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# Robust Mn(III) *N*-pyridylporphyrin-based biomimetic catalysts for hydrocarbon oxidations: Heterogenization on non-functionalized silica gel versus chloropropyl-functionalized silica gel

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## Abstract

Two classes of heterogenized biomimetic catalysts were prepared and characterized for hydrocarbon oxidations: (1) by covalent anchorage of the three Mn(III) *meso*-tetrakis(2-, 3-, or 4-pyridyl)porphyrin isomers by in situ alkylation with chloropropyl-functionalized silica gel (**SiI-Cl**) to yield **SiI-Cl/MnPY** (**Y = 1, 2, 3**) materials, and (2) by electrostatic immobilization of the three Mn(III) *meso*-tetrakis(*N*-methylpyridinium-2, 3, or 4-yl)porphyrin isomers (**MnPY, Y = 4, 5, 6**) on non-modified silica gel (**$SiO_2$**) to yield **$SiO_2$/MnPY** (**Y = 4, 5, 6)** materials. Silica gel used was of column chromatography grade and Mn porphyrin loadings were deliberately kept at a low level (0.3% w/w). These resulting materials were explored as catalysts for iodosylbenzene (PhIO) oxidation of cyclohexane, n-heptane, and adamantane to yield the corresponding alcohols and ketones; the oxidation of cyclohexanol to cyclohexanone was also investigated. The heterogenized catalysts exhibited higher efficiency and selectivity than the corresponding Mn porphyrins under homogeneous conditions. Recycling studies were consistent with low leaching/destruction of the supported Mn porphyrins. The **SiI-Cl/MnPY** catalysts were more efficient and more selective than **$SiO_2$/MnPY** ones; alcohol selectivity may be associated with hydrophobic silica surface modification reminiscent of biological cytochrome P450 oxidations. The use of widespread, column chromatography, amorphous silica yielded **SiI-Cl/MnPY** or **$SiO_2$/MnPY** catalysts considerably more efficient than the corresponding, previously reported materials with mesoporous Santa Barbara Amorphous No 15 (SBA-15) silica. Among the materials studied, in situ derivatization of Mn(III) 2-*N*-pyridylporphyrin by covalent immobilization on **SiI-Cl** to yield **SiI-Cl/MnP1** showed the best catalytic performance with high stability against oxidative destruction and reusability/recycle.


**Keywords:** porphyrin, silica gel, immobilization, oxyfunctionalization, alkane, biomimetic catalysis

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## Abbreviations

MnP, Mn porphyrin; MnPs, Mn porphyrins; CPTS, (3-chloropropyl)trimethoxysilane; Sil-Cl, 3-chloropropyl-functionalized silica gel; **(1)**, Mn(III) *meso*-tetrakis(2-pyridyl)porphyrin chloride (also known in the literature as MnT-2-PyPCl); **(2)**, Mn(III) *meso*-tetrakis(3-pyridyl)porphyrin chloride (also known in the literature as MnT-3-PyPCl), **(3)**, Mn(III) *meso*-tetrakis(4-pyridyl)porphyrin chloride (also known in the literature as MnT-4-PyPCl); MnP4, Mn(III) *meso*-tetrakis(*N*-methylpyridinium-2-yl)porphyrin chloride (also known in the literature as MnTM-2-PyPCl$_5$); MnP5, Mn(III) *meso*-tetrakis(*N*-methylpyridinium-3-yl)porphyrin chloride (also known in the literature as MnTM-3-PyPCl$_5$); MnP6, Mn(III) *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin chloride (also known in the literature as MnTM-4-PyPCl$_5$); MCM-41, mesoporous silica Mobil Composition Matter No 41; SBA-15, mesoporous silica Santa Barbara Amorphous No 15; DR-UV/VIS, diffuse reflectance UV/VIS spectroscopy; Cy-H, cyclohexane; Cy-ol, cyclohexanol; Cy-one, cyclohexanone; Adm, adamantane; Adm-1-ol, 1-adamantanol; Adm-2-ol, 2-adamantanol; 1-ol, 1-heptanol; 2-ol, 2-heptanol; 3-ol, 3-heptanol; 4-ol, 4-heptanol; 2-one, 2-heptanone; 3-one, 3-heptanone; 4-one, 4-heptanone.

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## Introduction

The three neutral Mn(III) *meso*-tetrakis(2-, 3-, or 4-pyridyl)porphyrin isomers [**(1)**, **(2)**, **(3)**] and their three methylated, cationic derivatives Mn(III) *meso*-tetrakis(*N*-methylpyridinium-2, 3, or 4-yl)porphyrins (**MnPY, Y = 4, 5, 6**) (Fig. 1) comprise a class of Mn porphyrins (MnPs) greatly studied as biomimetic models for oxidoreductase enzymes, such as, cytochromes P450, peroxidases, catalases, and superoxide dismutases, under homogeneous conditions.[1-11] Although these Mn porphyrins possess structural features, such as dangling pyridyl moieties on **(1)**, **(2)**, and **(3)** (suited for quaternization reactions) or permanent cationic *N*-methylpyridinium moieties on **MnPY** (Y = 4, 5, 6) (suited for electrostatic interactions), they remain little explored as heterogenized oxidation catalysts as compared to regular *meso*-tetraphenylporphyrin derivatives.[12,13] Among the isomers of these Mn porphyrins, most of the heterogenization work is centered on **(3)** and **MnP6**, given their traditionally easier preparation routes and commercial availability.

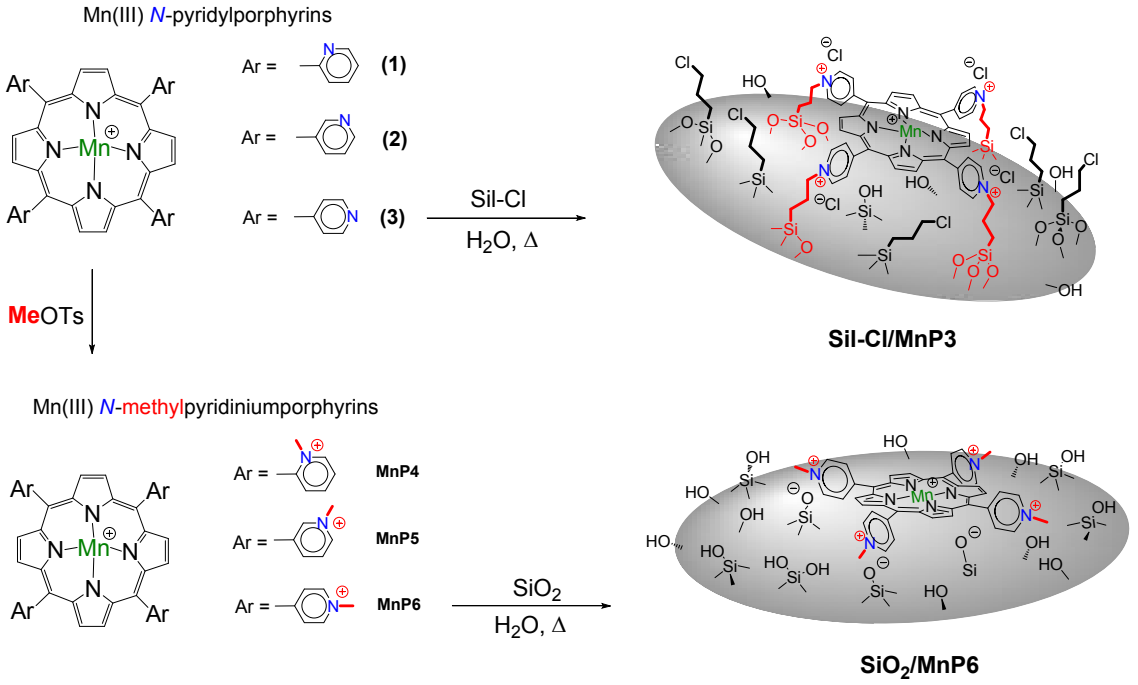


**Figure 1**. Schematic representation of the two classes of catalysts prepared and used in this work: in situ derivatization of neutral Mn porphyrin **(3)** by 3-chloropropyl-functionalized silica gel (**Sil-Cl**) to yield **Sil-Cl/MnP3** (related **(1)** and **(2)** isomers were anchored similarly); methyl tosylate (MeOTs) derivatization of (3) to yield cationic Mn porphyrin **MnP6** followed by immobilization on **silica gel**

(**$SiO_2$**) to yield **$SiO_2$/MnP6** (related **MnP4** and **MnP5** isomers were anchored similarly).

