

Selective oxidation of aromatic compounds with dioxygen and peroxides catalyzed by phthalocyanine supported catalysts

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Received 29 August 2001; accepted 24 October 2001

Abstract

This article summarizes our research in catalytic oxidation on the design and study of supported metallophthalocyanine catalysts. The catalytic properties of these materials were studied in the oxidation of 2-methylnaphthalene (2MN) to 2-methyl-1,4-naphthoquinone (Vitamin K₃, VK₃), 2,3,6-trimethylphenol (TMP) to trimethyl-1,4-benzoquinone (precursor of Vitamin E) and in the epoxidation of olefins. Iron tetrasulfophthalocyanine (FePcS) covalently grafted in the dimeric form yielded catalyst more active and selective than those containing monomeric species but suffered from a lack of stability transforming into less selective monomer complexes during catalysis. The stabilization of supported dimer form by covalent link of two adjacent phthalocyanine molecule through appropriate diamine spacer provided more selective and stable catalysts. Trimethyl-1,4-benzoquinone was obtained with 87% yield at 97% conversion of TMP. More demanding oxidation of 2MN afforded 45% yield of VK₃. Particular emphasis is placed on the mechanistic aspects of these oxidations using two mechanistic probes, 2-methyl-1-phenylpropan-2-yl hydroperoxide (MPPH) to distinguish between homolytic versus heterolytic cleavage of O–O bond during the formation of active species and thianthrene 5-oxide (SSO) to evaluate nucleophilic versus electrophilic character of formed active species. To illustrate a versatility of the phthalocyanine-based supported catalysts we prepared a novel phthalocyanine complex with eight triethoxysilyl substituents which can be directly anchored to the silica without any modification of the silica support. This new catalyst shows good catalytic activity in epoxidation of olefins by dioxygen in the presence of isobutyraldehyde. The same catalytic system was also active in the oxidation of phenols to biphenols with 86% yields. This catalytic system is complementary to previous one that selectively oxidizes phenols to quinones. An appropriate choice of the reaction conditions allows selective oxidation either to quinones or to biaryl compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron phthalocyanine; Supported catalyst; Catalytic oxidation; μ -Oxo dimer; Quinones

1. Introduction

The selective oxidation of aromatic compounds into quinones or biaryl products is an important goal in the synthesis of the fine chemicals. Such oxidations are currently performed with stoichiometric oxidants

such as Cr(VI) compounds [1]. The quest for effective catalytic methods that use clean oxidants such as peroxides or dioxygen remains an important challenge.

Phthalocyanine complexes of transition metals are attractive as potential oxidation catalysts because of their rather cheap and facile preparation in a large scale and their chemical and thermal stability. Their macrocyclic structure resembles that of porphyrin complexes widely used by nature in the active sites of oxygenase enzymes [2]. Not surprisingly, porphyrin

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catalytic chemistry is quite well-documented [3–6]. Extensive efforts have been directed at modeling catalytic activity using synthetic iron and manganese porphyrin complexes to elucidate the mechanism of dioxygen activation and the structure(s) of reactive intermediate(s). Mechanisms of catalytic oxidation of various organic substrates including alkanes and olefins by cytochrome P-450 and its chemical models based on porphyrin metal complexes were proposed, evidenced and now generally accepted. Several intermediate active species in catalytic cycle were postulated, identified and characterized by different spectroscopic techniques. There is a stark contrast between state of art of porphyrin and phthalocyanine oxidation chemistry. Although phthalocyanine complexes have been actively investigated as oxidation catalysts [7–15] their catalytic chemistry is practically not developed in terms of mechanisms and active species involved in these catalytic oxidations [10–12,14]. So, we are concentrating our efforts on the development of new catalytic methods for oxidation, in particular, of aromatic compounds and we are trying to investigate the mechanisms and active species involved in these oxidations.

