup>

So, with our aim focused on the development of efficient and stable catalytic systems for sequential transformations,<sup>[85,86,87]</sup> herein we report the synthesis and characterization of hybrid manganese(III) and chromium(III) halogenated porphyrin magnetic nanocomposites and their application as reusable catalysts in olefin epoxidation (using O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> as the oxidants) and in CO<sub>2</sub> cycloaddition to epoxides. Finally, an heterobimetallic dual catalyst, prepared by the appropriate amounts combining Mn(III)-porphyrin and Cr(III)-porphyrin hybrid materials was applied in sequential transformation of olefins into cyclic carbonates.

## Results and Discussion

Metalloporphyrin complexes (Figure 1) were prepared through condensation of pyrrole with substituted benzaldehydes, using optimized synthetic strategies developed by the Coimbra's group,<sup>[88-91]</sup> followed by metallation of free-base porphyrins, through modifications of the DMF/metal salt method.<sup>[92,93]</sup>

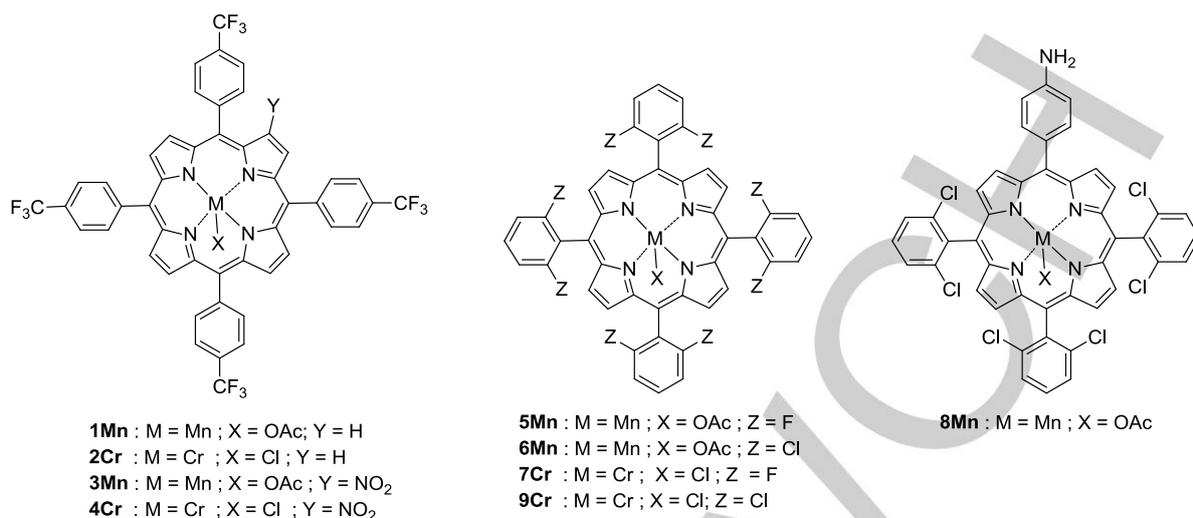
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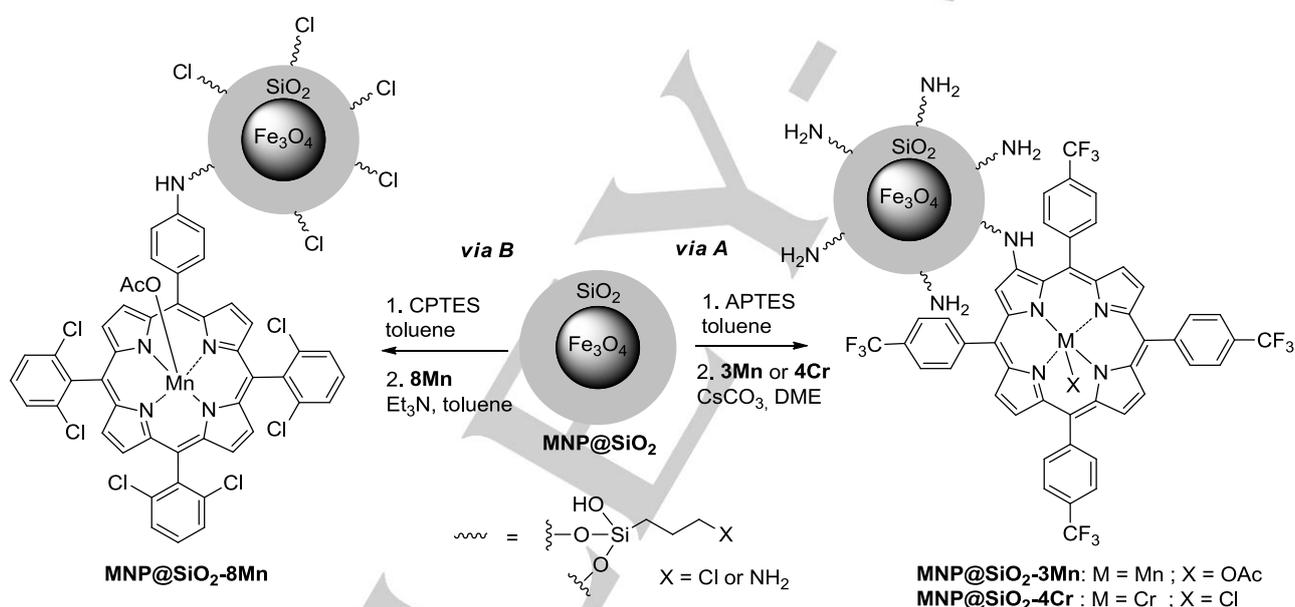
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**Figure 1.** Metalloporphyrin-based homogeneous catalysts and precursors.



**Scheme 1.** Preparation of hybrid metalloporphyrin-based magnetic materials **MNP@SiO<sub>2</sub>-3Mn**, **MNP@SiO<sub>2</sub>-4Cr** and **MNP@SiO<sub>2</sub>-8Mn**.

The hybrid metalloporphyrin-based heterogeneous catalysts were prepared using two different approaches: i) covalent attachment to aminopropyl-functionalized silica-coated magnetite nanoparticles *via*  $\beta$ -*ipso*-nitro aromatic nucleophilic substitution (Scheme 1, *via A*); ii) covalent grafting chloropropyl-functionalized silica coated magnetite nanoparticles *via* nucleophilic substitution (Scheme 1, *via B*). The synthesis of **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr** involved the previous nitration of *meso*-tetra(4-(trifluoromethyl)phenyl)porphyrin with copper(II) nitrate in an acetic anhydride/acetic acid mixture, followed by demetallation in acidic medium, which afforded  $\beta$ -nitro-*meso*-tetra(4-(trifluoromethyl)phenyl)porphyrin in 89% yield. Metal complexation was subsequently performed by reaction with manganese(II) acetate or chromium (II) chloride, in DMF, which afforded beta-mononitrated metalloporphyrins **3Mn** and **4Cr** in 79% and 84% isolated yields, respectively. Finally, covalent

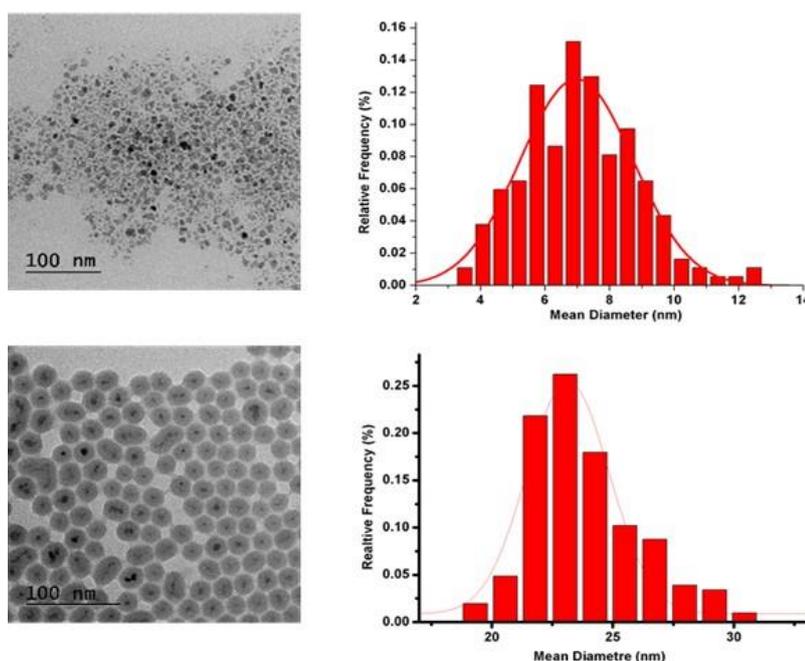
grafting onto the magnetic support was carried out by reacting each nitro-metalloporphyrin with the aminopropyl-functionalized silica-coated magnetite nanoparticles, using cesium carbonate as base and DME as solvent (Scheme 1, *via A*), which led to the desired hybrid materials **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr**. Likewise, the hybrid nanocomposite **MNP@SiO<sub>2</sub>-8Mn** was prepared accordingly to our recently described methodology,<sup>[51]</sup> by covalent linkage of the amine group at the *meso*-aryl position of the non-symmetric metalloporphyrin **8Mn** to the magnetic support, by reacting the silica-coated magnetite nanoparticles (**MNP@SiO<sub>2</sub>**)<sup>[94,95]</sup> with 3-chloropropyltriethoxysilane (CPTES) followed by addition of aminated metalloporphyrin **8Mn**, using Et<sub>3</sub>N as base (Scheme 1, *via B*).