Neutral Mn(III) *meso*-tetrakis(2-, 3-, or 4-pyridyl)porphyrins **(1)**, **(2)**, **(3)** are simple first-generation Mn porphyrins amenable to immobilization on haloalkane-functionalized materials through covalent bonding between the porphyrin pyridyl moieties and the support-based pendant organic halides, generating a cationic *N*-alkylpyridinium moiety of a **MnPY**-type structure with halide as counter-ion.[1,14,15] Thus, **(3)** has been successfully anchored on iodopropyl- and chloropropyl-functionalized silica gel (Sil-I and Sil-Cl, respectively)[14,15] or chloropropyl silica-coated magnetic nanoparticles[16] for alkene epoxidations and alkane hydroxylations. **(3)** supported on chloromethylated polystyrene yielded suitable catalysts for alkene epoxidation, alkane oxidation, sulfides oxidation, and carboxylic acid decarboxylation.[17-19] Of note, the Fe(III) analogue of **(3)** was immobilized on Sil-Cl and chloropropyl-functionalized Santa Barbara Amorphous No 15 mesoporous silica (SBA-15Cl) for the oxidative degradation of pentabromophenol.[20]

Mn(III) *N*-methylpyridiniumporphyrins (**MnPY, Y = 4, 5, 6**) are the simplest second-generation Mn porphyrins derived from **(1)**, **(2)**, and **(3)**, respectively (Fig. 1). They are a class of water-soluble cationic MnPs considerably more studied in catalysis than their neutral precursors **(1)**, **(2)**, **(3)**. Their immobilization on inert supports may be readily achieved by electrostatic interactions between the **MnPY** permanent positive pyridinium charges and a negative support surface.[3,12,21,] **MnPY**-based oxidative heterogenized catalysts have been prepared by anchoring theses cationic MnPs on supports, such as, non-modified amorphous silica gel,[12,22] imidazole- or- sulfonato-functionalized amorphous silica[23], Mobil Composition Matter No 41 (MCM-41) and Santa Barbara Amorphous No 15 (SBA-15) mesoporous silica,[1,3,24] amorphous- or hexagonal mesoporous silica (HMS)-coated magnetic nanoparticles,[3,25] and clays.[21,26] As compared to the corresponding homogenous systems, heterogenization of **MnP6** yielded generally better oxidation catalysts.[12,24,26]

Recently, a joint effort between our group and Nakagaki's group[1] resulted in 2 classes of mesoporous SBA-15-based materials exploiting these Mn porphyrins, i.e., **(1)**, **(2)**, and **(3)**, covalently derivatized by and heterogenized on

chloropropyl-functionalized mesoporous SBA-15 silica (**SBA-15Cl/MnPY**) and **MnPY** isomers electrostatically immobilized on non-functionalized mesoporous SBA-15 silica (**SBA-15/MnPY**). These materials were able to catalyze the cyclohexane (Cy-H) oxidation to cyclohexanol (Cy-ol) and cyclohexanone (Cy-one) by iodosylbenzene (PhIO) with moderate yields, good selectivity toward alcohol, and excellent recyclability. Cyclohexane and cyclohexanol are well-studied substrates for model oxidation reactions and of industrial and economic relevance[27-30] to the production of adipic acid and caprolactam, which are, in turn, used for the manufacture of nylons (nylon-66 and nylon-6).[27-29]

Herein we simplified and extended the scope of these heterogenized catalytic systems by replacing SBA-15-type silicas with cheaper, ordinary, column chromatography grade, amorphous silica gel as inert supports, to yield the corresponding classes of materials containing covalently bound cationic complexes (**SiI-Cl/MnPY, Y = 1, 2, 3**) and electrostatically immobilized cationic **MnPY** complexes (**$SiO_2$/MnPY, Y = 4, 5, 6**) (Fig. 1). Given the low cost and widespread availability of chromatographic silica in chemistry laboratories, these new **SiI-Cl/MnPY** and **$SiO_2$/MnPY** materials should be of broader interest and greater accessibility for oxidation catalysis than our previously reported SBA-15-based systems. Neutral **(1)**, **(2)**, and **(3)** and cationic MnPYs are the Mn porphyrin sources for the preparation of these heterogenized catalysts. Despite their different chemical nature prior to immobilization, the final porphyrinoid compounds supported on both SiI-Cl and $SiO_2$ surfaces are all MnPY-type, cationic Mn(III) *N*-alkylpyridylporphyrins (**SiI-Cl/MnPY** and **$SiO_2$/MnPY**, Fig.1).

All six solids were investigated as catalysts for PhIO-oxidation of cyclic alkanes (cyclohexane and adamantane) and a linear alkane (n-heptane). The oxidation of cyclohexanol to cyclohexanone was also investigated as a control reaction. The impact of the materials on catalytic efficiency, selectivity, and recyclability were also addressed with respect to: 1) the effect of MnP heterogenization (vs. homogenous systems); 2) the nature of the immobilized Mn porphyrin isomers, 3) catalyst oxidative stability; and 4) some hints on the effects of the support (**$SiO_2$** vs. **SiI-Cl**). Additionally, direct comparisons on the Cy-H oxidation data with the corresponding literature mesoporous SBA-15 silica systems[1] were undertaken.

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# Experimental

## General Information

All reagents and solvents were of commercial, high purity grade and detailed in the Electronic Supplementary Information (ESI, Section S1). Silica gel for column chromatography (**$SiO_2$**, high-purity grade, particle size of 70 230 mesh, median pore diameter 60 Å, Aldrich) was activated as described elsewhere.[31] **SiI-Cl** was prepared using a slightly modified literature procedure[32] and characterized[3,12,16-23,25,26,31,33-36] as described in ESI (Sections S2 and S3). Complexes **(1)**, **(2)**, **(3)**, and **MnPY** (**Y = 4, 5, 6**) were prepared by literature routes.[4,37,38-40] The isolated complexes in the chloride form were chromatographically and spectroscopically identical to the samples used in our previous study[1] to those reported elsewhere.[4,5,41,38,42-44] Tosylate ($OTs^-$) salts of **MnPY** (**Y = 4, 5, 6**) were prepared by ion exchange chromatography.[45] Details on MnP synthesis and characterization are given in ESI (Section S4 and S5). Iodosylbenzene (PhIO) was prepared from (diacetoxyiodo)benzene ($PhI(OAc)_2$, Aldrich) as reported elsewhere.[46] PhIO was stored under refrigeration and its active oxygen content was determined periodically by iodometry. All equipment for analytical and physical measurements are given in ESI (Section S1).

## Preparation of SiI-Cl/MnPY (Y = 1, 2, 3) materials

The detailed preparations of these materials are given in ESI (Section S6). Briefly, 19.55 μmol of **(1)** (as a 0.405 mmol $L^{-1}$ aqueous solution) and 5.00 g of **SiI-Cl** were refluxed under mechanical stirring for 24 h until a full discoloration of the supernatant and a darkening of the solids were observed. The suspension was filtered and the solid was washed with small portions of $H_2O$ until the presence of MnP in the washings was not detected by UV/VIS spectroscopy; the washing procedure was repeated with MeOH, EtOH, and $CHCl_3$ (in this order). All washings were collected to allow for the spectrophotometric determination of non-immobilized **(1)**. The resulting solid was oven dried at 80 $^0$C for 24 h to yield 4.86 g of **SiI-Cl/MnP1** as a light orange material. The amount of Mn porphyrin immobilized onto **SiI-Cl** was determined indirectly by analyzing spetrophotometrically the recovered Mn porphyrin in reaction supernatant and washing solutions as reported elsewhere.[1-3] Mn porphyrin loading (in μmol MnP

per g of **SiI-Cl**) was calculated as the ratio between the immobilized amount of MnP and the starting mass of **SiI-Cl**. The immobilization yield was defined as the ratio between the amounts of immobilized versus starting MnP. Preparations of **SiI-Cl/MnP2** and **SiI-Cl/MnP3** as light green solids were carried out similarly (see ESI, Section S6 for details).

These reactions were repeated by different coauthors, using independently prepared samples, to check for reproducibility. No apparent differences were observed between corresponding **SiI-Cl/MnPY (Y = 1, 2, 3)** batches.

**Preparation of $SiO_2$/MnPY (Y = 4, 5, 6) materials**

The synthesis and workup procedures for the electrostatic heterogenization of the chloride salts of cationic **MnPY** isomers (**Y = 4, 5, 6**) onto **$SiO_2$** were similar to that described for the **SiI-Cl/MnPY** materials, except that the nature of the starting reagents were changed and the reaction time was shortened to 3 h (see ESI, Section S7, for details). MnPY loadings and immobilization yields were determined as described above.

**Oxidation reactions**

A detailed description of the methodology used for the oxidation reactions is given in ESI (Sections S8 and S9). Briefly, 2 mL vials were charged with predefined amounts of PhIO, catalyst, 1:1 MeCN:$CHCl_3$ solvent, and substrate, and sealed with a teflon/silicone septum and a screw cap. The oxidation reactions were carried out at room temperature (*ca.* 26 ºC), under air, in the absence of light, with magnetic stirring. The reactions were quenched at 90 min with 50 µL of a saturated sodium tetraborate and sodium sulfite aqueous solution (see ESI, Section S9). Then, 50 µL of a 28 mmol $L^{-1}$ solution of a GC internal standard in MeCN:$CHCl_3$ (1:1, v/v) was added. The products of the reactions were quantified by gas chromatography (GC). Bromobenzene (PhBr) was used as internal standard for the reactions with cyclohexane, cyclohexanol, and adamantane as substrates, while 1-octanol was used in the reactions of n-heptane oxidation.The reported yields for all products represent an average of least three replicates and were calculated based on the initial amount of PhIO (limiting reactant), considering the following stoichiometry: 1 mol of PhIO per mol of alcohol and 2

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mols of PhIO per mol of aldehyde or ketones.[1,4,12] For the homogeneous systems (using non-immobilized MnP), MnP destruction (bleaching) was determined spectrophotometrically after quenching the reaction.

For the recycling studies, the solid catalysts were recovered by centrifugation, washed with $CHCl_3$, EtOH, MeOH, and $H_2O$ (in this order), dried at 80 ºC for 6 h, and, then, reused in a new oxidation run. The reaction media and collected washings were analyzed by UV/VIS spectroscopy to verify whether there was leaching of MnPs from the solid catalysts.

The control reactions were carried out in the absence of catalysts but containing (i) PhIO+substrate+solvent, (ii) support+substrate+solvent (labeled **SiI-Cl** or **$SiO_2$** entries), (iii) supports+PhIO+substrate+solvent (labeled **$SiO_2$**/PhIO or **SiI-Cl**/PhIO entries).

## Results and discussion

### Characterization of SiI-Cl and $SiO_2$ supports

**SiI-Cl** was synthesized by chemical functionalization of chromatographic grade amorphous silica gel (**$SiO_2$**) with CPTS by the heterogeneous route.[32] The amount of choropropyl moieties on the silica surface was estimated by elemental analysis of carbon (3.72%) and chlorine (2.91%), which is consistent with a functionalization of 930 μmol $g^{-1}$, considering the a stoichiometry of three carbon atoms per chlorine atom. Both **SiI-Cl** and **$SiO_2$** were also characterized by fourier-transform infrared spectroscopy, thermogravimetric analysis, textural analyses, scanning electron microscopy, transmission electron microscopy, and $^{29}Si$ and $^{13}C$ nuclear magnetic resonance spectroscopies. The results agree with literature data and the corresponding discussions are presented in ESI (Section S3).