The heterogenization of transition metal complexes onto inorganic supports is an interesting approach to prepare selective heterogeneous catalysts for clean catalytic methods. Different methods can be used to immobilize the complexes onto inorganic support. Metallophthalocyanines have been fixed onto zeolites [16] and zeolites embedded in polydimethylsiloxane membranes [14,15], activated carbon black [17], MCM-41-type molecular sieves [18–20] and by sol–gel processing [21,22]. Covalent grafting of metallophthalocyanines onto silicas [23–27] or onto organic copolymers [28] presents another possible

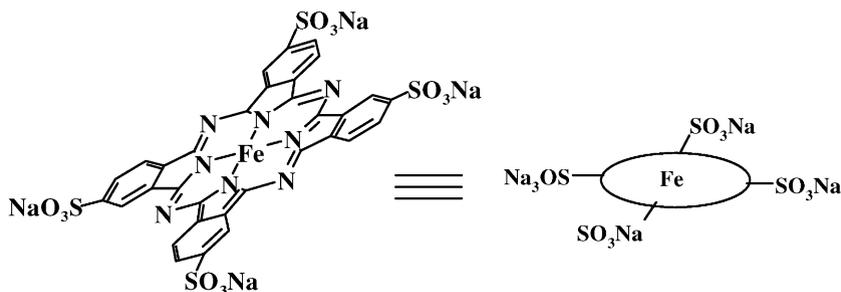
approach. We have recently shown that the controlled covalent anchoring of phthalocyanine complexes onto silicas in dimeric form gave selective heterogeneous catalysts for the oxidation of aromatic compounds to quinones [13,29]. The heterogenization of metal complexes of porphyrins onto different supports has also been published [30–33].

The present paper reports on the application of phthalocyanine-based heterogeneous catalysts in the oxidation of aromatic compounds. We have studied the dependence of the catalytic activity and selectivity on the structure of phthalocyanine complex and on the structural organization of catalytic sites. We discuss here possible mechanisms of the formation of active species from monomeric and dimeric forms of iron tetrasulfophthalocyanine (FePcS) and *t*-butylhydroperoxide to explain their different catalytic properties in oxidation of aromatic compounds. To achieve this we used two mechanistic probes: thi-anthrene 5-oxide to estimate the electronic character of active species (electrophilic versus nucleophilic) and 2-methyl-1-phenylpropan-2-yl hydroperoxide (MPPH) for heterolytic versus homolytic O–O bond cleavage of peroxide with both monomeric and dimeric forms of supported FePcS.

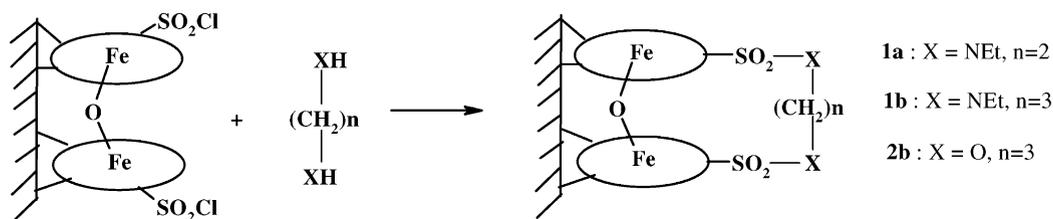
2. Results and discussion

2.1. Designing a dimeric phthalocyanine supported catalyst for the selective oxidation of aromatic compounds

Recently we described controlled procedures for the covalent grafting of FePcS (Scheme 1) onto amino-modified silicas either in a monomer or dimer form



Scheme 1. Structure of FePcS.



Scheme 2. Strategy of stabilization of a dimer structure by covalent linking of two adjacent phthalocyanine molecules.