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## Characterization of catalysts based on metalloporphyrins hybrid magnetic nanoparticles

The hybrid nanocomposites were characterized by inductively coupled plasma atomic emission spectroscopy (ICP), UV-visible spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FTIR) and thermogravimetry-differential scanning calorimetry (TG/DSC). The physical/chemical characterization data of **MNP@SiO<sub>2</sub>-8Mn** was in agreement with that previously

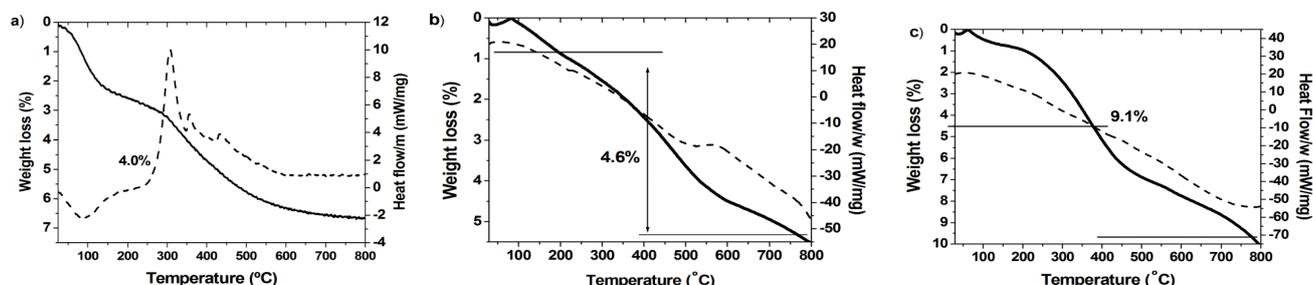
described by some of us.<sup>[51]</sup> Transmission electron microscopy (TEM) images (Figure 2) showed that the silica-coated magnetite nanoparticles (**MNP@SiO<sub>2</sub>**) display a spherical morphology, having an average diameter of  $23 \pm 2$  nm, which is substantially higher than that of the uncoated magnetite nanoparticle **MNP** ( $7 \pm 2$  nm). The metal content of the hybrid materials was determined by ICP, which indicated a Mn percentage of 0.026% in **MNP@SiO<sub>2</sub>-3Mn**, a Cr percentage of 0.260% in **MNP@SiO<sub>2</sub>-4Cr** and a Mn percentage of 0.090% in **MNP@SiO<sub>2</sub>-8Mn**.



**Figure 2.** Transmission electron microscopy (TEM) images and the corresponding particle size distribution histograms of: a) **MNP**; b) **MNP@SiO<sub>2</sub>**

The quantification of the organic content in the nanocomposite materials was carried out by TG/DSC measurements in the range 25 °C-800 °C (Figure 3). All diagrams present an endothermic peak between 30 °C and 175 °C, attributed to weight loss of physically adsorbed water and solvents. Another weight loss of 4.0% was observed for **MNP@SiO<sub>2</sub>-NH<sub>2</sub>** (Figure 3a), attributed to the decomposition of aminopropyl groups grafted at the surface of silica-coated magnetite nanoparticle matrix (1.1% of NH<sub>2</sub> corresponding to 0.68 mmol g<sup>-1</sup>). In the TG/DSC curves of **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr** (Figure 3b and 3c,

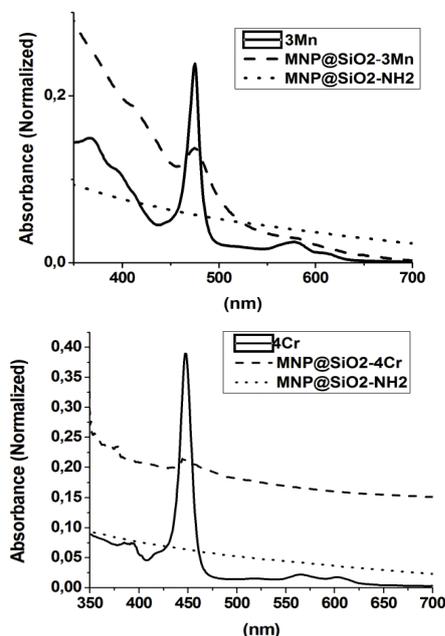
respectively), additional weight losses (with exothermic peaks) occurred between 225 °C and 780 °C, which were considered to essentially arise from decomposition of metalloporphyrins **3Mn** or **4Cr**. By comparison with the TG/DSC curve of **MNP@SiO<sub>2</sub>-NH<sub>2</sub>**, the weight losses of **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr** were of 0.6% and 5.1%, respectively, which allowed determining the amount of metalloporphyrins **3Mn** (0.0057 mmol g<sup>-1</sup>) and **4Cr** (0.050 mmol g<sup>-1</sup>), grafted onto the magnetic support. These values are in agreement with those obtained by ICP.



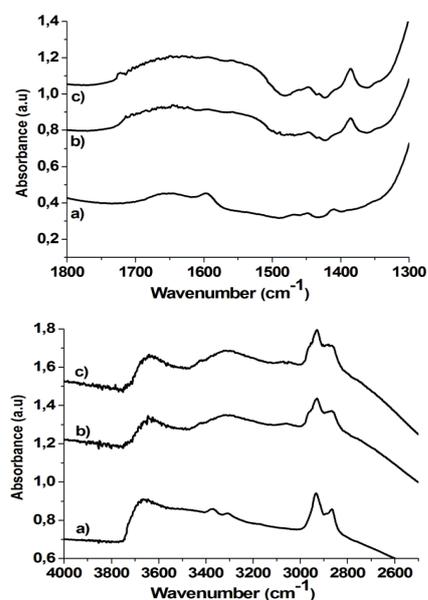
**Figure 3.** TG-DSC curves (weight loss - solid line; heat flow - dashed line) of: a) **MNP@SiO<sub>2</sub>-NH<sub>2</sub>**; b) **MNP@SiO<sub>2</sub>-3Mn**; c) **MNP@SiO<sub>2</sub>-4Cr**.

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The UV–Vis absorption spectra of **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr** (Figure 4) clearly show the Soret bands at 471 nm and at 448 nm, typical of manganese (III) and chromium(III) porphyrins, respectively, in similarity with the corresponding non-immobilized metalloporphyrins **3Mn** and **4Cr**.



**Figure 4.** Normalized UV-Vis absorption spectra of **MNP@SiO<sub>2</sub>-3Mn** (up) and **MNP@SiO<sub>2</sub>-4Cr** (down) dispersed in CH<sub>3</sub>CN:H<sub>2</sub>O (1:1), compared with metalloporphyrins **3Mn** and **4Cr** in CHCl<sub>3</sub>.



**Figure 5.** Infrared spectra of: a) **MNP@SiO<sub>2</sub>-NH<sub>2</sub>**; b) **MNP@SiO<sub>2</sub>-3Mn** and c) **MNP@SiO<sub>2</sub>-4Cr**, in the regions 4000-2500 cm<sup>-1</sup> (up) and 1800-1325 cm<sup>-1</sup> (down).

The effective grafting of metalloporphyrins **3Mn** and **4Cr** onto the magnetic support was confirmed by infrared analysis of the hybrid materials **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr**, in contrast with the aminopropyl-functionalized silica, **MNP@SiO<sub>2</sub>-NH<sub>2</sub>** (Figure 5). In the interval 4000-2500 cm<sup>-1</sup> (Figure 5, up), all IR spectra show broad bands between 3750-3300 cm<sup>-1</sup>, which are typical of terminal silanol and hydroxyl groups in interaction, and additional signals at 2950-2850 cm<sup>-1</sup>, which are characteristic of C–H stretching vibrations. The spectrum of **MNP@SiO<sub>2</sub>-NH<sub>2</sub>** presents two clear bands at 3300-3400 cm<sup>-1</sup> (Figure 5, up) and one broad band close to 1600 cm<sup>-1</sup> (Figure 5, down), typical of N–H stretching of primary amines and N–H bending, respectively. In the interval 1300-1700 cm<sup>-1</sup> (Figure 5, d), both spectra of **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr** present characteristic peaks at: 1450 cm<sup>-1</sup> (C–H bending), 1410 cm<sup>-1</sup> (Si–CH<sub>2</sub> bending) and 1350–1400 cm<sup>-1</sup> (C–F stretching), indicating the presence of trifluoromethyl-based porphyrins in the nanocomposite materials. It should be noted that, instead of two bands in the region 3300-3400 cm<sup>-1</sup>, both spectra of **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr** present a broad band, attributed to N–H stretching of secondary amines, which corroborate the covalent attachment of the metalloporphyrins, through amino groups, onto the surface of the magnetic support.

#### Catalytic epoxidation

The metalloporphyrin-based homogeneous catalysts were first evaluated in styrene epoxidation, using molecular oxygen or H<sub>2</sub>O<sub>2</sub> as non-pollutant oxidants, in order to appraise the effects of the metal center, porphyrin structure and oxygen source. In a typical epoxidation reaction with O<sub>2</sub>, a round bottom flask was loaded with the appropriate amounts of styrene, the desired metalloporphyrin catalyst and isobutyraldehyde as co-reductant. The solution was stirred at room temperature (25 °C), under O<sub>2</sub> bubbling, for 90 min. Substrate conversion, along with TON calculations and selectivity were determined by GC analysis, using chlorobenzene as internal standard and the results are presented in Table 1.

All manganese(III)-porphyrin catalysts **1Mn**, **5Mn** and **6Mn** (Table 1, entries 2-4) led to practically full conversions (99%) in 90 min, presenting TON's of up to 10531, and high selectivity for epoxide formation (86-92%), with benzaldehyde being formed as side-product in just 8-14%. Moreover, no significant effects of the porphyrin *meso*-aryl substituents were observed in the catalytic activity. Contrarily, a strong influence of the central metal was identified, being chromium(III)-porphyrin catalysts **2Cr**, **7Cr** and **9Cr** significantly less active and selective towards epoxide, with formation of benzaldehyde in up to 30%, as previously observed<sup>[96]</sup> (Table 1, entries 5-7). The effect of porphyrin structure and central metal on the mechanism of epoxidation reactions with O<sub>2</sub> have been object of several publications.<sup>[97,98]</sup> Our study corroborates previous observations, where the use of molecular oxygen as oxygen donor requires, in general, the presence of an electron source.<sup>[99]</sup> Herein, we observed that the presence of

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isobutyraldehyde is crucial to obtain an active catalytic system *via* high-valent metal oxo species (Table 1, entry 4), which points toward the involvement of the Mukaiyama's mechanism.<sup>[51,99,100]</sup>

UV-Vis analyses showed degradation of around 30% of the Cr(III)-porphyrin catalysts **2Cr** and **7Cr**, after 90 min, while

Mn(III)-porphyrin catalysts **1Mn**, **5Mn** and **6Mn** suffer degradation of up to 85% (SI, FiguresS1–S5).