### Preparation of SiI-Cl/MnPY (Y = 1, 2, 3) and $SiO_2$/MnPY (Y = 4, 5, 6).

Two classes of heterogenized catalysts were prepared either by in situ derivatization and covalent immobilization of **(1)**, **(2)**, or **(3)** on **SiI-Cl** to yield **SiI-Cl/MnPY** catalysts (Fig. 1), or by electrostatic immobilization of **MnPY** (**Y = 4, 5, 6**) on **$SiO_2$** to yield **$SiO_2$/MnPY** catalysts (Fig. 1). The immobilization of MnPX on SiI-Cl explores the quaternization of the *N*-pyridyl moieties of MnPX directly

by the surface chloropropyl groups of Sil-Cl, mimicking, thus, a regular, organic halide-based alkylating agent (Fig. 1). Conversely, for the immobilization process of MnPY onto $SiO_2$, MnPX was initially quaternized *via* *N*-pyridyl methylation to yield MnPY,[38,40] which was then immobilized onto $SiO_2$ by exploring the cationic nature of the MnPY *N*-methylpyridinium moieties and the anionic nature of $SiO_2$ surface.[1,2,12,13]

The MnP immobilization yields and the MnP loadings on **Sil-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) were calculated by the difference between the initial amount of MnP used in the reaction and the amount of unreacted MnP recovered in the reaction supernatant and washings (Table 1). The amount of unreacted, recovered MnP in the various washings was determined spectrophotometrically, as in related systems.[1-3] Attempts to quantify MnP in the solids by UV/VIS (by destroying the silica matrix with aqueous NaOH) or directly by diffuse reflectance UV/VIS (DR-UV/VIS) were unsuccessful. Attempts to quantify Mn content by atomic absorption spectroscopy gave unreliable results in our hands so far, most likely due to unoptimized method for sample treatment.

**Table 1.** Isolation yields, MnP immobilization yields and MnP loadings related to the **Sil-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) solids.

| Solids | Isolation yield /% | Immobilization yield /%[a] | MnP Loading /μmol $g^{-1}$ [a] |
|---|---|---|---|
| Sil-Cl/MnP1 | 97 | 92±5 | 4.3±0.9 |
| Sil-Cl/MnP2 | 98 | 90±3 | 4.1±0.1 |
| Sil-Cl/MnP3 | 98 | 97±2 | 5.9±0.9 |
| $SiO_2$/MnP4 | ~100 | ~100 | 5.2 |
| $SiO_2$/MnP5 | ~100 | ~100 | 4.6 |
| $SiO_2$/MnP6 | 99 | ~100 | 5.0 |

[a] mean and standard deviation.

In situ derivatization and covalent immobilization yield of MnPs onto Sil-Cl were on average greater than 90%, whereas electrostatic immobilization of MnPY onto $SiO_2$ was essentially quantitative (Table 1), which is in direct contrast with the related SBA-15 and HMS systems where immobilization yields were ~60% and ~28% on average, respectively, for similar MnP loadings.[1-3] The

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immobilization yields of *ca.* 100% for the three cationic MnPY (Y = 4, 5, 6) isomers indicates that higher loads of MnP on $SiO_2$ may be achieved, but this was not investigated herein; materials of high metalloporphyrin loads have not resulted in better oxidation catalysts in previous studies.[13]

Immobilization of neutral **(1), (2), (3)** onto non-modified silica gel (**$SiO_2$**), which lacks the possibility for in situ covalent derivatization of these Mn porphyrins, yielded MnP-containing materials of little interest, as weakly adsorbed **(1), (2), or (3)** were essentially fully leached with a variety of organic solvents (MeOH, EtOH, MeCN, and mixtures with $CH_2Cl_2$ or $CHCl_3$); this is consistent with the reported behavior of these neutral MnPs toward regular chromatographic $SiO_2$ and related data on mesoporous SBA-15 silica.[1,4] Conversely, all attempts to release MnP from **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) materials *via* extraction with either water or organic solvents (MeOH, MeCN, EtOH, $CHCl_3$) were unsuccessful, revealing the stability of these materials against MnP leaching. Release of MnP from these materials was achieved only under drastic conditions *via* silica matrix dissolution with concentrated aqueous NaOH. The present study was focused, thus, on the **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) materials.

The presence of MnPs on **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) was confirmed by diffuse reflectance UV/VIS (DR-UV/VIS) of the materials, given the high molar absorptivity of MnPs (see ESI, Section S4 and S5) and their characteristic spectral features.[9] Other routine characterization techniques as elemental analysis, infrared spectroscopy, and thermoanalysis were not able to detect the anchored MnPs due to their low loadings of about 0.3% (w/w). These limitations are consistent with previous heterogenized MnP studies.[2,13,21]

The DR-UV/VIS spectra of the three **SiI-Cl/MnPY** (**Y = 1, 2, 3**) solids share similar spectral profiles with the corresponding non-immobilized **(1), (2), (3)** isomers (Fig. 2), which indicates that the structure of the porphyrin ring was preserved during immobilization. Indeed, alkylation reactions of the peripheral pyridyl moieties of Mn(III) *N*-pyridylporphyrins are accompanied by little spectral profile changes (see ESI, Section S4). This behavior was also observed in our previous work with mesoporous SBA-15 silica as support.[1] Only **SiI-Cl/MnP3**, which incorporates the *para* isomer, showed a redshift of the Soret band (Fig.

2e), possibly due to a perturbation of the π-electrons of the porphyrin macrocycle provoked by the easier interaction with the support.[21,47,48]

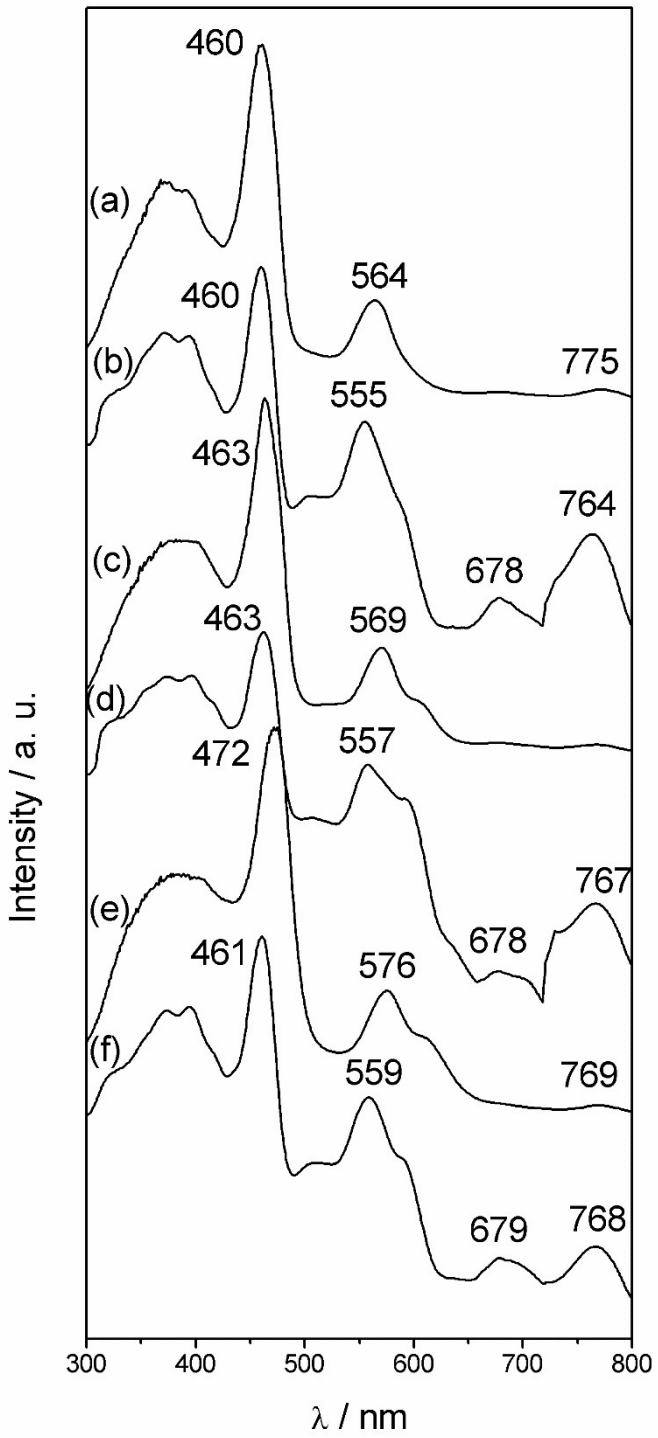


**Figure 2.** DR-UV/VIS spectra of the (a) **SiI-Cl/MnP1**, (b) **(1)**, (c) **SiI-Cl/MnP2**, (d) **(2)**, (e) **SiI-Cl/MnP3**, and (f) **(3)**. The spectra of non-immobilized MnPs were recorded as solids dispersed on barium sulfate.