[13,29]. Surprisingly, dimeric μ -oxo FePcS was more active and selective for the oxidation of 2-methylnaphthalene (2MN) to Vitamin K₃ (VK₃) and for the 2,3,6-trimethylphenol (TMP) to trimethyl-1,4-benzoquinone (TMQ) (precursor of Vitamin E). However, during catalytic reactions, the selective dimeric catalyst was gradually transformed to the less selective monomeric species, as indicated by DR UV–VIS analysis of recycled catalyst [13]. This resulted in a decrease of quinone yield. Consequently, stabilization of the dimeric structure of FePcS is required to prevent deactivation through monomer formation. One approach to the stabilization of dimer structure is to covalently link phthalocyanine units using free chlorosulfonyl groups left after immobilization through an appropriate spacer [33]. To achieve this we used *N,N'*-diethylethylenediamine (catalyst **1a**), *N,N'*-diethyl-1,3-propanediamine (**1b**) and 1,3-propanediol (**2b**) (Scheme 2). We have also prepared MnPcS-SiO₂ supported catalyst. Treatment of MnPcS-SiO₂ with *N,N'*-diethyl-1,3-propanediamine resulted in catalyst **3b**. The modified supported catalysts were tested for the oxidation of TMP and their catalytic performance was compared with those of unmodified monomer m-FePcS-SiO₂ and dimer d-FePcS-SiO₂ supported catalyst (Table 1). The modified supported catalysts were very active in TMP oxidation, providing quasi-complete conversions after 2 h. The diol modified catalyst was less selective than dimer catalyst d-FePcS-SiO₂. Supported catalysts **1a** and **1b** treated with diamines were found to be more selective resulting in 82 and 87% quinone yields, respectively. In the case of MnPcS supported catalyst the treatment with diethyl-1,3-propanediamine was beneficial for catalytic activity, the conversion was increased from 36 to 98%. However, the selectivity of TMP oxidation was still low. Manganese-based

Table 1

Catalytic oxidation of TMP by TBHP in 1,2-dichloroethane at 30 °C

Catalyst	Conversion (%)	Yield of quinone ^a (%)
m-FePcS-SiO ₂	95	42
d-FePcS-SiO ₂	96	77
1a	91	82
1b	97	87
2b	95	56
MnPcS-SiO ₂	36	26
3b	98	23

^a Based on converted substrate. Reaction time: 2 h.

catalysts were also less efficient in the oxidation of 2MN, conversions being only 3 and 32% for MnPcS-SiO₂ and **3b**, respectively.

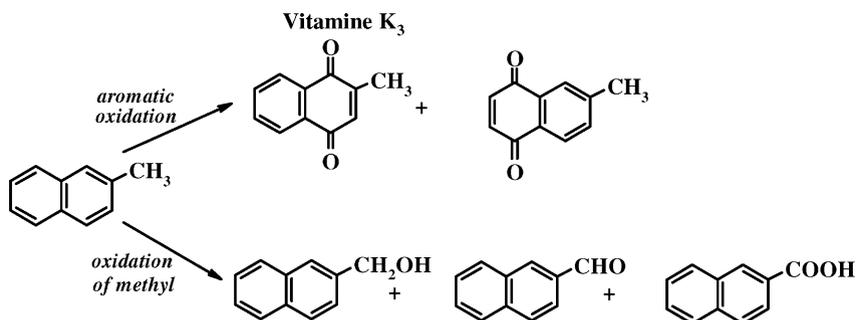
The oxidation of 2MN can occur either on the methyl group or on the aromatic rings to give 2-naphthol, 2-naphthaldehyde, 2-naphthoic acid and 2-quinones (Scheme 3). Along with these compounds, products of radical coupling as well as over-oxidation products can be formed. That is why 2-methyl-1,4-naphthoquinone can be generally obtained in moderate yields. The data on 2MN oxidation in presence of iron-based catalysts are collected in Table 2. Modification of supported catalysts with

Table 2

Catalytic oxidation of 2MN by TBHP in acetonitrile at 40 °C

Catalyst	Conversion (%)	Yield of VK ₃ ^a (%)	Total yield of quinones (%)
m-FePcS-SiO ₂	58	11	14
d-FePcS-SiO ₂	78	24	35
1a	70	45	65
1b	73	23	33
2b	72	21	29

^a Based on converted substrate. Reaction time: 24 h.



Scheme 3. Oxidation of 2MN.