**Table 1.** Epoxidation of styrene using metalloporphyrins as homogeneous catalysts.<sup>[a]</sup>

Entry	Catalyst	Oxidant [O]	Conv. <sup>[b]</sup> (%)	Epoxide select. (%)	TON <sup>[c]</sup>
1	-	O <sub>2</sub>	3	78	319
2	Mn(III)OAc-TPPpCF <sub>3</sub> ( <b>1Mn</b> )	O <sub>2</sub>	99	88	10531
3	Mn(III)OAc-TDFPP ( <b>5Mn</b> )	O <sub>2</sub>	99	86	10531
4	Mn(III)OAc-TDCPP ( <b>6Mn</b> )	O <sub>2</sub>	99 (0) <sup>[d]</sup>	92	10531
5	Cr(III)Cl-TPPpCF <sub>3</sub> ( <b>2Cr</b> )	O <sub>2</sub>	15	70	1595
6	Cr(III)Cl-TDFPP ( <b>7Cr</b> )	O <sub>2</sub>	17	73	1807
7	Cr(III)Cl-TDCPP ( <b>9Cr</b> )	O <sub>2</sub>	14	72	1488
8	Mn(III)OAc-TPPpCF <sub>3</sub> ( <b>1Mn</b> )	H <sub>2</sub> O <sub>2</sub>	4	90	24
9	Mn(III)OAc-TDCPP ( <b>6Mn</b> )	H <sub>2</sub> O <sub>2</sub>	99	98	594
10	-	H <sub>2</sub> O <sub>2</sub>	0	-	-

[a] Reaction conditions using O<sub>2</sub> as oxidant (entries 1-6): catalyst, styrene, isobutyraldehyde (1:10638:53191), CH<sub>2</sub>Cl<sub>2</sub> (2 mL), O<sub>2</sub> bubbling, T = 25 °C, t = 90 min. Reaction conditions using H<sub>2</sub>O<sub>2</sub> as oxidant (entries 7-9): catalyst, styrene, NH<sub>4</sub>OAc (1 : 600 : 387), CH<sub>3</sub>CN (20 mL), T = 25 °C, t = 45 min; H<sub>2</sub>O<sub>2</sub> (30% w/w) solution in CH<sub>3</sub>CN (1:10) was added to the reaction mixture (2.25 mL aliquots every 15 min). [b] Conversions calculated by GC based on chlorobenzene as internal standard. [c] Turnover number (TON) calculated by mol<sub>products</sub>/mol<sub>catalyst</sub>. [d] In absence of isobutyraldehyde.

The effect of the oxidant was then appraised on the catalytic activity and stability, with the manganese(III) porphyrins **1Mn** and **6Mn** being further applied as catalysts in the same reaction, but using hydrogen peroxide as alternative oxygen source, which does not require any co-reductant (Table 1, entries 8-9). In a model epoxidation experiment, the substrate, the selected metalloporphyrin catalyst and ammonium acetate (axial ligand), were dissolved in acetonitrile and stirred at room temperature. Then, aliquots of a solution of hydrogen peroxide (30% w/w) in CH<sub>3</sub>CN (1:10) were added to the reaction mixture, every 15 min, along 45 min. A significant effect of the porphyrin structure was found, evidenced by the best performance of catalyst **6Mn** (MnOAc-TDCPP), which produced full conversion in 45 min with excellent selectivity for epoxide formation (98%), while a conversion of only 4% was observed with catalyst **1Mn** (MnOAc-TPPpCF<sub>3</sub>). In this case, the difference of activity may be explained by the higher stability of **6Mn** (MnOAc-TDCPP) when compared with of **1Mn** (MnOAc-TPPpCF<sub>3</sub>), as corroborated by UV-Vis (SI, Figure S3 and S5). The mechanism of H<sub>2</sub>O<sub>2</sub> epoxidation reaction, reported by some of us<sup>[78,79]</sup> and other authors,<sup>[80,81]</sup> points out that, under the above mentioned reaction conditions (**6Mn** MnOAc-

TDCPP, aprotic solvent and ammonium acetate as axial ligand), the Mn(V)=O oxo species is the active species obtained directly from the reaction of **6Mn** Mn(III)TDCPP with H<sub>2</sub>O<sub>2</sub> (peroxidase route).

From the studies in homogeneous phase, Mn(III) metalloporphyrins were found to be the most promising epoxidation catalysts, when using O<sub>2</sub> as oxidant, presenting higher activity and selectivity to epoxides than the Cr(III) counterparts, probably due to the formation of highly stable and consequently poorly active Cr(V)=O species.<sup>[96]</sup> Regarding the epoxidation reactions using hydrogen peroxide as oxygen source, significant conversion was only obtained with **6Mn** (MnOAc-TDCPP), containing 2,6-dichlorophenyl groups in the *meso* positions. However, both strategies led to a significant catalyst's degradation. Therefore, to overcome the catalysts instability and allow their recycling and reuse, the hybrid heterogeneous catalysts **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-8Mn**, were then selected to be applied in styrene epoxidation, using molecular oxygen or hydrogen peroxide as the oxidants. The results are presented in Table 2.

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Using O<sub>2</sub> as the oxidant, heterogeneous hybrid catalyst **MNP@SiO<sub>2</sub>-8Mn** gave rise to high conversions and selectivity in the order of 94% for epoxide formation (Table 2, entry 3), while that **MNP@SiO<sub>2</sub>-3Mn** showed low conversion in order to 34% and selectivity 85% for epoxide. However, when hydrogen peroxide was used as oxygen source, only the catalyst containing *meso*-2,6-dichloro-phenyl substituents at the porphyrin structure, **MNP@SiO<sub>2</sub>-8Mn**, led to high activity (SI, Figure S7), while the trifluoromethyl-based manganese(III) porphyrin hybrid catalyst, **MNP@SiO<sub>2</sub>-3Mn**, was completely inactive. These results are in close agreement with those previously observed in homogeneous phase (Table 1, entries 7-8 and Table 2, entries 2 and 4). The recyclability of **MNP@SiO<sub>2</sub>-8Mn** was then appraised, after

magnetic recovery of the catalyst followed by washing of the solid material with the solvent used in the catalytic reaction. When using O<sub>2</sub> as the oxidant, the catalyst **MNP@SiO<sub>2</sub>-8Mn** showed excellent reusability along five consecutive cycles, almost without loss of activity or selectivity for epoxide formation (Figure 6). Therefore, besides the high activity and selectivity, it is worth noting the stability of Mn(III) porphyrin magnetic material, **MNP@SiO<sub>2</sub>-8Mn**, with no catalyst leaching being observed, as demonstrated by ICP analyses of the liquid supernatant, which showed a negligible metal content in solution (<0.1 μg mL<sup>-1</sup>). This stabilizing effect may be attributed to the influence of the magnetic support in preventing the formation of catalytic inactive oxo-dimeric metalloporphyrin species.<sup>[101]</sup>

Table 2. Evaluation of heterogeneous hybrid metalloporphyrin-based iron magnetic catalysts in styrene epoxidation, using molecular oxygen or hydrogen peroxide as oxidants.<sup>[a]</sup>

Entry	Catalyst	Oxidant [O]	Conv. <sup>[b]</sup> (%)	Epoxide select. (%)	TON <sup>[c]</sup>
1	<b>MNP@SiO<sub>2</sub>-3Mn</b>	O <sub>2</sub>	34	85	3616
2	<b>MNP@SiO<sub>2</sub>-3Mn</b>	H <sub>2</sub> O <sub>2</sub>	2	41	12
3	<b>MNP@SiO<sub>2</sub>-8Mn</b>	O <sub>2</sub>	99	94	10531
4	<b>MNP@SiO<sub>2</sub>-8Mn</b>	H <sub>2</sub> O <sub>2</sub>	91	92	546

[a] Reaction conditions using O<sub>2</sub> as the oxidant: catalyst, styrene, isobutyraldehyde, chlorobenzene (1 : 10638 : 53191 : 4148), CH<sub>2</sub>Cl<sub>2</sub> (2 mL), O<sub>2</sub> bubbling, T = 25 °C, t = 140 min. Reaction conditions using H<sub>2</sub>O<sub>2</sub> as the oxidant: catalyst, styrene, NH<sub>4</sub>OAc (1 : 600 : 387) and CH<sub>3</sub>CN (20 mL), T = 25 °C, t = 45 min; H<sub>2</sub>O<sub>2</sub> (30% w/w) diluted with CH<sub>3</sub>CN (1:10) was added to the reaction mixture in 450 μL aliquots every 15 min. [b] Conversions calculated by GC based on chlorobenzene as internal standard. [c] Turnover number (TON) calculated by mol<sub>products</sub>/mol<sub>catalyst</sub>.

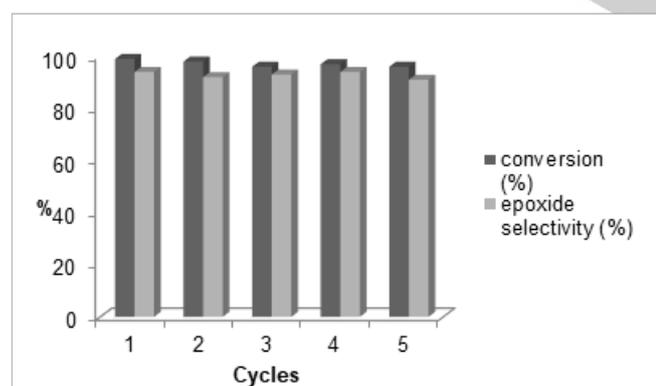


Figure 6. Recycling experiments of **MNP@SiO<sub>2</sub>-8Mn** in styrene epoxidation with O<sub>2</sub>.