The DR-UV/VIS spectra of the three **$SiO_2$/MnPY** (**Y = 4, 5, 6**) solids are showed in Fig. 3. Again, the Soret band and the Q bands on these spectra were similar to those of the corresponding non-supported **MnPY**, indicating that the overall electronic structure of these systems is little affected by the electrostatic immobilization. This is consistent with previous observations on mesoporous SBA-15 and HMS systems.[1-3]

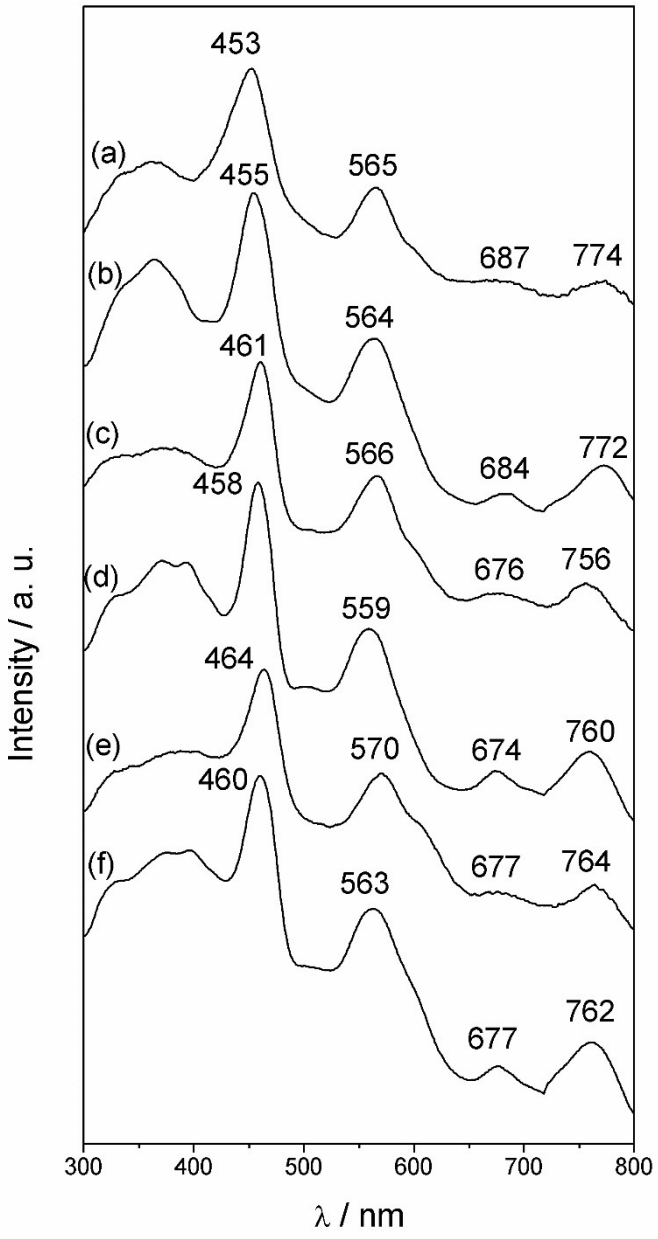


**Figure 3.** DR-UV/VIS spectra of (a) **$SiO_2$/MnP4,** (b) **MnP4**, (c) **$SiO_2$/MnP5**, (d) **MnP5**, (e) **$SiO_2$/MnP6**, and (f) **MnP6**. The spectra of non-immobilized MnPs were recorded as solids dispersed on barium sulfate.

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## Catalytic biomimetic oxidations

The oxyfunctionalization of alkanes by C-H bond activation and/or selective oxidation under mild conditions remains a challenge in academia and industry and a much sought-after subject in catalysis.[28-30,49-52] The efficiency of **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) materials as catalysts for C–H activation *via* alkane hydroxylation was evaluated in typical metalloporphyrin-based model reactions using cyclohexane, n-heptane, and adamantane as substrates and iodosylbenzene (PhIO) as oxidant (Fig. 4). Oxidation of cyclohexanol was also carried out to uncover some features of ketone formation in these systems. In all cases, reactions with the corresponding non-immobilized MnPs (**(1)**, **(2)**, **(3)** or **MnPY**) under homogeneous conditions were carried out to evaluate the role played by the support on catalytic efficiency and reaction selectivity. Chloride salts of the cationic **MnPY** (**X = 4, 5, 6**) isomers are, however, poorly soluble in 1:1 (v/v) MeCN:$CHCl_3$ solvent mixture used in the oxidation reactions. Thus, the corresponding tosylate salts of **MnPY**, which are soluble in MeCN:$CHCl_3$ solvent mixtures, were used in the homogeneous reactions. Herein, the product yields for alkane oxidations were calculated based on the initial amount of PhIO (limiting reactant), considering a 1:1 stoichiometry for alcohols and 2:1 stoichiometry for aldehyde and ketones.[1,4,12]

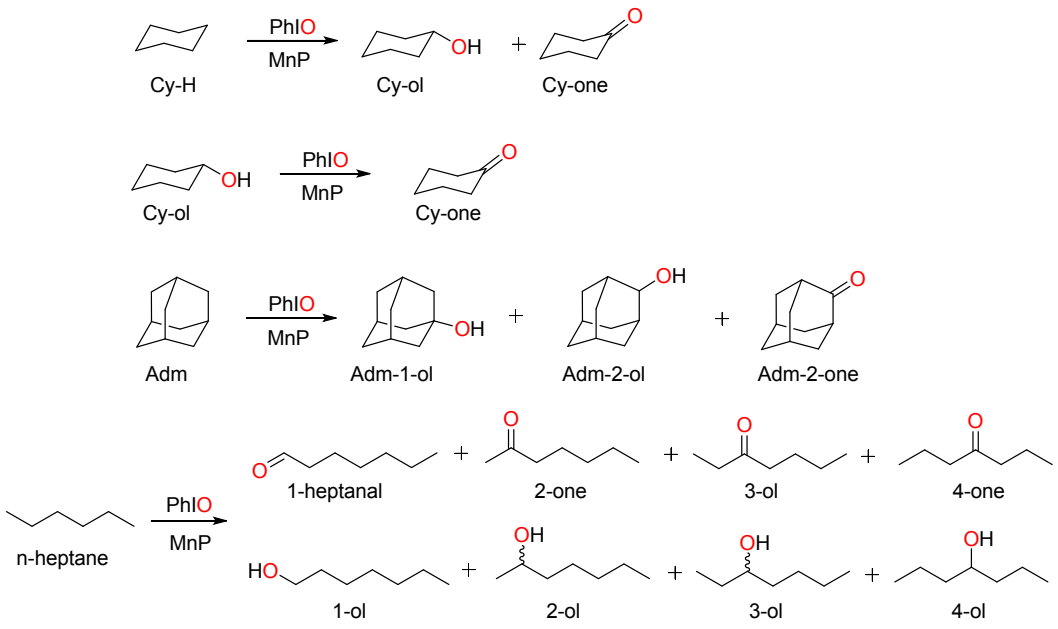


**Figure 4.** Reaction schemes for the oxidation of cyclohexane (Cy-H), cyclohexanol (Cy-ol), n-heptane, and adamantane (Adm) catalyzed by homogeneous and immobilized MnPs studied in this work.

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## Cyclohexane as model substrate

Cyclohexanol (Cy-ol) and cyclohexanone (Cy-one) yields and Cy-ol selectivity for cyclohexane (Cy-H) oxidation catalyzed by the heterogenized materials **Sil-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) for three independent catalytic cycles are presented in Figures 5 and 6, respectively. The data for all control reactions, including the homogeneous systems with the non-immobilized Mn porphyrins, are given in ESI (Section 10, Fig. S15). All reactions were carried out using a MnP/PhIO/Cy-H molar ratio of 1:10:4628. In the control reactions of Cy-H with PhIO alone, **$SiO_2$**/PhIO, or **Sil-Cl**/PhIO, a low total yield (Cy-ol + Cy-one) of about 2% was observed, indicating that the supports $SiO_2$ or Sil-Cl were unable to catalyze efficiently the PhIO-oxidation of cyclohexane in the absence of Mn porphyrin (ESI, Section 10, Fig. S15).

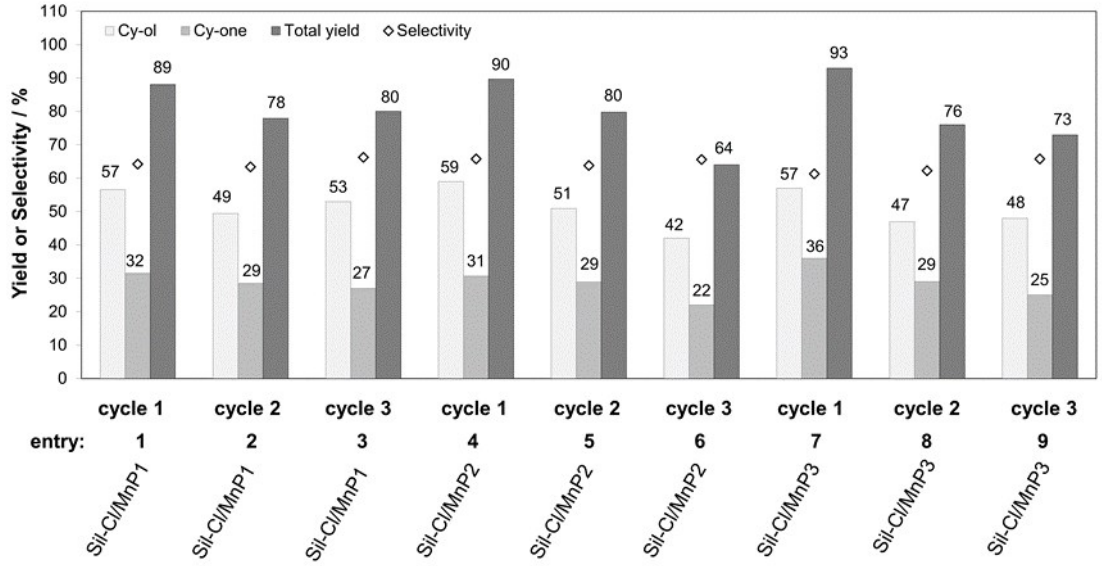


**Figure 5**. First (cycle 1), second (cycle 2), and third (cycle 3) cycles of cyclohexane oxidation reactions by PhIO catalyzed by the supported materials **Sil-Cl/MnPY** (**Y = 1, 2, 3**). After completion of each cycle, the catalysts were recovery and reused. Reactions conditions: MnP/PhIO/Cy-H molar ratio of 1:10:4628 (0.2 μmol of MnP, 2.0 μmol of PhIO, 930.0 μmol of Cy-H), MeCN:$CHCl_3$ mixture (1:1, v/v) as solvent, magnetic stirring, 26 ºC, 90 min, and air atmosphere. Yields calculated based on the starting PhIO. 2 mol of PhIO were considered for the formation of 1 mol of Cy-one. Total yield = Cy-ol + Cy-one. Selectivity = 100 x [Cy-ol/(Cy-ol + Cy-one)].