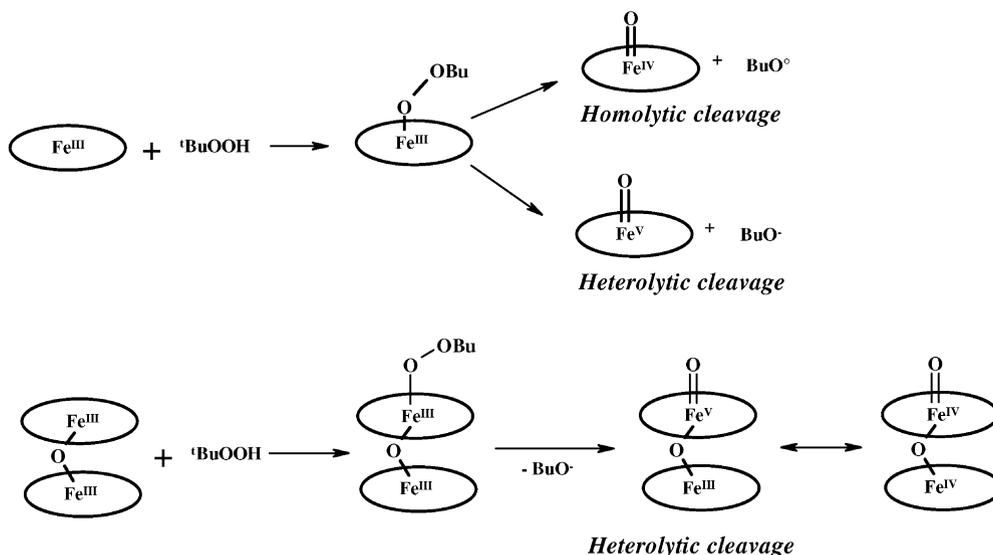
N,N'-diethyl-1,3-propanediamine or 1,3-propanediol practically does not influence their catalytic properties in the more demanding oxidation of 2MN. However, *N,N'*-diethylethylenediamine modified catalyst **1b** exhibits increased selectivity. The yield of VK₃ was 45%, total selectivity of quinones being 65%. The results indicate that catalytic properties of supported dimeric catalysts can be tuned by appropriate modification of the catalytic sites. Several other examples of catalytically active μ -oxo dimer complexes have been published (for a discussion, see [33]). It should be noted that three forms of μ -oxo bridged phthalocyanine complexes have been prepared which can be distinguished by X-ray powder patterns, UV–VIS, NMR, IR and Mössbauer spectral data, and their different magnetic behavior [34–37]. Three structures of μ -oxo dimers have been proposed differing either in geometrical organization (parallel or bent phthalocyanine moieties) or in Fe oxidation state (two or three). However, in spite of abundant experimental data, the nature of three isomeric μ -oxo dimers still remains unknown. It is clear that catalytic properties of dimeric phthalocyanines should depend on their structure. The speculation that different dimer forms of FePcS on the surface having different catalytic properties could be obtained in case of **1a**, **1b** and **2b** catalysts is very tempting, but we have no experimental data to support it. However, it is quite possible that the catalytic properties of these modified FePcS supported catalysts are very sensitive to the structural organization of catalytic sites. No doubt that further efforts are needed to elucidate the structures of μ -oxo bridged phthalocyanines and to understand the influence of structural parameters on their catalytic properties.

It should be noted that VK₃ is still prepared by stoichiometric oxidation of 2MN by CrO₃–H₂SO₄ system in 38–40% yields producing large amounts of toxic chromium containing wastes. Several homogeneous catalytic methods including methyltrioxorhenium [38,39], metalloporphyrin [40], metallophthalocyanine [41] and metalloporphyrazines [42] catalysts have been developed for 2MN oxidation. The FePcS supported catalysts in combination with peroxides could be an interesting heterogeneous alternative for aromatic oxidation of 2MN to VK₃.

2.2. Proposed mechanism of the formation of active species from *m*-FePcS-SiO₂ and *d*-FePcS-SiO₂

The reason for better catalytic properties of dimer FePcS-SiO₂ catalyst in aromatic oxidation is not yet well understood. The data on the mechanisms and metal-oxo complexes involved in oxidations are scarce in the case of phthalocyanines. In the homogeneous oxidation of chlorinated phenols by FePcS/H₂O₂ system a nucleophilic PcSFe^{III}-OO⁻ complex was proposed to be the active species [9,10]. Another possible active species could be a high-valent oxo iron complex, having two redox equivalents above the Fe^{III} state. Several lines of evidence indicate that it is not the case for the FePcS/H₂O₂ [43]. An electrophilic PcSFe^{IV}=O complex (one redox equivalent above the Fe^{III} state) was proposed to be the active species involved in homogeneous oxidation of aromatics by FePcS/H₂O₂ [12].