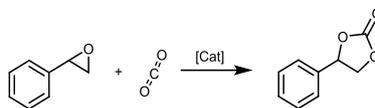
Contrarily, when hydrogen peroxide was used as oxidant, the catalyst **MNP@SiO<sub>2</sub>-8Mn** showed limited reusability, with a sharp decrease in epoxide yield being observed after the third run (SI, Figure S8). This might be due to metalloporphyrin degradation in

the presence of hydroxyl radicals. Blank experiments, carried out using silica-functionalized magnetite nanoparticles (**MNP@SiO<sub>2</sub>-Cl** and **MNP@SiO<sub>2</sub>-NH<sub>2</sub>**) as catalysts, either with O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> as the oxidants, led to conversions below 1%, which discards the involvement of the magnetic supports as the reaction's catalysts. In conclusion, the porphyrin magnetic-nanocomposite **MNP@SiO<sub>2</sub>-8Mn** was a stable, active and reusable catalyst for styrene epoxidation using O<sub>2</sub>.

#### Catalytic CO<sub>2</sub> cycloaddition to epoxides

The metalloporphyrin-based homogeneous catalysts were then evaluated in the CO<sub>2</sub> addition to styrene oxide, in order to appraise the effects of the metal and porphyrin structure on the catalytic activity and selectivity. The reactions were performed under moderate conditions (10 bar CO<sub>2</sub>, 80 °C), using 0.07 mol% catalyst, with and without bis(triphenylphosphine)iminium chloride (PPNCI) as the co-catalyst. The results are collected in Table 3. All Mn(III)-porphyrin catalysts presented low conversions in the absence of co-catalyst but, with the addition of PPNCI, a significant increase in their catalytic activity was observed (Table 3, entries 2-7). The ligand's structure had a moderate

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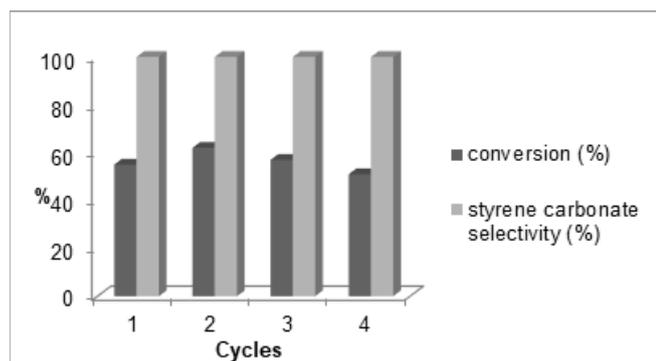
Entry	Catalyst	Co-catalyst	Conv. <sup>[b]</sup> (%)	TON	TOF (h <sup>-1</sup> )
1	–	PPNCl	30	429	18
2	MnOAc-TPPpCF <sub>3</sub> ( <b>1Mn</b> )	–	11	157	7
3	MnOAc-TPPpCF <sub>3</sub> ( <b>1Mn</b> )	PPNCl	88	1257	52
4	MnOAc-TDFPP ( <b>5Mn</b> )	–	5	71	3
5	MnOAc-TDFPP ( <b>5Mn</b> )	PPNCl	77	1100	46
6	MnOAc-TDCPP ( <b>6Mn</b> )	–	10	142	5
7	MnOAc-TDCPP ( <b>6Mn</b> )	PPNCl	90	1286	54
8	CrCl-TPPpCF <sub>3</sub> ( <b>2Cr</b> )	–	88	1257	52
9	CrCl-TPPpCF <sub>3</sub> ( <b>2Cr</b> )	PPNCl	100 (91) <sup>[c]</sup>	1429 (1300) <sup>[c]</sup>	60 (260) <sup>[c]</sup>
10	CrCl-TDFPP ( <b>7Cr</b> )	–	86	1229	51
11	CrCl-TDFPP ( <b>7Cr</b> )	PPNCl	100 (88) <sup>[c]</sup>	1429 (1257) <sup>[c]</sup>	60 (251) <sup>[c]</sup>
12	CrCl-TDCPP ( <b>9Cr</b> )	–	78	1128	47
13	CrCl-TDCPP ( <b>9Cr</b> )	PPNCl	100 (81) <sup>[c]</sup>	1429 (1157) <sup>[c]</sup>	60 (231) <sup>[c]</sup>

[a] Reaction conditions: styrene oxide (35 mmol, 4 mL); catalyst: 0.07 mol%; co-catalyst (when indicated): 0.07 mol% PPNCl; T = 80 °C; P (CO<sub>2</sub>) = 10 bar; t = 24 h. [b] Conversions calculated by GC based on chlorobenzene as internal standard. Selectivity for styrene carbonate, as determined by crude <sup>1</sup>H NMR, was 100% in all cases. [c] t = 5 h.

influence in the activity of the Mn(III) porphyrins, with the trifluoromethylphenyl (**1Mn**) and 2,6-dichlorophenyl-based (**6Mn**) catalysts being more active than the 2,6-difluorophenyl metalloporphyrin catalyst (**5Mn**), either with or without the use of PPNCl as co-catalyst. In addition, full selectivity for the cyclic carbonate product was observed with all Mn(III) catalytic systems, under the studied conditions (10 bar CO<sub>2</sub>, 80 °C). On the other hand, the Cr(III)-porphyrin catalysts were much more active than their Mn(III) analogues, both with or without co-catalyst. In the absence of any additive, the catalysts **2Cr**, **7Cr** and **9Cr** led to conversions of 88%, 86% and 78% in 24 h, respectively (Table 3, entries 8, 10 and 12). Remarkably, the addition of PPNCl led to a significant increase on the activity of the Cr(III)-porphyrin catalysts **2Cr**, **7Cr** and **9Cr** (Table 3, entries 9, 11 and 13). The best catalytic system is **2Cr**/PPNCl, displaying 91% conversion in just 5 h, with full selectivity for the formation of styrene carbonate. UV-Vis analysis of crude mixtures showed practically no catalyst degradation, after 24 h, in all cases. Based on the results in homogeneous phase, the trifluoromethyl-based chromium(III) hybrid nanocomposite **MNP@SiO<sub>2</sub>-4Cr** was selected as heterogeneous catalyst, to be applied in CO<sub>2</sub> addition to styrene oxide, under similar reaction conditions. Following a standard

procedure, the magnetic catalyst (490 mg, 0.0245 mmol Cr) was introduced in a glass vial inside the autoclave, together with the co-catalyst, PPNCl (0.0245 mmol). After pressurization with CO<sub>2</sub> (10 bar), the reaction was conducted for 24 h, under vigorous stirring. The hybrid catalyst **MNP@SiO<sub>2</sub>-4Cr** produced a conversion of 55% in 24 h, with close to full selectivity for the formation of styrene carbonate (SI, Figure S8). Then, the heterogeneous catalyst was recovered using an external magnet, it was washed with CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub>, dried under vacuum and reused in the next run. Remarkably, the nanocomposite showed a notable reusability in four consecutive cycles, without significant loss of activity or selectivity for styrene carbonate (Figure 7). A blank experiment was carried out, using the aminopropylsilyl-functionalized magnetic nanoparticle (**MNP@SiO<sub>2</sub>-NH<sub>2</sub>**) as catalyst but practically no conversion (<1%) was observed after 24 h, which indicates that the immobilized Cr(III)-porphyrin is effectively acting as the reaction's catalyst. In sum, these results show that the hybrid Cr(III)-porphyrin magnetic nanocomposite **MNP@SiO<sub>2</sub>-4Cr** is a stable and reusable catalyst for CO<sub>2</sub> cycloaddition to styrene epoxide, with high selectivity for cyclic carbonate formation.

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**Figure 7.** Recycling experiments of **MNP@SiO<sub>2</sub>-4Cr** in CO<sub>2</sub> addition to styrene oxide.

Sequential epoxidation/CO<sub>2</sub> cycloaddition

**Table 4.** Sequential epoxidation/CO<sub>2</sub> cycloaddition, catalyzed by homogeneous Mn(III) (**6Mn**) and Cr(III)-porphyrin (**2Cr**) catalysts.<sup>[a]</sup>

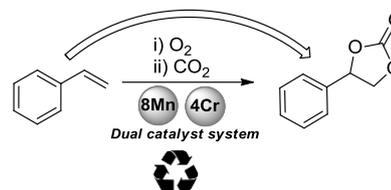
Entry	Substrate	Conversion <sup>[b]</sup> (%)	Product (%)
1		99	70
2		99	47
3		99	<1
4		93	68
5		99	48

[a] Reaction conditions for epoxidation: catalyst, styrene, NH<sub>4</sub>OAc (1 : 600 : 387), CH<sub>3</sub>CN (20 mL), T = 25 °C, t = 45 min; H<sub>2</sub>O<sub>2</sub> (30% w/w) solution in CH<sub>3</sub>CN (1:10) was added to the reaction mixture (2.25 mL aliquots every 15 min). Reaction conditions for CO<sub>2</sub> addition reaction: catalyst and co-catalyst (PPNCI): 0.07 mol%; T = 80 °C; P (CO<sub>2</sub>) = 10 bar; t = 24 h [b] Conversions calculated by GC based on chlorobenzene as internal standard.

In the search of efficient methodologies for the "direct" transformation of olefins into cyclic carbonates, different approaches were studied. Sequential epoxidation/CO<sub>2</sub> addition reactions were first appraised in homogeneous phase, with styrene being selected as model olefin substrate.

Initially, hydrogen peroxide was selected as the oxidant and the epoxidation step was carried out with the manganese(III)-porphyrin catalyst **6Mn**, under the conditions presented in Table 1. After 45 min, the solvent was partially evaporated and the resulting mixture was transferred, without any further purification, to a stainless steel autoclave containing the chromium(III)-porphyrin catalyst **2Cr** and the co-catalyst PPNCI. The subsequent CO<sub>2</sub> addition proceeded along 24 h, under the conditions described in Table 3 (10 bar CO<sub>2</sub>, 80 °C), leading to the formation of the desired styrene carbonate in 70% yield (Table 4, entry 1). Therefore, the scope of this sequential methodology was expanded to a set of different aryl and alkyl olefins, including 4-chlorostyrene, 4-methylstyrene, 2-vinylnaphthalene and 1-hexene. Remarkably, full conversion of the initial olefin was achieved in all cases, with moderate to good selectivity for cyclic carbonate formation (47-70%) (Table 4, entries 2-5) and (SI, Figures S9-11). The only exception was obtained with 4-methylstyrene, for which a complex mixture of benzylic oxidation products, formed during the epoxidation step, was observed, leading to very low selectivity (<1%) for cyclic carbonate formation (Table 4, entry 3). A different approach was then appraised, using molecular oxygen as the oxidant (and isobutyraldehyde as co-reductant), again with manganese(III)-porphyrin **6Mn** as the epoxidation catalyst, under the reaction conditions described in Table 1. After 90 min at 25 °C under O<sub>2</sub> bubbling, the chromium(III)-porphyrin catalyst **2Cr** and the co-catalyst PPNCI, was added. The subsequent CO<sub>2</sub> addition proceeded along 24 h, under the conditions described in Table 3 (10 bar CO<sub>2</sub>, 80 °C). GC/MS analysis of the crude showed the complete conversion of the initial olefin substrate but a complex mixture of products was obtained, without any evidence of cyclic carbonate formation. This was attributed to the epoxide ring opening in the presence of isobutyric acid formed in the first step.