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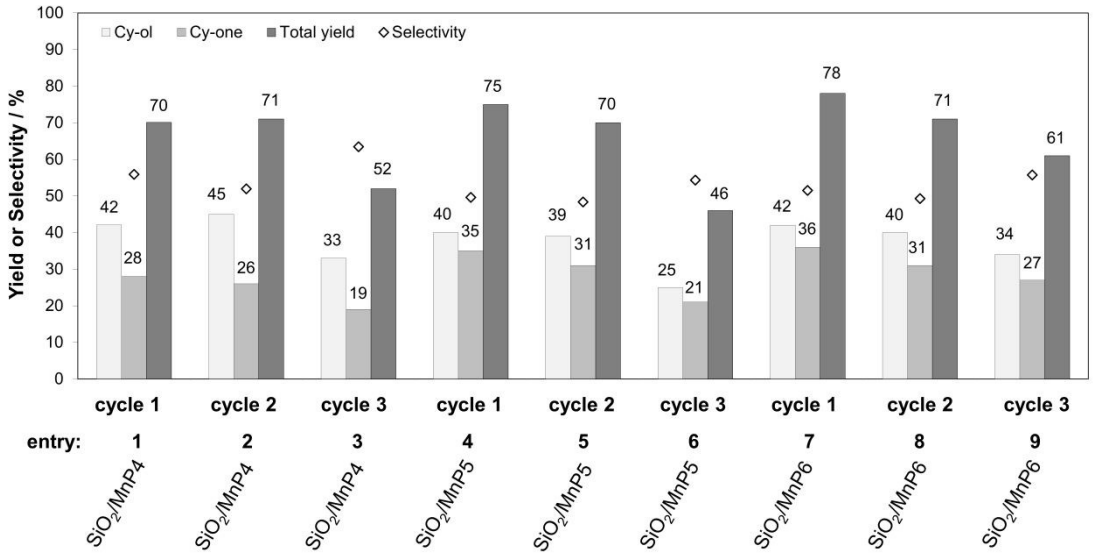


**Figure 6**. First (cycle 1), second (cycle 2), and third (cycle 3) cycles of cyclohexane oxidation reactions by PhIO catalyzed by the supported materials **$SiO_2$/MnPY** (**Y = 4, 5, 6**). After completion of each cycle, the catalysts were recovery and reused. The reaction conditions were identical to those of Figure 5. Yields calculated based on the starting PhIO. 2 mol of PhIO were considered for the formation of 1 mol of Cy-one. Total yield = Cy-ol + Cy-one. Selectivity = 100 x [Cy-ol/(Cy-ol + Cy-one)].

A comparison between the supported MnPs systems (on either **SiI-Cl** or **$SiO_2$**) (Figs. 5 and 6) with their corresponding non-immobilized MnP counterparts (ESI, Fig. S15) reveals a considerable increase in the total oxidation yield (Cy-ol + Cy-one) for all heterogenized systems **SiI-Cl/MnPY** or **$SiO_2$/MnPY**. A likely explanation, which is supported by recycling experiments (see below) is related to the increased oxidative stability of MnPs upon immobilization on either **SiI-Cl/MnPY** (**Y = 1, 2, 3**) or **$SiO_2$/MnPY** (**Y = 4, 5, 6**) materials as compared with their corresponding homogeneous systems. Of note, **(1), (2), (3)** and **MnPY** (**Y = 4, 5, 6**) in homogeneous systems showed oxidative destruction (bleaching) of about 70%, as determined spectrophotometrically in the end of the reactions. The role of inert supports in the increased oxidative stability of MnPs is well documented.[12,26,53,54]

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The highest Cy-ol selectivities were observed in the **SiI-Cl/MnPY** (**Y = 1, 2, 3**) solids and this may also be related to a role played by the nature of the support. **SiI-Cl/MnPY** solids (Fig. 5, entries 1, 4, and 7) showed an overall 10% higher selectivity and 20% higher total yield than **$SiO_2$/MnPY** solids (Fig. 6, entries 1, 4, and 7). As suggested in the SBA-15 related systems,[1] this may tentatively be related to the lipophilic character of **SiI-Cl** (given the excess surface chloropropyl moieties) as compared to the more polar nature of unmodified **$SiO_2$**. This may facilitate the access of apolar Cy-H substrate) and the replacement of polar Cy-ol product from the catalytic center, resembling the protein role in cytochromes P450.[11] Proper experiments need, however, to be designed and carried out to unambiguously assess this surface lipophilic effects on catalysis.

**SiI-Cl/MnPY** (**Y= 1, 2, 3**) catalysts based on cheap, ordinary, chromatographic silica were more efficient and equally selective for cyclohexane oxidation than the more elaborate SBA-15Cl-based catalyst counterparts.[1] The total oxidation yields achieved with **SiI-Cl/MnP1**, **SiI-Cl/MnP2**, and **SiI-Cl/MnP3** were of 89, 91, and 93%, respectively (Fig. 5, entries 1, 4, and 7), which contrasts with those of 54, 62, and 72% reported for SBA-15Cl-based catalysts SBA-15Cl/MnP1, SBA-15Cl/MnP2, and SBA-15Cl/MnP3, respectively.[1] This difference in overall efficiency between **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and SBA-15Cl/MnPY (Y = 1, 2, 3) may be related to the localization of the MnPs on the supports. Lower yields with mesoporous SBA-15Cl/MnPY (Y = 1, 2, 3) materials have suggested that MnP is probably buried inside the mesoporous, hindering access of substrate and oxidant.[1] Conversely, for **SiI-Cl/MnPY** catalysts, we speculate that MnPs are predominantly exposed on the material surface, favoring the catalytic reaction.[55-57] A similar behavior was observed with the **$SiO_2$/MnPY** catalysts when compared to their analogous SBA-15/MnPY materials: total yields achieved with **$SiO_2$/MnPY** solids (aprox. 74%, Fig. 6, entries 1, 4, and 7) were remarkably higher than those with SBA-15/MnPY materials (aprox. 45%).[1]

**SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) were evaluated in recycling reactions (Fig. 5 and 6). All immobilized catalysts maintained a high overall yield, particularly in cycle 2, with some loss in efficiency on cycle 3. The Cy-ol selectivity of the reactions were essentially unaffected, at least during 3

cycles. These results are in direct contrast to those of SBA-15 systems, where overall yields were reduced by aprox. 50% in the second cycle already.[1]

**SiI-CI/MnP1** material was the most robust catalyst among all supported MnPs, showing an efficiency loss of only 10% (Fig. 5, entries 1-3) during the three oxidation reaction cycles. **$SiO_2$/MnP4** and **$SiO_2$/MnP6** catalysts had an efficiency loss of 18% and 16%, respectively (Fig. 6, entries 4-6 and 7-9). Conversely, **$SiO_2$/MnP5** catalyst showed the largest loss (*ca.* 29%) in efficiency by the end of the third reaction cycle (Fig. 6, entries 1-3). The decrease in catalytic efficiency throughout the recycling reactions was ascribed to oxidative destruction of supported MnP (bleaching) along the oxidation cycles, as in other related systems.[58,59] MnP leaching was considered of lower impact (if any) as no sign of MnP in the reaction supernatant or catalyst washing solvents has been detected by UV/VIS spectroscopy.

The oxidative stability of the heterogenized catalysts (**SiI-CI/MnPY** and **$SiO_2$/MnPY**) was evaluated using a more drastic condition with a PhIO/MnP molar ratio of 100 in the first reaction cycle (cycle A) followed by the standard reaction condition with a PhIO/MnP molar ratio of 10 in the second reaction cycle (cycle B), as similarly carried out in the literature SBA-15-based systems.[1] The non-immobilized catalysts were also studied under homogeneous conditions with PhIO/MnP molar ratio of 100 (cycle A) for comparison with the corresponding heterogenized systems. All data for these reactions are presented in ESI (Section 11, Figs. S16 and S17). The PhIO, **SiI-CI**/PhIO, and **$SiO_2$**/PhIO control systems (without MnP) showed less than 1% Cy-ol and Cy-one formation.

All catalysts showed low catalytic efficiency with a high PhIO/MnP molar ratio of 100 (Cycle A; ESI Fig. S16). Upon catalyst reuse under standard PhIO/MnP ratio of 10 (Cycle B; ESI Fig. S17), all catalysts recovered, at least partially, the efficiency recorded in Figs. 5 and 6. A more general discussion and some hypotheses[1,21,54,60-63] on these results are presented in ESI (Section 11). Briefly, they indicate that (a) the materials are to some extent reasonably stable against oxidative degradation under large excess PhIO; (b) SiO2-based materials were more resist than the corresponding SiI-Cl ones, in agreement with previous data on the SBA-15-based catalysts;[1] (c) the remarkable stability of **SiI-CI/MnP1** and **$SiO_2$/MnP4** may be associated with the recurring porphyrin-based biomimetic feature known as “the *ortho* effect”,[4,38,54,64-66] in which the *ortho*,

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surface-derived 2-*N*-propylpiridinium groups on **SiI-Cl/MnP1** (Fig. 1) and the *ortho* 2-*N*-methylpiridinium groups on **$SiO_2$/MnP4** (Fig. 1) may hamper oxidative attack to vulnerable porphyrin *meso* positions.