Comparison of electrochemical data for porphyrin and phthalocyanine complexes indicates that the higher oxidation states of the central transition metal



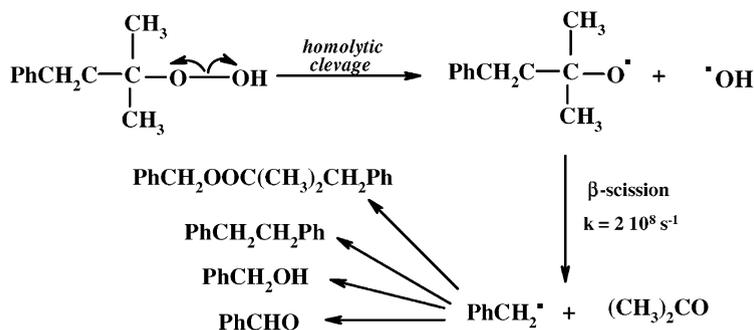
Scheme 4. Proposed mechanisms of the formation of active species from monomeric and dimeric forms of FePcS and TBHP.

ions are more readily accessible in the porphyrin series than in the phthalocyanine one [44]. Consequently, phthalocyanine ligand tends to stabilize the lower oxidation states of metal ion compare to porphyrin. In the same oxidation state metallophthalocyanines should be stronger oxidants than their porphyrin analogues. When using t BuOOH as an oxidant one can suggest the initial formation of $\text{PcSFe}^{\text{III}}\text{-OO}^t\text{Bu}$ complex (Scheme 4). Both kinds of the cleavage of O–O bond (homolytic and heterolytic) are operating in porphyrin series, depending on the structure of porphyrin ligand and peroxide and reaction conditions [45]. In the case of $\text{PcSFe}^{\text{III}}\text{-OO}^t\text{Bu}$ peroxo complex homolytic cleavage of O–O bond to give $\text{PcSFe}^{\text{IV}}\text{=O}$ and $t\text{BuO}^\bullet$ should be favored to heterolytic pathway to produce $\text{PcSFe}^{\text{V}}\text{=O}$, since Fe^{V} oxidation state is less accessible in phthalocyanine complex than in porphyrin one. In the case of dimeric FePcS peroxo complex a heterolytic cleavage of O–O bond with parallel formation of $t\text{BuO}^-$ rather than a radical should be much more favorable than in the case of monomeric FePcS due to delocalization of the charge on two iron atom of dimer (Scheme 4). As a result, a higher selectivity of the dimer FePcS catalyst could be explained by the formation of the active species without concomitant production of radical species leading to side reactions. The difference in the intrinsic reactivity of the

proposed $\text{PcSFe}^{\text{IV}}\text{=O}$ and $\text{PcSFe}^{\text{IV}}\text{-O-Fe}^{\text{IV}}(\text{PcS})\text{=O}$ species could also be responsible for a difference in the selectivity of 2MN and TMP oxidation mediated by monomer and dimer FePcS catalyst. To check this hypothesis we decided to study properties of active species generated from monomer and dimer FePcS complexes using two mechanistic probes, MPPH and thianthrene 5-oxide (SSO).

2.3. MPPH as a mechanistic probe

In recent years Ingold and co-workers showed that MPPH is a very useful mechanistic probe to distinguish between free alkoxy radical chemistry and radical-free high valent iron-oxo mechanism [46,47]. The alkoxy radical derived from this peroxide via homolytic O–O bond cleavage undergoes extremely rapid β -scission (Scheme 5) and so this radical is too short-lived to abstract hydrogen atom from substrate. This method was successfully used to demonstrate the radical nature of putative monooxygenase mimic based on simple iron non-heme complexes and t -alkyl hydroperoxides [48] and to study heterolytic versus homolytic O–O cleavages of t -alkyl hydroperoxides by Fe(III) porphyrins [45,49]. So, we synthesized MPPH and used this oxidant for oxidation of TMP in the presence both m-FePcS-SiO₂ and d-FePcS-SiO₂