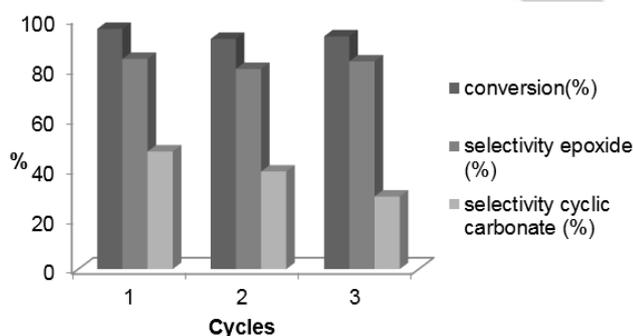
Therefore, from a critical analysis of the above results and aiming at the development of efficient and reusable catalytic system to sequentially promote the "direct" transformation of olefins into cyclic carbonate, the hybrid metalloporphyrin magnetic nanocomposites **MNP@SiO<sub>2</sub>-8Mn** and **MNP@SiO<sub>2</sub>-4Cr** were combined and evaluated as a heterogeneous bimetallic dual catalytic system for styrene epoxidation with molecular oxygen, followed by CO<sub>2</sub> cycloaddition (Figure 8).



**Figure 8.** Sequential heterogeneous bimetallic dual catalytic system for direct transformation of styrene into styrene cyclocarbonate using O<sub>2</sub> and CO<sub>2</sub>.

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So, a mixture containing the two hybrid materials **MNP@SiO<sub>2</sub>-8Mn** (66 mg,  $8.16 \times 10^{-4}$  mmol) and **MNP@SiO<sub>2</sub>-4Cr** (122 mg,  $6.08 \times 10^{-3}$  mmol Cr) was placed inside the reaction vessel. The epoxidation reaction was carried out using molecular oxygen as the oxidant and isobutyraldehyde as the co-reductant, under the reaction conditions described in Table 2. After 140 minutes, the magnetic hybrid catalyst (containing both Mn(III) and Cr(III)-porphyrin nanoparticles) was collected in the reactor walls with an external magnet and the reaction crude was treated with an aqueous solution of sodium hydrogen carbonate to remove the isobutyric acid formed as side-product. After separation, the organic phase was transferred to the autoclave, containing already the recovered magnetic catalysts and the co-catalyst PPNCI. The reactor was then pressurized with CO<sub>2</sub> (10 bar) and cycloaddition step was conducted at 80 °C, for 24 h. GC/MS analyses determined complete conversion of the olefin, with formation of styrene carbonate as the major product (up to 52%). After the catalyst's recovery using an external magnet, the hybrid material was washed several times with different solvents, dried under vacuum and reused in the next run, which involved both epoxidation and CO<sub>2</sub> addition as sequential steps. Remarkably, the hybrid material could be reused in several additional consecutive sequential epoxidation/CO<sub>2</sub> addition cycles, without loss of catalytic activity and just a slight decrease of selectivity for the formation of cyclic carbonate (Figure 9), which demonstrated the recyclability of this heterobimetallic dual catalytic system. From the final product selectivity we may infer that the mechanism of the overall sequential reaction should be similar to the one described for individual steps, where Mn(V)=O oxo species is the epoxidation active species, obtained by Mukayama oxygen/aldehyde activation mechanism, and the CO<sub>2</sub> addition to the epoxide is catalyzed by the Cr(III) porphyrin (stronger Lewis acid), assisted by the nucleophile PPNCI as previously described by some of us.<sup>[83]</sup>



**Figure 9.** Recycling experiments of the dual catalytic system **MNP@SiO<sub>2</sub>-8Mn+MNP@SiO<sub>2</sub>-4Cr** in styrene sequential epoxidation/CO<sub>2</sub> addition.

## Conclusions

The work presented herein allowed the development of active and selective metalloporphyrin-based homogeneous and heterogeneous catalysts for epoxidation/CO<sub>2</sub> addition sequential reactions, aiming at the direct transformation of olefins into cyclic carbonates. Studies of the styrene epoxidation reaction in

homogeneous phase have allowed us to conclude that, regardless of the oxidant used (molecular oxygen or hydrogen peroxide), the manganese(III) porphyrins are more active and selective than their chromium(III) counterparts. Furthermore, using O<sub>2</sub> as the oxidant, the catalyst 6Mn (MnOAc-TDCPP) was shown to be the most active, selective and stable epoxidation catalyst. On the other hand, chromium(III) metalloporphyrins proved to be the most active catalysts for CO<sub>2</sub> addition to styrene oxide, among the synthesized metalloporphyrins, the best results being obtained with 2Cr (CrCl-pCF<sub>3</sub>TPP). Within our main goal of developing sustainable chemical processes, the most promising catalysts for each individual reaction were immobilized in magnetic nanoparticles, to obtain the corresponding reusable heterogeneous hybrid catalysts, which were characterized by several physical/chemical techniques.

Although the use of H<sub>2</sub>O<sub>2</sub> as the oxidant, in homogeneous phase, has allowed the direct transformation of a set of different olefins into the respective cyclic carbonates in good yields, using the catalysts 6Mn and 2Cr in each epoxidation and CO<sub>2</sub> cycloaddition steps, respectively, the corresponding heterogeneous catalysts were shown to lose significant activity after each recycling experiment. Advantageously, the hybrid catalyst **MNP@SiO<sub>2</sub>-8Mn** presented a good performance in styrene epoxidation using O<sub>2</sub> as oxidant, maintaining its efficiency in five consecutive cycles. Remarkable, for the first time we developed an efficient and reusable heterobimetallic catalytic system, through appropriate combination of two hybrid materials, **MNP@SiO<sub>2</sub>-8Mn** and **MNP@SiO<sub>2</sub>-4Cr**, to sequentially promote the transformation of styrene into epoxide followed by the CO<sub>2</sub> cycloaddition reaction. This dual catalyst could be recycled and reused in three consecutive cycles without significant loss of activity or selectivity. Studies on the preparation of immobilized catalysts, with different metals and different ligands are underway in our laboratory, with a view to the development and optimization of tandem (one-pot) oxidative carboxylation processes.

## Experimental Section

Reagents and solvents were purchased from Sigma-Aldrich (Portugal) and Fluorochem (England). Commercial styrene oxide was distilled prior to use. <sup>1</sup>H-NMR spectra were recorded on a Bruker Avance III spectrometer, or a Bruker DRX-400 spectrometer, both operating at 400.13 MHz (chemical shifts are expressed in ppm using CDCl<sub>3</sub> as solvent). The MALDI-TOF MS data were obtained on a Bruker Daltonics Flex Analysis apparatus. The UV-vis absorption spectra, in solution, were recorded on a Hitachi U-2010 and the absorption spectra of solid samples were obtained by diffuse reflectance using a Cary 5000 UV-Vis-NIR spectrophotometer equipped with an integrating sphere. The infrared spectra were obtained using a Pike Miracle spectrometer and each spectrum were performed with a resolution of 4 cm<sup>-1</sup> (64 scans). The samples were pressed into thin wafers (20-25 mg cm<sup>-2</sup>) and heated in an IR glass cell up to 160 °C using a heating rate of 10 K min<sup>-1</sup> during 1h, under vacuum (10 Pa) before spectra acquisition in transmission mode. A Philips CM 200 apparatus (accelerating voltage of 200 kV) was used for TEM analyses and size distributions of the hybrid materials were determined by a statistical size distribution via manual analysis of enlarged images with Imagetool sware (Version 3.0) programme. An Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Thermo X Series apparatus was used for ICP analysis. Thermogravimetric

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analyses were obtained using a Parkin-Elmer STA6000 simultaneous TG/DSC instrument from 25 °C to 800 °C as maximum temperature. HP-Agilent 6890 chromatographer, equipped with ionization detector (FID) was used for gas chromatography analysis using chlorobenzene as internal standard. GC-MS spectra were obtained in a Hewlett-Packard 5973 MSD spectrometer, using EI (70 eV), coupled to a Hewlett-Packard Agilent 6890 chromatographer, equipped with a HP-5 MS column (30 m × 0.25 mm × 0.25 μm). A Bruker Microtof instrument was used for mass spectral analyses.

### Synthesis of metalloporphyrin catalysts

The symmetric porphyrins 5,10,15,20-tetra(2,6-difluorophenyl) porphyrin (TDFPP), 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin (TDCPP) and 5,10,15,20-tetra(4-trifluoromethylphenyl) porphyrin (*p*-CF<sub>3</sub>TTP), as well as the non-symmetric 5-(4-aminophenyl)-10,15,20-tri(2,6-dichlorophenyl)porphyrin (NH<sub>2</sub>-TDCPP) were prepared according to our optimized synthetic methods.<sup>[51,88-91]</sup> Then, the free-base porphyrins were reacted with the desired metal salts (manganese(II) acetate tetrahydrate or chromium(II) chloride), following literature procedures, to afford the metalloporphyrin complexes **1Mn**, **2Cr**, **5Mn**, **6Mn**, **7Cr**, **8Mn** and **9Cr**. Their characterization data was in agreement with the reported literature.<sup>[82,83,93,102]</sup>

### 2-Nitro-5,10,15,20-tetra(4-trifluoromethylphenyl)porphyrinato copper(II) (9Cu)

A solution of copper(II) nitrate trihydrate (0.27 g, 1.12 mmol) in acetic anhydride/acetic acid mixture (50/10 mL) was added to a chloroform solution (500 mL) of 5,10,15,20-tetra-(4-trifluoromethylphenyl)porphyrin (*p*-CF<sub>3</sub>TTP) (500 mg, 0.56 mmol). The reaction was conducted at 60 °C for 24 h. Then, the solution was concentrated under vacuum and washed with a saturated solution of sodium hydrogen carbonate (2x), water (2x) and dried with anhydrous sodium sulfate. The crude was then purified by silica gel column chromatography, using dichloromethane:*n*-hexane (2:1) as the eluent. The complex 2-nitro-5,10,15,20-tetra-(4-trifluoromethylphenyl)porphyrinato copper(II) (**9Cu**) was isolated in 84 % yield (466 mg, 0.47 mmol). HRMS (ESI-FIA-TOF): calcd. for C<sub>48</sub>H<sub>23</sub>F<sub>12</sub>N<sub>5</sub>O<sub>2</sub>Cu 992.0956; found: 992.0954.