**Cyclohexanol as model substrate**

**SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) were evaluated as catalysts in the oxidation of Cy-ol to Cy-one by PhIO as a means to verify whether Cy-one produced during the cyclohexane oxidation could result from Cy-ol product being further oxidized. In these studies using Cy-ol as substrate, the amount of initial Cy-ol was established considering the maximum theoretical concentration of Cy-ol corresponding to a 100% yield in the cyclohexane oxidations, that is, a stoichiometric molar Cy-ol/MnP of 10:1. Cy-one yields were based on the initial PhIO (limiting reactant), considering 1 mol of PhIO for the formation of 1 mol of Cy-one.

All materials were able to catalyze the Cy-ol oxidation to Cy-one to some extent (Fig. 7), indicating, thus, that the ketone formed in the cyclohexane oxidation may be derived from Cy-ol product reoxidation. Metalloporphyrin-catalyzed oxidation of alcohol to ketones has been addressed.[67-69] However, the formation of ketone in alkane oxidations *via* alternative mechanisms, involving radical reactions[55,70,71] cannot be completely ruled out.[72] Regardless of the mechanism(s), in the Cy-ol oxidations catalyzed by **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**), the Cy-one yields were relatively high and comparable to those of the cyclohexane oxidation (Fig. 5). Among these systems, **SiI-Cl/MnP1** and **SiI-Cl/MnP3** showed slightly better catalytic performances than the others (Fig. 7, entry 4 and 6).

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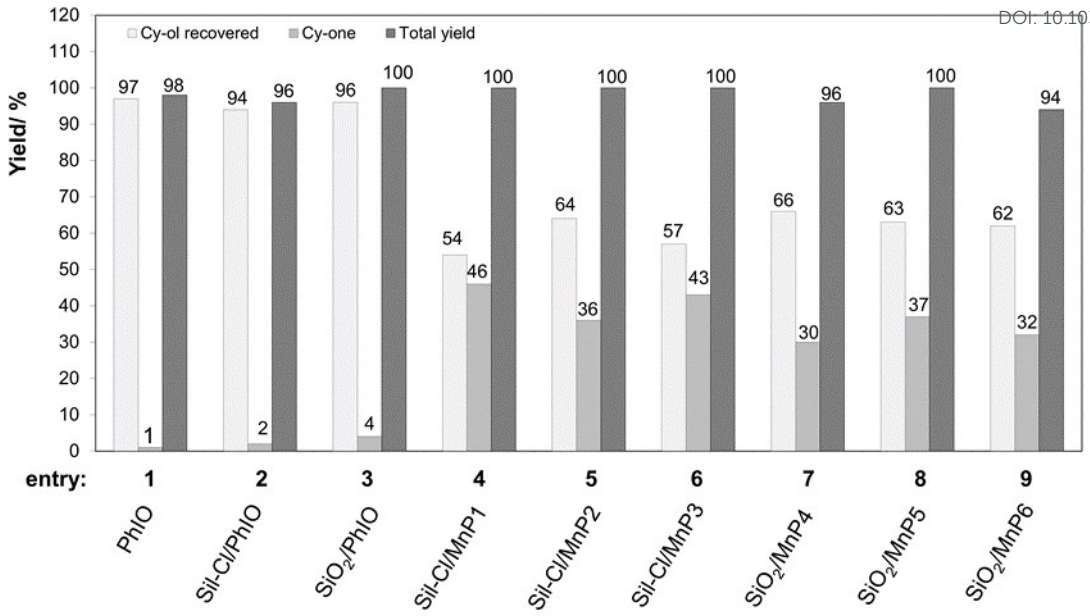


**Figure 7.** Cyclohexanol oxidation by PhIO catalyzed by supported materials **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**), including the control reactions (PhIO, **SiI-Cl**/PhIO, and **$SiO_2$**/PhIO). The reaction conditions were identical to those of Figure 5 except that Cy-ol replaced cyclohexane and the MnP/PhIO/Cy-ol molar ratio was of 1:10:10. Yields calculated based on the starting PhIO. 1 mol of PhIO was considered for the formation of 1 mol of Cy-one. Total yield = Cy-ol + Cy-one.

These preliminary results on Cy-ol oxidation indicate that the heterogenized MnP materials **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) are potentially effective catalysts for alcohol oxidation and deserve, thus, further investigation.[73,74]

**n-Heptane as model substrate**

n-Heptane is a fairly stable acyclic alkane difficult to be oxyfunctionalized due to the inertness of its C–H bonds, whose energies are higher for the primary carbons (101±1.8 kcal $mol^{-1}$) than for the secondary ones (98±1.8 kcal $mol^{-1}$).[75] The selective oxidation of linear alkanes at the primary carbons is highly sought and remains a challenge.

The heterogenized catalysts **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) were evaluated for the PhIO-oxidation reactions of n-heptane using a

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MnP/PhIO/n-heptane molar ratio of 1:10:5000. The formation of eight oxidation products (Fig. 4) were detected and independently quantified in all reactions: 1-heptanol (1-ol), 2-heptanol (2-ol), 3-heptanol (3-ol), 4-heptanol (4-ol), 1-heptanal, 2-heptanone (2-one), 3-heptanone (3-one), and 4-heptanone (4-one). No attempts were undertaken to resolve the stereochemistry of 2-ol and 3-ol. This range of oxidation product has been partially reported with related immobilized metalloporphyrin-based catalytic systems.[2,76-78] The n-heptane oxidations were evaluated for **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) catalytic efficiency, reaction chemo- and regioselectivity, and catalyst recycling. The product yields for three oxidation cycles with **SiI-Cl/MnP1** and **$SiO_2$/MnP4**, as representatives of each catalyst class, is presented in Figure 8. Data for the other materials along with the homogeneous systems are in ESI (Section 12, Figs. S18 – S20).

In the first cycle of n-heptane oxidation reactions, the control systems (PhIO, **$SiO_2$**/PhIO, and **SiI-Cl**/PhIO) led to total product yield lower than 5% (data not shown). Conversely, total oxidation yields in the 66 – 95% range with the supported catalysts **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) under heterogeneous conditions (Fig. 8 and ESI Figs. S18 and S19) were unusually high for n-heptane oxidation catalyzed by metalloporphyrin-based materials.[5,25] The high catalytic efficiency of these material is also in direct contrast with the 33 – 68% total yield range found with the non-immobilized catalysts under homogeneous conditions (ESI, Fig. S20). This substantial increase in total oxidation yield with the heterogenized catalysts **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) is likely associated with the remarkable impact of the support on stabilizing the anchored MnPs against oxidative degradation, as observed in the cyclohexane systems. Of note, non-immobilized MnPs were bleached by approx. 40% [for **(1)**, **(2)**, **(3)**] and 50% (for **MnP4**, **MnP5**, **MnP6**), respectively, during n-heptane oxidation.

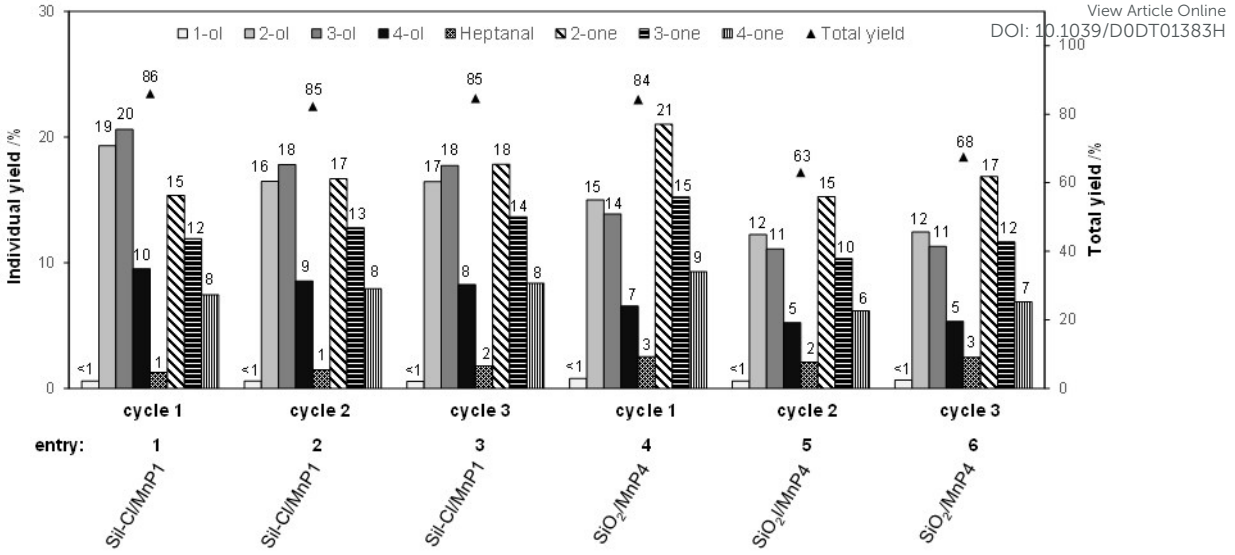


**Figure 8.** First cycle (cycle 1), second (cycle 2), and third (cycle 3) cycles of n-heptane oxidation reactions by PhIO catalyzed by the supported materials **SiI-Cl/MnP1** and **$SiO_2$/MnP4**. After completion of each cycle, the catalysts were recovery and reused. Reactions conditions: MnP/PhIO/n-heptane molar ratio of 1:10:5000 (0.2 μmol of MnP, 2.0 μmol of PhIO, 1000.0 μmol of n-heptane), MeCN:$CHCl_3$ mixture (1:1, v/v) as solvent, magnetic stirring, 26 ºC, 90 min, and air atmosphere. Yields calculated based on the starting PhIO. 2 mol of PhIO were considered for the formation of 1 mol of ketone or aldehyde. Total yield = 1-ol + 2-ol + 3-ol + 4-ol + 1-heptanal + 2-one + 3-one + 4-one.