### 2-Nitro-5,10,15,20-tetra(4-trifluoromethylphenyl)porphyrin (10)

A solution of sulfuric acid 98% (10 mL) was added dropwise to a chloroform solution (200 mL) of **9Cu** (500 mg, 0.50 mmol). The reaction was kept at 25 °C for 1 h. Then, the crude was carefully neutralized with a saturated solution of sodium bicarbonate and distilled water. The organic solution was dried with anhydrous sodium sulfate. After filtration and solvent evaporation, the crude was purified by silica gel column chromatography, using dichloromethane:*n*-hexane (2:1) as the eluent. The 2-nitro-5,10,15,20-tetra(4-trifluoromethylphenyl)porphyrin (**10**) was isolated in 88% yield (415 mg, 0.44 mmol). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, 298 K): δ = 9.01 (s, 1H, β-H), 8.96–8.86 (m, 4H, β-H), 8.70–8.67 (m, 2H, β-H), 8.37–8.32 (m, 8H, Ar-H), 8.09–8.06 (m, 6H, Ar-H), 7.99 (d, *J* = 8.0 Hz, 2H, Ar-H), -2.68 ppm (s, 2H). HRMS (ESI-FIA-TOF): calcd. for C<sub>48</sub>H<sub>25</sub>F<sub>12</sub>N<sub>5</sub>O<sub>2</sub> 931.1817; found: 932.1889.

### 2-Nitro-5,10,15,20tetra(4trifluoromethylphenyl)porphyrinato manganese(III) acetate (3Mn)

Manganese(II) acetate tetrahydrate (880 mg, 3.6 mmol) was added to a round bottom flask containing **10** (300 mg, 0.32 mmol), dissolved in dimethylformamide (20 mL). The reaction was kept under stirring at 150 °C for 4h. The solution was then concentrated under vacuum and washed with a saturated solution of sodium hydrogen carbonate (2x), water (2x) and dried with anhydrous sodium sulfate. The crude was purified by silica gel column chromatography, using ethyl acetate as the eluent, providing 2-nitro-5,10,15,20-tetra(4-trifluoromethylphenyl)porphyrinato manganese

(III) acetate (**3Mn**) in 78% yield (292 mg, 0.28 mmol). HRMS (ESI-FIA-TOF): calcd. for C<sub>50</sub>H<sub>26</sub>F<sub>12</sub>N<sub>5</sub>O<sub>4</sub>Mn [M-OAc]: 984.1041; found: 984.0883.

### 2-Nitro-5,10,15,20-tetra(4-trifluoromethylphenyl)porphyrinato chromium(III) chloride (4Cr)

Chromium(II) chloride (181 mg, 1.48 mmol) was added to a round bottom flask containing **10** (350 mg, 0.37 mmol) dissolved in dimethylformamide (20 mL). The reaction was kept under stirring, at 150 °C for 5 h. Finally, the crude was concentrated under vacuum and washed with a saturated solution of sodium hydrogen carbonate (2x), water (2x) and dried with anhydrous sodium sulfate. The crude product was purified using silica gel column chromatography with ethyl acetate as eluent yielding 2-nitro-5,10,15,20-tetra(4-trifluoromethylphenyl)porphyrinatochromium (III) chloride (**4Cr**) in 89% yield (335 mg, 0.33 mmol). HRMS (ESI-FIA-TOF): calcd. for C<sub>48</sub>H<sub>23</sub>ClCrF<sub>12</sub>N<sub>5</sub>O<sub>2</sub> [M+1]: 1017.0754; found: 1017.0837

### Preparation of hybrid metalloporphyrin magnetite nanocomposites

In a round bottom flask, the aminopropylsilyl-functionalized magnetite material **MNP@SiO<sub>2</sub>-NH<sub>2</sub>** (1 g), previously prepared as described elsewhere, was added to a solution of **3Mn** (230 mg, 0.22 mmol) or **4Cr** (250 mg, 0.24 mmol) and cesium carbonate (310 mg, 0.95 mmol) in dry 1,2-dimethoxyethane (50 mL). The mixtures were heated until 85 °C for 24 h. Then, the magnetic solid materials were collected using an external magnet and washed several times with acetonitrile, ethyl acetate and dichloromethane to rinse away excess of non-immobilized metalloporphyrins. Finally, the resulting hybrid metalloporphyrin magnetic nanocomposites **MNP@SiO<sub>2</sub>-3Mn** and **MNP@SiO<sub>2</sub>-4Cr** were dried under vacuum for 48 h. A similar procedure was adopted to prepare the **MNP@SiO<sub>2</sub>-8Mn**,<sup>[51]</sup> through reaction of **8Mn** with chloropropylsilyl-functionalized magnetite nanoparticles.<sup>[103]</sup>

### Procedure for catalytic epoxidation with O<sub>2</sub>

A dichloromethane solution (2 mL), containing the olefin substrate (0.5 mmol), the metalloporphyrin catalyst (4.7×10<sup>-5</sup> mmol metal), isobutyraldehyde (0.18 g, 2.5 mmol) and chlorobenzene (21 mg, 0.19 mmol) was introduced into a stainless steel autoclave. Then, the reaction was stirred, at 25 °C, under oxygen bubbling, for the appropriate time (90 min with homogeneous catalysts or 140 min with heterogeneous catalysts). Conversion and selectivity were determined by GC, using chlorobenzene as internal standard. The products' identification was performed by GC/MS and GC analysis against standards.

### Procedure for catalytic epoxidation with H<sub>2</sub>O<sub>2</sub>

The olefin substrate (4.5 mmol), ammonium acetate (225 mg, 2.91 mmol), the metalloporphyrin catalyst (7.48×10<sup>-3</sup> mmol metal) and chlorobenzene (44 mg, 0.39 mmol) were dissolved in acetonitrile (20 mL). The mixture was introduced into a glass vial and a hydrogen peroxide (2 mmol) solution (30% w/w), diluted with acetonitrile (1:10), was slowly added to the reaction mixture, in 2.25 mL aliquots, until complete substrate conversion. The reaction was conducted at 25 °C, under stirring, for the desired time (45 min with homogeneous catalysts or 24 h with heterogeneous catalysts). Conversion and selectivity were determined by GC, using chlorobenzene as internal standard. The products' identification was performed by GC/MS and GC analysis against standards.

### Procedure for catalytic CO<sub>2</sub> addition to epoxides

The metalloporphyrin catalyst (2.45×10<sup>-2</sup> mmol) and the co-catalyst PPNCI (2.45×10<sup>-2</sup> mmol) (when indicated) were placed inside a 100 mL stainless steel autoclave and kept for 3 h under vacuum, at 80 °C. Then, styrene epoxide (4 mL, 35 mmol), previously dried over alumina and stored under inert atmosphere, was introduced via *cannula* into the autoclave. The autoclave was pressurized with CO<sub>2</sub> (10 bar) and the reaction was conducted under stirring, at 80 °C, for 24 h. At the end, the autoclave was

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cooled in an ice bath and slowly depressurized. Conversion was determined by GC, using chlorobenzene as internal standard and selectivity was determined by  $^1\text{H}$  NMR, through integral ratio.

#### Recycling and reuse of heterogeneous magnetic catalysts

After the first run of each catalytic experiment, the heterogeneous catalysts **MNP@SiO<sub>2</sub>-3Mn**, **MNP@SiO<sub>2</sub>-8Mn** or **MNP@SiO<sub>2</sub>-4Cr** were steadily separated from the crude mixtures, using an external magnet, followed by decantation of supernatant solution. Then, the solid magnetic material was washed with  $\text{CH}_2\text{Cl}_2$  (4 mL) (3x) and  $\text{CH}_3\text{CN}$  (4 mL) (3x), dried under vacuum, at 60 °C, for 2h and reused in the next run.

#### Procedure for homogeneous sequential epoxidation/CO<sub>2</sub> cycloaddition with O<sub>2</sub> as the oxidant

A dichloromethane solution (2 mL) containing styrene (1 mL, 8.69 mmol), the catalyst **6Mn** (0.8 mg,  $8.16 \times 10^{-4}$  mmol), isobutyraldehyde (3.1 g, 43.4 mmol), and chlorobenzene (21 mg, 0.19 mmol) was introduced in an autoclave. The reaction was conducted with stirring at 25 °C, under oxygen bubbling, for 4 h. Meanwhile, the catalyst **2Cr** (5.9 mg,  $6.08 \times 10^{-3}$  mmol) and PPNCI ( $6.08 \times 10^{-3}$  mmol) were placed inside a 100 mL stainless steel autoclave and kept for 3 h under vacuum, at 80 °C. Then, the epoxidation crude mixture was transferred via *cannula* into the autoclave. The reactor was pressurized with CO<sub>2</sub> (10 bar) and the reaction was conducted at 80 °C for 24 h. At the end, the autoclave was cooled in an ice bath and slowly depressurized. The products' identification was performed by GC/MS and GC analysis against standards. Conversion was determined by GC, using chlorobenzene as internal standard and selectivity was determined by  $^1\text{H}$  NMR, through peak integral ratio.

#### Procedure for homogeneous sequential epoxidation/CO<sub>2</sub> cycloaddition with H<sub>2</sub>O<sub>2</sub> as the oxidant

The olefin substrate (4.5 mmol), ammonium acetate (225 mg, 2.91 mmol), the catalyst **6Mn** (7.5 mg,  $7.48 \times 10^{-3}$  mmol) and chlorobenzene (44 mg, 0.39 mmol), were dissolved in  $\text{CH}_3\text{CN}$  (20 mL). The mixture was then introduced into an autoclave and an aqueous hydrogen peroxide (2 mmol) solution (30% w/w), diluted with acetonitrile (1:10), was slowly added to the reaction mixture, in 2.25 mL aliquots, every 15 min. The reaction was conducted with stirring at 25 °C, for 45 min. Then, the crude mixture was dried over anhydrous sodium sulfate, concentrated to a total volume of 2.5 mL and stored under inert atmosphere. Meanwhile, the catalyst **2Cr** (3.0 mg,  $3.15 \times 10^{-3}$  mmol) and the co-catalyst PPNCI (1.8 mg,  $3.15 \times 10^{-3}$  mmol) were placed inside a 100 mL stainless steel autoclave and kept for 3 h under vacuum, at 80 °C. Then, the epoxidation crude mixture was transferred via *cannula* into the autoclave. The reactor was pressurized with CO<sub>2</sub> (10 bar) and the reaction was conducted at 80 °C for 24 h. At the end, the autoclave was cooled in an ice bath, and slowly depressurized. Conversion was determined by GC, using chlorobenzene as internal standard and selectivity was determined by  $^1\text{H}$  NMR, through peak integral ratio.

#### Procedure for heterogeneous sequential epoxidation/CO<sub>2</sub> cycloaddition

Styrene (1 mL, 8.69 mmol), the hybrid catalysts **MNP@SiO<sub>2</sub>-8Mn** (66 mg,  $8.16 \times 10^{-4}$  mmol Mn) and **MNP@SiO<sub>2</sub>-4Cr** (122 mg,  $6.08 \times 10^{-3}$  mmol Cr), isobutyraldehyde (3.1 g, 43.4 mmol), chlorobenzene (0.4 g, 3.32 mmol) and dichloromethane were introduced into a glass vial, inside an autoclave and the reaction was conducted with stirring at 25 °C, under oxygen bubbling, for 4 h. After this period, the hybrid solid material (containing both catalysts **MNP@SiO<sub>2</sub>-8Mn** and **MNP@SiO<sub>2</sub>-4Cr**) was collected in the autoclave walls, using an external magnet, and the liquid was decanted. Then, PPNCI ( $6.08 \times 10^{-3}$  mmol) was added to the stainless steel autoclave containing the hybrid magnetic catalysts and the reactor was kept under vacuum, at 80 °C, for 3 h. Next, the crude mixture obtained in the epoxidation step was treated with a saturated sodium hydrogen carbonate

solution (30 mL). After phase separation, the organic phase was dried over alumina and introduced, via *cannula*, inside the stainless steel autoclave containing the recovered hybrid catalysts. Then, the reactor was pressurized with CO<sub>2</sub> (10 bar) and the reaction was conducted at 80 °C for 24 h. At the end, the autoclave was cooled and slowly depressurized. Finally, the mixture of magnetic catalysts (**MNP@SiO<sub>2</sub>-8Mn** and **MNP@SiO<sub>2</sub>-4Cr**) was separated from the reaction mixture using an external magnet. The recovered solid material was washed with dichloromethane (4 mL) (3x), dried in vacuum for 2 h at 60 °C and reused in the next run. Conversion was determined by GC, using chlorobenzene as internal standard and selectivity was determined by  $^1\text{H}$  NMR, through peak integral ratio.

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- [1] X. Lim, *Nature* **2015**, *526*, 628-630.
- [2] J. A. Martens, A. Bogaerts, N. De Kimpe, P. A. Jacobs, G. B. Marin, K. Rabaey, M. Saeys, S. Verhelst, *ChemSusChem* **2017**, *10*, 1039-1055.
- [3] Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nature Commun.* **2015**, *6*, 5933.
- [4] J. Artz, T. E. Müller, K. Thener, *Chem. Rev.* **2018**, *118*, 434-504.
- [5] E. Alper, O. Y. Orhan, *Petroleum* **2017**, *3*, 109-126.
- [6] E. Vessally, M. Babazadeh, A. Hosseini, S. Arshadi, L. Edjlali, *J. CO<sub>2</sub> Util.* **2017**, *21*, 491-502.
- [7] Q.-W. Song, Z.-H. Zhou, L.-N. He, *Green Chem.* **2017**, *19*, 3707-3728.
- [8] M. Aresta, A. Dibenedetto, E. Quaranta, *J. Catal.* **2016**, *343*, 2-45.
- [9] K. M. K. Yu, I. Curcic, J. Gabriel, S. C. E. Tsang, *ChemSusChem* **2008**, *1*, 893-899.
- [10] R. R. Shaikh, S. Pompraprom, V. D'Elia, *ACS Catal.* **2018**, *8*, 419-450.
- [11] X.-D. Lang, L.-N. He, *Chem. Rec.* **2016**, *16*, 1337-1352.
- [12] V. B. Saptal, B. M. Bhanage, *Curr. Opin. Green Sustainable Chem.* **2017**, *3*, 1-10.
- [13] C. Martin, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353-1370.
- [14] J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663-674.
- [15] A. A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951-976.
- [16] T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312-1330.
- [17] M. North, R. Pasquale, C. Young, *Green Chem.* **2010**, *12*, 1514-1539.
- [18] C. J. Whiteoak, A. W. Kleij, *Synlett.* **2013**, *24*, 1748-1756.
- [19] H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf, T. Werner, *Top. Curr. Chem.* **2017**, *375*, 50.
- [20] M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann, F. E. Kuhn, *ChemSusChem* **2015**, *8*, 2436-2454.
- [21] C. J. Whiteoak, A. Nova, F. Maseras, A. W. Kleij, *ChemSusChem* **2012**, *5*, 2032-2038.