The overall superior efficiency of **SiI-Cl/MnPY** (**Y = 1, 2, 3**) catalysts over **$SiO_2$/MnPY** (**Y = 4, 5, 6**) observed in Cy-H oxidations (Figs. 5 and 6) was more pronounced on the n-heptane systems, except that **$SiO_2$/MnP4** was as highly efficient as the **SiI-Cl/MnPY** (**Y = 1, 2, 3**) catalysts (Fig. 8 and ESI Figs. S18 and S19). Another relevant feature of these materials revealed by the n-heptane oxidations relates to the remarkable change in chemoselectivity within these two classes of catalysts (Fig. 8 and Table 2). Whereas the **$SiO_2$/MnPY** (**Y = 4, 5, 6**) materials were more selective toward the carbonyl products (ketones and aldehyde), **SiI-Cl/MnPY** (**Y = 1, 2, 3**) catalysts were more selective toward n-heptanols, corroborating once more the Cy-H data on the role played by the surface chloropropyl chain moieties of **SiI-Cl** support in the oxidation reactions. Additionally, it is worth noting that non-immobilized **(1)**, **(2)**, and **(3)** shows chemoselectivity toward carbonyl products (Table 2 and ESI Fig. S20), indicating

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that a full inversion in n-heptane oxidation chemoselectivity is observed upon MnP immobilization on the **SiI-Cl** support to yield **SiI-Cl/MnPY** (**Y = 1, 2, 3**) catalysts. As described for the Cy-H oxidation reactions, it is suggested that the chloropropyl chains on **SiI-Cl** renders **SiI-Cl/MnPY** (**Y = 1, 2, 3**) catalysts likely more lipophilic, facilitating the approach of n-heptane to the materials surface and the access to the MnP catalytic sites, thus resulting in a high chemoselectivity for alcohol. The possible role of surface chloropropyl chains in repealing n-heptanols from the catalyst active sites, preventing, thus, further oxidation to carbonyl products cannot be fully assessed or ruled out at the moment without further investigation.

**Table 2.** Chemoselectivity and Regioselectivity of n-heptane PhIO-oxidations catalyzed by **SiI-Cl/MnPY (Y = 1, 2, 3)** and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) under heterogeneous conditions or by non-immobilized MnPs under homogeneous conditions. The reaction conditions are indicated in Figure 8.

| Entry | Catalyst | Total yield /% | | Chemoselect.[c] /% | Regioselectivity[g] /% | | |
|---|---|---|---|---|---|---|---|
| | | C-OH[a] | C=O[b] | | ω-1[d] | ω-2[e] | ω-3[f] |
| 1 | **SiI-Cl/MnP1** | 50 | 36 | 58 | 34 | 32 | 33 |
| 2 | **SiI-Cl/MnP2** | 51 | 40 | 56 | 33 | 32 | 34 |
| 3 | **SiI-Cl/MnP3** | 51 | 44 | 54 | 32 | 32 | 35 |
| 4 | **$SiO_2$/MnP4** | 36 | 48 | 43 | 36 | 30 | 32 |
| 5 | **$SiO_2$/MnP5** | 24 | 42 | 36 | 34 | 30 | 34 |
| 6 | **$SiO_2$/MnP6** | 24 | 42 | 36 | 34 | 28 | 36 |
| 7 | **(1)** | 16 | 46 | 26 | 26 | 32 | 41 |
| 8 | **(2)** | 23 | 44 | 35 | 21 | 32 | 46 |
| 9 | **(3)** | 19 | 42 | 31 | 22 | 32 | 44 |
| 10 | **MnP4** | 11 | 15 | 43 | 35 | 28 | 33 |
| 11 | **MnP5** | 11 | 20 | 35 | 22 | 31 | 43 |
| 12 | **MnP6** | 15 | 18 | 45 | 32 | 32 | 35 |

[a] C-OH (alcohols) = 1-ol + 2-ol + 3-ol + 4-ol. [b] C=O (ketones + aldehyde) = 1-heptanal + 2-one + 3-one + 4-one. [c] Chemoselectivity = (C-OH)/[C-OH + C=O). [d] ω-1: sum of 2-ol and 2-one, [e] ω-2: sum of 3-ol and 3-one, [f] ω-3: sum of 4-ol and 4-one. [g] Normalized regioselectivity (ω-1) = 100 x [(2-ol + 2-one)/2]/{[(1-ol+1-heptanal)/3] + [(2-ol + 2-one)/2]

+ [(3-ol + 3-one)/2] + (4-ol + 4-one)}, normalized regioselectivity (ω-2) and normalized regioselectivity (ω-3) were calculated analogously.

n-Heptane is a substrate that allows also for the evaluation of regioselectivity associated with the catalyzed oxidations. Considering that n-heptane primary carbons ω (C1 and C7 positions) have a total of 6 C-H bonds, the secondary carbons ω-1 (C2 and C6 positions) and ω-2 (C3 and C5 positions) have a total of 8 C-H bonds, and central secondary carbon ω-3 (C4 position) has only 2 C-H bonds, all regioselectivities associated with ω, ω-1, ω-2, and ω-3 carbons were normalized to account for the statistical probability of n-heptane oxidation on each position (Table 2). The regioselectivity of oxidations catalyzed by the heterogenized catalysts **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) was under thermodynamic control, that is, oxyfunctionalization of the primary carbons was very low (ω regioselectivity was lower than 2% in all cases) and ω-1 (sum of 2-ol and 2-one), ω-2 (sum of 3-ol and 3-one), and ω-3 (sum of 4-ol and 4-one) regioselectivities were nearly the same, indicating that there was no oxidation preference among the secondary carbons. Thus, the silica support or surface organic chain of **SiI-Cl** did not exert any significant influence (if any) in guiding the orientation of n-heptane toward the catalytic center.

After the first oxidation cycle, the supported catalysts **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) were centrifuged, washed with $CHCl_3$, EtOH, MeOH, and $H_2O$, dried at 80 ºC for 24 h, and reused (cycle 2) under the same reaction condition as those of the first cycle (Fig. 8 and ESI Figs. S18 and S19). This process was repeated once more, giving rise to a third cycle (cycle 3) (Fig. 8 and ESI Figs. S18 and S19). The robustness of **SiI-Cl/MnP1** and **SiI-Cl/MnP3** as oxidation catalysts, as observed earlier in the cyclohexane systems, was also confirmed in the n-heptane reactions; the total oxidation yields associated with these catalysts were very high (in the 82 – 95% range) and just slightly affected by reuse for at least three oxidation cycles. The corresponding *meta* MnP isomer-based heterogenized catalysts **SiI-Cl/MnP2** and **$SiO_2$/MnP5**, however, showed considerable loss of efficiency upon recycling (ESI Fig. S18), as also observed in the cyclohexane oxidations. In general, the **SiI-Cl/MnPY** (**Y = 1, 2, 3**) catalysts were more resistant against oxidative deactivation than the corresponding **$SiO_2$/MnPY** (**Y = 4, 5, 6**) materials.

Despite the catalytic efficiency of **SiI-Cl/MnPY** (**Y = 1, 2, 3**) being little affected by catalyst recycle in n-heptane oxidations, the chemoselectivity of these reactions were compromised along the three reuses, particularly from the 1st to the 2nd cycles (Table 2, entries 1–3; and ESI Tables S4 and S5, entries 1–3). Such a selectivity decrease was not observed in cyclohexane oxidation catalyzed by these **SiI-Cl/MnPY** (**Y = 1, 2, 3**) materials. Given the closer structural similarity of the surface chloropropyl moieties to n-heptane rather than to cyclohexane, it is tempting to suggest that some partial destruction of these surface chloropropyl groups (as a somewhat competing substrate during n-heptane oxidation), may be likely responsible to decrease the lipophilicity of SiI-Cl surface. This, hence, would facilitate the access of n-heptanols to the MnP catalytic center, promoting their further oxidation to the corresponding carbonyl derivatives and, finally, compromising chemoselectivity for alcohols upon catalyst reuse. Whereas the putative cumulative oxidation of surface chloropropyl moieties would decrease chemoselectivity, it may also represent a sacrificial means to protect surface MnP against oxidative destruction, which is, thus, consistent with little effect on **SiI-Cl/MnPY** (**Y = 1, 2, 3**) catalyst efficiency upon recycling. Conversely, it is worth noting that the chemoselectivity of the n-hexane oxidations catalyzed by **$SiO_2$/MnPY** (**Y = 4, 5, 6**) remains essentially unchanged upon recycling; **$SiO_2$** support, as opposed to **SiI-Cl**, is not prone to PhIO modification and the decrease in catalyst efficiency observed with the **$SiO_2$/MnPY** (**Y = 4, 5, 6**) systems may be a result of direct surface **MnPY** degradation during reuse; this is consistent with a direct effect on efficiency, but of little impact on chemoselectivity.

Catalyst recycling exert little effect on regioselectivity of n-heptane oxidation catalyzed by **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) (Table 2 and ESI Tables S4, and S5).

**Adamantane as model substrate**

The adamantane is a substrate bulkier and conformationally more rigid than cyclohexane and n-heptane. The oxidation in its tertiary carbons results in 1-adamantanol (Adm-1-ol), whereas oxidation in its secondary carbons results in either 2-adamantanol (Adm-2-ol) or adamantanone (Adm-2-one), as depicted in Figure 4.[54,79-82]

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Figure 9 summarizes the data obtained on adamantane oxidation catalyzed by the heterogenized catalysts **SiI-CI/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) and their homogeneous MnP counterparts. Control experiments (PhIO, **SiI-CI**/PhIO, and **$SiO_2$**/PhIO) in absence of catalysts showed total oxidation yields as little as 6%. Under homogeneous conditions, **(1)**, **(2)**, and **(3)** isomers were equally efficient among themselves (45% on average; Fig. 9 entries 1-3) and more efficient than homogeneous **MnPY** (**Y = 4, 5, 6**) (25% on average, Fig. 9, entries 7-9). A considerable increase in catalytic efficiency was achieved upon heterogenization, as observed previously in the cyclohexane and n-heptane systems; total oxidation yields for adamantane oxidations catalyzed by **SiI-CI/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) ranged from 55% to 81% (Fig. 9, entries 4-6, 10-12). Such an efficiency improvement may be attributed to the role played by the support in increasing the oxidative stability of immobilized MnPs. Total oxidation yields achieved with **SiI-CI/MnPY** (**Y = 1, 2, 3**) catalysts (77% on average, Fig. 9, entries 4-6) were approx. 15% greater than those with **$SiO_2$/MnPY** (**Y = 4, 5, 6**) catalysts (62% on average, Fig. 9, entries 10-12), which may tentatively be related to the lipophilicity of **SiI-CI** surface as discussed for the cyclohexane and n-heptane oxidations.