## FULL PAPER

- [22] M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing, C. Detrembleur, *Catal. Sci. Technol.* **2017**, *7*, 2651-2684.
- [23] Q. He, J. W. O'Brien, K. A. Kitselman, L. E. Tompkins, G. C. T. Curtis, F. M. Kerton, *Catal. Sci. Technol.*, **2014**, *4*, 1513-1528.
- [24] V. B. Saptal, B. M. Bhanage, *ChemCatChem* **2016**, *8*, 244-250.
- [25] A. Decortes, A. M. Castilla, A. W. Kleij, *Angew. Chem. Int. Ed.* **2010**, *49*, 9822-9837.
- [26] X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, *41*, 1462-1484.
- [27] V. D'Elia, J. D. A. Pelletier, J.-M. Basset, *ChemCatChem* **2015**, *7*, 1906-1917.
- [28] J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, *Green Chem.* **2015**, *17*, 1966-1987.
- [29] X.-H. Ji, N.-N. Zhu, J.-G. Ma, P. Cheng, *Dalton Trans.* **2018**, *47*, 1768-1771.
- [30] S.-S. Yu, X.-H. Liu, J.-G. Ma, Z. Niu, P. Cheng, *J. CO<sub>2</sub> Util.* **2016**, *14*, 122-125.
- [31] M. North, P. Villuendas, *ChemCatChem* **2012**, *4*, 789-794.
- [32] Y. Chen, R. Luo, Q. Xu, J. Jiang, X. Zhou, H. Ji, *ACS Sustainable Chem. Eng.* **2018**, *6*, 1074-1082.
- [33] Y. Qin, H. Guo, X. Sheng, X. Wang, F. Wang, *Green Chem.* **2015**, *17*, 2853-2858.
- [34] C. Maeda, S. Sasaki, T. Ema, *ChemCatChem* **2017**, *9*, 946-949.
- [35] Y. Chen, R. Luo, Q. Xu, W. Zhang, X. Zhou, H. Ji, *ChemCatChem* **2017**, *9*, 767-773.
- [36] X. Jiang, F. Gou, X. Fu, H. Jing, *J. CO<sub>2</sub> Util.* **2016**, *16*, 264-271.
- [37] A. Farhadian, M. B. G. Afshani, A. B. Miyardan, M. R. Nabid, N. Safari, *ChemistrySelect* **2017**, *2*, 1431-1435.
- [38] Z. Dai, Q. Sun, X. Liu, C. Bian, Q. Wua, S. Pan, L. Wang, X. Meng, F. Deng, F.-S. Xiao, *J. Catal.* **2016**, *338*, 202-209.
- [39] A. Chen, P. Ju, Y. Zhang, J. Chen, H. Gao, L. Chen, Y. Yu, *RSC Adv.* **2016**, *6*, 96455-96466.
- [40] F. Zadehahmadi, F. Ahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, R. Kardanpour, *J. Mol. Catal. A: Chem.* **2015**, *398*, 1-10.
- [41] X. Sheng, H. Guo, Y. Qin, X. Wang, F. Wang, *RSC Adv.* **2015**, *5*, 31664-31669.
- [42] D. Bai, Q. Wang, Y. Song, B. Li, H. Jing, *Catal. Commun.* **2011**, *12*, 684-688.
- [43] C. Maeda, J. Shimonishi, R. Miyazaki, J. Hasegawa, T. Ema, *Chem. Eur. J.* **2016**, *22*, 6556-6563.
- [44] J. He, J. Ling, P. Chiu, *Chem. Rev.* **2014**, *114*, 8037-8128.
- [45] F. Cavani, J. H. Teles, *ChemSusChem* **2009**, *2*, 508-534.
- [46] A. Fingerhut, O. V. Serdyuk, S. B. Tsogoeva, *Green Chem.* **2015**, *17*, 2042-2058.
- [47] S.-C. Chua, X. Xu, Z. Guo, *Process Biochem.* **2012**, *47*, 1439-1451.
- [48] *Modern Oxidation Methods*, J.-E. Bäckvall (Ed.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2004**.
- [49] J. C. Barona-Castaño, C. C. Carmona-Vargas, T. J. Brocksom, K. T. de Oliveira, *Molecules* **2016**, *21*, 310.
- [50] A. Farokhi, H. Hosseini-Monfared, *New J. Chem.* **2016**, *40*, 5032-5043.
- [51] L. D. Dias, R. M. B. Carrilho, C. A. Henriques, G. Piccirillo, A. Fernandes, L. M. Rossi, M. F. Ribeiro, M. J. F. Calvete, M. M. Pereira, *J. Porphyrins Phthalocyanines* **2018**, *22*, 2-11.
- [52] R. A. Baglia, J. P. T. Zaragoza, D. P. Goldberg, *Chem. Rev.* **2017**, *117*, 13320-13352.
- [53] K. Berijani, H. Hosseini-Monfared, *Inorg. Chim. Acta* **2018**, *471*, 113-120.
- [54] A. Farokhi, H. Hosseini Monfared, *J. Catal.* **2017**, *352*, 229-238.
- [55] M. Zhao, C.-D. Wu, *Catal. Commun.* **2017**, *99*, 146-149.
- [56] K. Berijani, H. Hosseini-Monfared, *Mol. Catal.* **2017**, *433*, 136-144.
- [57] P. Sakthipriya, N. Ananthi, *J. Porphyrins Phthalocyanines* **2016**, *20*, 730-737.
- [58] T. Omagari, A. Suzuki, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2016**, *138*, 499-502.
- [59] P. J. Thomassen, S. Varghese, E. J. A. Bijsterveld, P. Thordarson, J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *Eur. J. Org. Chem.* **2015**, 5246-5253.
- [60] J. W. Brown, Q. T. Nguyen, T. Otto, N. N. Jarenwattananon, S. Glöggler, L.-S. Bouchard, *Catal. Commun.* **2015**, *59*, 50-54.
- [61] S. Rayati, F. Nejabat, *New J. Chem.* **2017**, *41*, 7987-7991.
- [62] X.-L. Yang, C.-D. Wu, *Inorg. Chem.* **2014**, *53*, 4797-4799.
- [63] L. Cuesta-Aluja, A. M. Masdeu-Bultó, *ChemistrySelect* **2016**, *1*, 2065-2070.
- [64] J. Sun, L. Liang, J. Sun, Y. Jiang, K. Lin, X. Xu, R. Wang, *Catal. Surv. Asia.* **2011**, *15*, 49-54.
- [65] N. Eghbali, C.-J. Li, *Green Chem.* **2007**, *9*, 213-215.
- [66] P. Ramidi, C. M. Felton, B. P. Subedi, H. Zhou, Z. R. Tian, Y. Gartia, B. S. Pierce, A. Ghosh, *J. CO<sub>2</sub> Util.* **2015**, *9*, 48-57.
- [67] J. Sun, S. Fujita, B. M. Bhanage, M. Arai, *Catal. Today* **2004**, 93-95, 383-388.
- [68] C. C. Rocha, T. Onfroy, F. Launay, *C. R. Chimie* **2015**, *18*, 270-276.
- [69] M. Aresta, E. Quaranta, A. Ciccarese, *J. Mol. Catal.* **1987**, *41*, 355-359.
- [70] D. Bai, H. Jing, *Green Chem.* **2010**, *12*, 39-41.
- [71] M. Aresta, A. Dibenedetto, *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 399-409.
- [72] M. Aresta, A. Dibenedetto, I. Tommasi, *Appl. Organometal. Chem.* **2000**, *14*, 799-802.
- [73] D. Xiang, X. Liu, J. Sun, F.-S. Xiao, J. Sun, *Catal. Today.* **2009**, *148*, 383-388.
- [74] J. Sun, S. Fujita, F. Zhao, M. Hasegawa, M. Arai, *J. Catal.* **2005**, *230*, 398-405.
- [75] K. Jasiak, T. Krawczyk, M. Pawlyta, A. Jakóbk-Kolon, S. Baj, *Catal. Lett.* **2016**, *146*, 893-901.
- [76] J.-L. Wang, J.-Q. Wang, L.-N. He, X.-Y. Dou, F. Wu, *Green Chem.* **2008**, *10*, 1218-1223.
- [77] J. Sun, S. Fujita, B. M. Bhanage, M. Arai, *Catal. Commun.* **2004**, *5*, 83-87.
- [78] S. L. H. Rebelo, M. M. Q. Simões, M. G. P. M. S. Neves, A. M. S. Silva, J. A. S. Cavaleiro, A. F. Peixoto, M. M. Pereira, M. R. Silva, J. A. Paixão, A. M. Beja, *Eur. J. Org. Chem.* **2004**, 4778-4787.
- [79] S. L. H. Rebelo, M. M. Pereira, M. M. Q. Simões, M. G. P. M. S. Neves, J. A. S. Cavaleiro, *J. Catal.* **2005**, *234*, 76-87.
- [80] R. de Paula, M. M. Q. Simões, M. G. P. M. S. Neves, J. A. S. Cavaleiro, *J. Mol. Catal. A: Chem.* **2011**, *345*, 1-11.
- [81] A. Franck, C. Fertinger, R. Eldik, *Chem. Eur. J.* **2012**, *18*, 6935-6949.
- [82] L. Cuesta-Aluja, J. Castilla, A. M. Masdeu-Bultó, C. A. Henriques, M. J. F. Calvete, M. M. Pereira, *J. Mol. Catal. A: Chem.* **2016**, *423*, 489-494.
- [83] R. M. B. Carrilho, L. D. Dias, R. Rivas, M. M. Pereira, C. Claver, A. M. Masdeu-Bultó, *Catalysts* **2017**, *7*, 210.
- [84] S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan, A. B. Holmes, *Macromolecules* **2000**, *33*, 303-308.
- [85] A. R. Almeida, R. M. B. Carrilho, A. F. Peixoto, A. R. Abreu, A. Silva, M. M. Pereira, *Tetrahedron* **2017**, *73*, 2389-2395.
- [86] L. Damas, G. N. Costa, J. C. Ruas, R. M. B. Carrilho, A. R. Abreu, G. Aquino, M. J. F. Calvete, M. Pineiro, M. M. Pereira, *Curr. Microwave Chem.* **2015**, *2*, 53-60.
- [87] M. M. Pereira, A. C. B. Neves, M. J. F. Calvete, L. D. Dias, A. Fernandes, *Catal. Today*, **2013**, *218*, 99-106.
- [88] R. A. W. Johnstone, M. L. P. J. Nunes, M. M. Pereira, A. M. A. R. Gonsalves, A. C. Serra, *Heterocycles* **1996**, *43*, 1423-1437.
- [89] C. A. Henriques, S. M. A. Pinto, G. L. B. Aquino, M. Pineiro, M. J. F. Calvete, M. M. Pereira, *ChemSusChem* **2014**, *7*, 2821-2824.
- [90] M. Silva, A. Fernandes, S. S. Bebiano, M. J. F. Calvete, M. F. Ribeiro, H. D. Burrows, M. M. Pereira, *Chem. Commun.* **2014**, *50*, 6571-6573.
- [91] M. J. F. Calvete, L. D. Dias, C. A. Henriques, S. M. A. Pinto, R. M. B. Carrilho, M. M. Pereira, *Molecules* **2017**, *22*, 741.
- [92] P. Chen, M. H. Chisholm, J. C. Gallucci, X. Zhang, Z. Zhou, *Inorg. Chem.* **2005**, *44*, 2588-2595.

## FULL PAPER

- [93] D. Lahaye, K. Muthukumaran, C-H. Hung, D. Gryko, J. S. Rebouças, I. Spasojevic, I. Batinic-Haberle, J. S. Lindsey, *Bioorg. Med. Chem.* **2007**, *22*, 7066-7086.
- [94] C. A. Henriques, A. Fernandes, L. M. Rossi, M. F. Ribeiro, M. J. F. Calvete, M. M. Pereira, *Adv. Funct. Mater.* **2016**, *26*, 3359-3368.
- [95] L. M. Rossi, L. L. R. Vono, F. P. Silva, P. K. Kiyohara, E. L. Duarte, J. R. Matos, *Appl. Catal. A: Gen.* **2007**, *330*, 139-144.
- [96] J. Muzart, *Chem. Rev.* **1992**, *92*, 113-140.
- [97] R. A. Baglia, J. P. T. Zaragoza, D. P. Goldberg, *Chem. Rev.* **2017**, *117*, 13320-13352.
- [98] X. Huang, J. T. Groves, *Chem. Rev.* **2018**, *118*, 2491-2553.
- [99] W. Nam, H. J. Kim, S. H. Kim, R. Y. N. Ho, J. S. Valentine, *Inorg. Chem.* **1996**, *35*, 1045-1049.
- [100] B. B. Wentzel, P. L. Alsters, M. C. Feiters, R. J. M. Nolte, *J. Org. Chem.* **2004**, *69*, 3453-3464.
- [101] C. Sun, B. Hu, Z. Liu, *Chem. Eng. J.* **2013**, *232*, 96-103.
- [102] T. G. Traylor, A. R. Miksztal, *J. Am. Chem. Soc.* **1989**, *111*, 7443-7448.
- [103] C. A. Henriques, S. M. A. Pinto, J. Pina, C. Serpa, A. Fernandes, L. M. Rossi, M. F. Ribeiro, M. M. Pereira, M. J. F. Calvete, *Dalton Trans.* **2016**, *45*, 16211-16220.

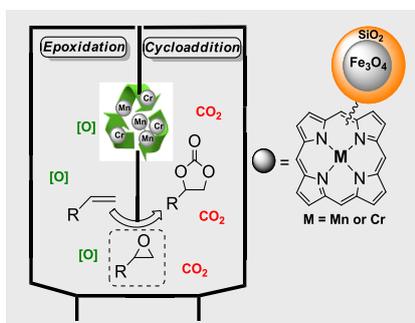
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Layout 1:

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**The search for more efficient catalytic processes and CO<sub>2</sub> industrial applications are key challenges in Chemistry:**

Development of an efficient catalytic system for valorization of CO<sub>2</sub> through sequential transformation epoxidation/CO<sub>2</sub> cycloaddition of simple olefins into valuable cyclic carbonates by hybrid metalloporphyrin magnetic catalysts is reported.



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**Hybrid-Metalloporphyrin Magnetic Nanoparticles as Catalysts for Sequential Transformation of Alkenes and CO<sub>2</sub> into Cyclic Carbonates**