In all systems, hydroxylation was the main reaction observed giving rise to Adm-1-ol and Adm-2-ol. Except in the **$SiO_2$/MnPY** (**Y = 4, 5, 6**) systems, in which further Adm-2-ol oxidation led to Adm-2-one in yields as low as 5% (Fig. 9, entries 10-12), the formation of ketone in all other systems was lower than 1%, if any. Whereas such small but measurable effect may perhaps be related to the hydrophilic nature of $SiO_2$ support in **$SiO_2$/MnPY** (**Y = 4, 5, 6**) catalysts, analyses of chemoselectivity were of little relevance in these adamantane-based model reactions.

Regarding reaction regioselectivity, all catalysts studied herein were selective toward hydroxylation of adamantane, chiefly at its tertiary carbon to yield Adm-1-ol, following a similar behavior reported to other non-supported and supported metalloporphyrin-based systems.[54,79-81] The high preference toward Adm-1-ol is ascribed to the lower C–H bond strength of adamantane tertiary carbon, which results in its higher reactivity.[79,82-84] In all systems, regioselectivity was normalized with respect to the statistical probability of the oxidation associate

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with the number of C–H bonds, i.e., 4 tertiary C-H bonds to yield Adm-1-ol, and 12 secondary C-H bonds to yield Adm-2-ol and Adm-2-one.

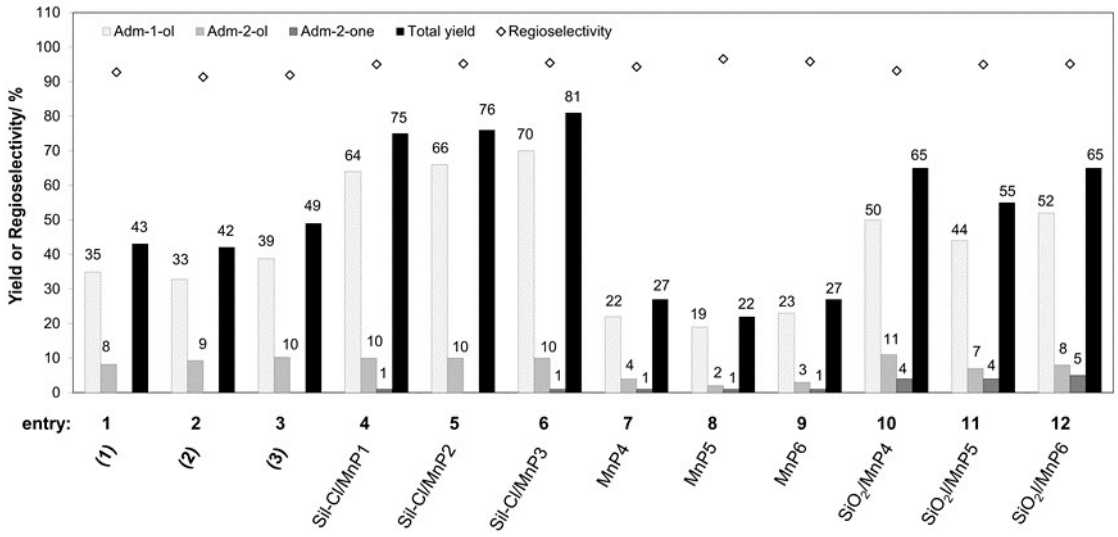


**Figure 9.** First cycle (cycle 1) of adamantane oxidation by PhIO catalyzed by the non-immobilized MnPs and the supported materials **SiI-Cl/MnPY (Y = 1**, **2**, **3)** and **$SiO_2$/MnPY** (**Y = 4**, **5**, **6**). Reactions conditions: MnP/PhIO/Adm molar ratio of 1:10:500 (0.2 μmol of MnP, 2.0 μmol of PhIO, 100.0 μmol of Adm), MeCN:$CHCl_3$ mixture (1:1, v/v) as solvent, magnetic stirring, 26 ºC, 90 min, and air atmosphere. Total yield = Adm-1-ol + Adm-2-ol + Adm-2-one. Yields calculated based on the starting PhIO. 2 mol of PhIO were considered for the formation of 1 mol of Adm-2-one. Normalized regioselectivity = 100 x (Adm-1-ol)/[(Adm-1-ol) + (Adm-2-ol)/3 + (Adm-2-one)/3].

The total yield and regioselectivity of **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) catalysts were not changed over the three reaction cycles (Fig. 9 and ESI, Section 13, Figs. S21 and S22).

Reuse of the supported catalysts **SiI-Cl/MnPY** (**Y = 1, 2, 3**) and **$SiO_2$/MnPY** (**Y = 4, 5, 6**) for two more cycles (cycles 2 and 3, ESI Figs. S21 and S22) revealed that the reaction yields were little affected by catalyst recycling, corroborating the results with the other model substrates that these materials are particularly catalytically robust and resistant against oxidative degradation. The small changes observed in product distribution upon catalyst recycling were essentially limited to the **SiI-Cl/MnPY** (**Y = 1, 2, 3**) systems, in which Adm-2-one

yields increased from less than 1% in the first cycle to *ca* 4% in the third cycle; this was, however, of little impact on chemoselectivity as 1- and 2- adamantanol account for more than 95% of total oxidation yields. Finally, it is worth noting that the high efficiency and robustness observed for the **SiI-Cl/MnP1** and **SiI-Cl/MnP4** catalysts in cyclohexane and n-heptane oxidations were also observed in the adamantane oxidation reactions.

## Conclusions

Chloropropyl-functionalized silica (**SiI-Cl**) was used as support for direct derivatization and covalent immobilization (quaternization reaction) of the three Mn(III) *N*-pyridylporphyrin isomers in aqueous medium to yield **SiI-Cl/MnPX** (**X= 1, 2, 3**). Additionally, **$SiO_2$/MnPY** (**Y= 4, 5, 6**) solids were prepared by the electrostatic immobilization of the three cationic Mn(III) *N*-methylpyridiniumporphyrin isomers on non-modified **$SiO_2$**.

The materials were evaluated as PhIO-oxidation catalysts for alkane functionalization using cyclohexane, n-heptane, and adamantane as model substrates. The strong bonding of MnPs with the inorganic matrices (**SiI-Cl** and **$SiO_2$**) resulted in heterogenized materials highly stable against leaching.

The supported materials **SiI-Cl/MnPY** (**Y = 1**, **2**, **3**) and **$SiO_2$/MnPY** (**Y = 4**, **5**, **6**) showed good to excellent catalytic efficiency in all model substrate oxidations. **SiI-Cl/MnPY** (**Y = 1**, **2**, **3**) catalysts based on cheap, ordinary, chromatographic silica were more efficient and equally selective for cyclohexane oxidation than related literature SBA-15-based catalysts. The **SiI-Cl/MnPY** (**Y = 1**, **2**, **3**) and **$SiO_2$/MnPY** (**Y = 4**, **5**, **6**) systems were also able to catalyze cyclohexanol oxidation indicating that they are promising catalysts for alcohol oxidation.

The supports played important roles in the catalytic efficiency, chemo- and regioselectivity, and oxidative stability of heterogenized MnPs on the **SiI-Cl/MnPY** (**Y = 1**, **2**, **3**) and **$SiO_2$/MnPY** (**Y = 4**, **5**, **6**) materials. Although regular chromatographic silicas are not expected to yield regioselectively noteworthy catalysts, the study on the oxidation of n-heptane was particularly revealing on the impact the surface modification exerted on catalyst properties. In these n-

heptane oxidations, **SiI-Cl/MnPY** (**Y = 1**, **2**, **3**) catalysts showed chemoselectivity for alcohols, whereas **$SiO_2$/MnPY** (**Y = 4**, **5**, **6**) catalysts promoted chemoselectivity for carbonyl compounds (ketones and aldehyde).

Overall, **SiI-Cl/MnP1** stood out as particularly resistant against oxidative destruction and catalytically robust in cyclohexane, n-heptane, and adamantane model-substrate oxidations, without significant loss of either efficiency or selectivity for at least three oxidation cycles.

## Conflicts of interest

There are no conflicts to declare.

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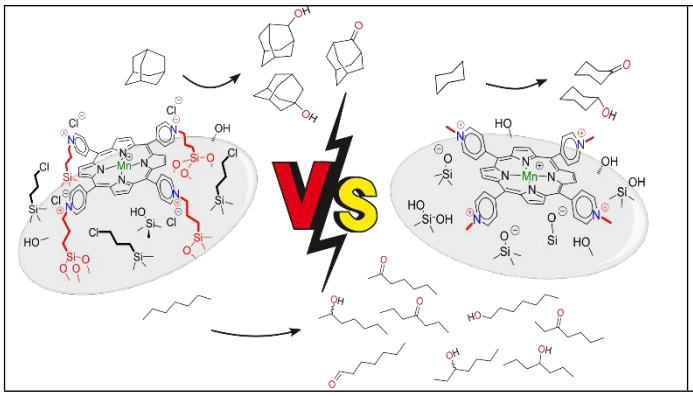

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Simple neutral and cationic Mn porphyrins were immobilized on ordinary chromatographic silica or chloropropyl-functionalized silica supports to yield efficient and reusable biomimetic catalysts for C–H activation and oxyfunctionalization of alkanes