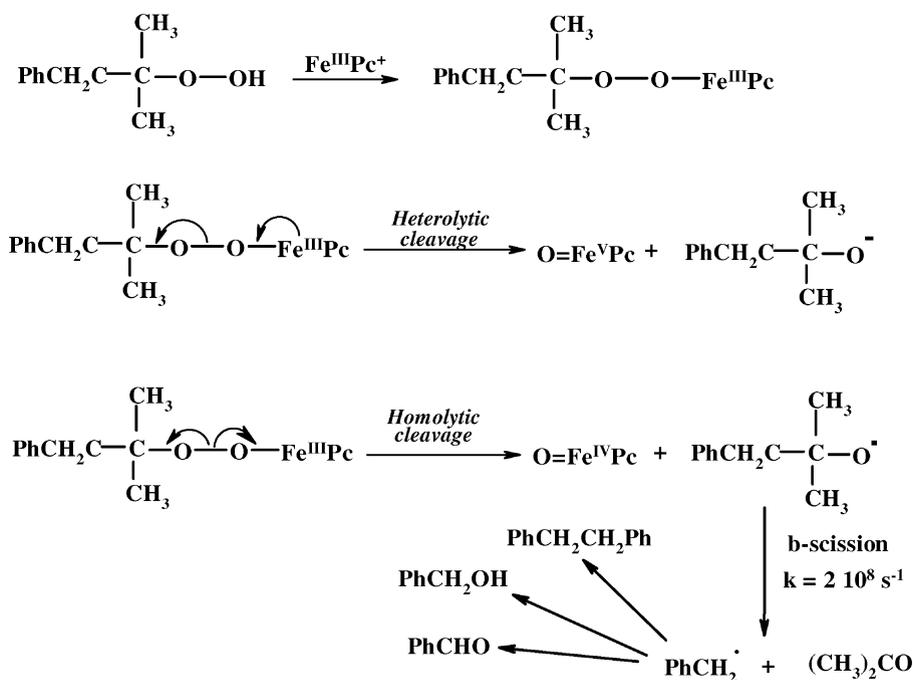
Scheme 5. MPPH as a mechanistic probe.

catalysts (Scheme 6). The oxidation was slightly slower than with TBHP, but 97–98% conversions were obtained after 2 h of reaction under 30 °C. The reactions were quenched by the addition of excess triphenylphosphine which rapidly and quantitatively converts the remaining hydroperoxide to the corresponding alcohol. Analysis of the reaction products by GC and GC–MS method showed that amount of the products issued from the benzyl radical was much

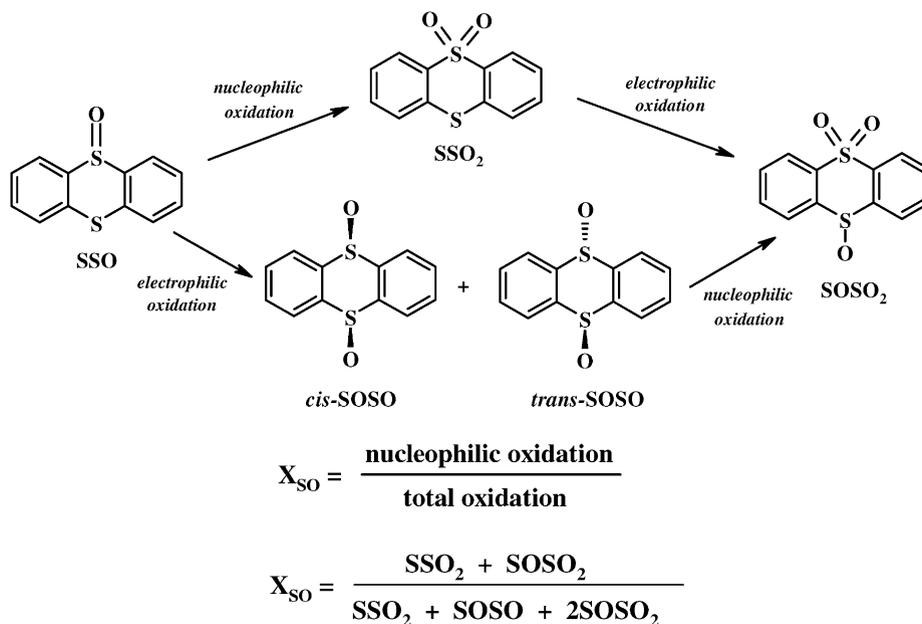
higher with monomer FePcS-SiO₂ catalyst. Thus, the amounts of benzaldehyde and benzyl alcohol obtained in the presence of the monomer catalyst were 2.0- and 3.3-fold more than those obtained with dimer catalyst:

$$\frac{\text{PhCHO}_{\text{m-FePcS}}}{\text{PhCHO}_{\text{d-FePcS}}} = 2.0, \quad \frac{\text{PhCH}_2\text{OH}_{\text{m-FePcS}}}{\text{PhCH}_2\text{OH}_{\text{d-FePcS}}} = 3.3$$

This finding indicate a general trend that is in agreement with proposed mechanism of the formation of



Scheme 6. Heterolytic and homolytic cleavages of O–O bond of MPPH–FePcS peroxy complex.



Scheme 7. Thianthrene 5-oxide as a mechanistic probe for assessing the electronic character of oxygen-transfer agents.

active species: homolytic cleavage of O–O peroxide bond is more abundant in the presence of m-FePcS supported catalyst as compared to the d-FePcS one.

2.4. Thianthrene 5-oxide as a mechanistic probe

The oxidation of thianthrene 5-oxide (SSO) has been used as a mechanistic probe to determine the electronic character of oxygen transfer agents by means of their X_{SO} values (Scheme 7) [50–54]. Thianthrene 5-oxide is preferentially oxidized at sulfide site by electrophilic oxidants and at sulfoxide site by nucleophilic ones. Thus, low values X_{SO} parameter ($X_{SO} < 0.3$) signify electrophilic character of oxidant and high ones ($X_{SO} > 0.7$) nucleophilic character [52,53]. Control experiment showed that no reaction occurred in the absence of phthalocyanine supported catalyst. The obtained values of X_{SO} parameter for monomer and dimer catalysts and literature data on relevant oxidants are listed in Table 3. Thianthrene probe indicated that both active species derived from monomeric ($X_{SO} = 0.47$) and dimeric ($X_{SO} = 0.37$) supported complexes are neither typical electrophilic nor typical nucleophilic oxygen transfer agents.

However, dimeric FePcS active species possesses a more stronger electrophilic character as compared to monomeric FePcS active species.

The actual X_{SO} values are not to be taken as a quantitative measure of nucleophilic versus electrophilic character but rather as a qualitative trend to compare properties of oxygen transfer agents [50]. Thus, more electrophilic property of the active species generated from dimer FePcS-SiO₂ catalyst ($X_{SO} = 0.37$)

Table 3
Oxygen transfer parameter for the oxidation of thianthrene 5-oxide by heterogeneous and homogeneous oxidants

Oxidant	X_{SO}	Reference
m-FePcS-SiO ₂	0.47	This work
d-FePcS-SiO ₂	0.37	This work
Fe(TPPF)/PhIO	0.28	[54]
Dimethyldioxirane	0.09–0.13	[52]
O ₃	0.24	[52]
m-CPBA	0.36	[50]
PhIO/CH ₂ Cl ₂	0.70	[54]
H ₂ O ₂ /1N HCl/Et ₂ O	1.00	[54]
Ti-MCM-41/H ₂ O ₂	0.06	[53]
Ti-MCM-41/TBHP	0.17	[53]

compared to monomer catalyst FePcS-SiO₂ ($X_{SO} = 0.47$) is in accordance with proposed mechanisms of the formation of active species (Scheme 4). Indeed, PcSFe^{IV}-O-Fe^{IV}(PcS)=O species (two redox equivalents above Fe(III) state) should be more electrophilic compared to PcSFe^{IV}=O species (one redox equivalent above Fe(III) state) due to the presence of second Fe(IV) atom having electron-withdrawing character.

2.5. Preparation of a novel phthalocyanine for direct covalent grafting on to silica: modulation of catalytic properties

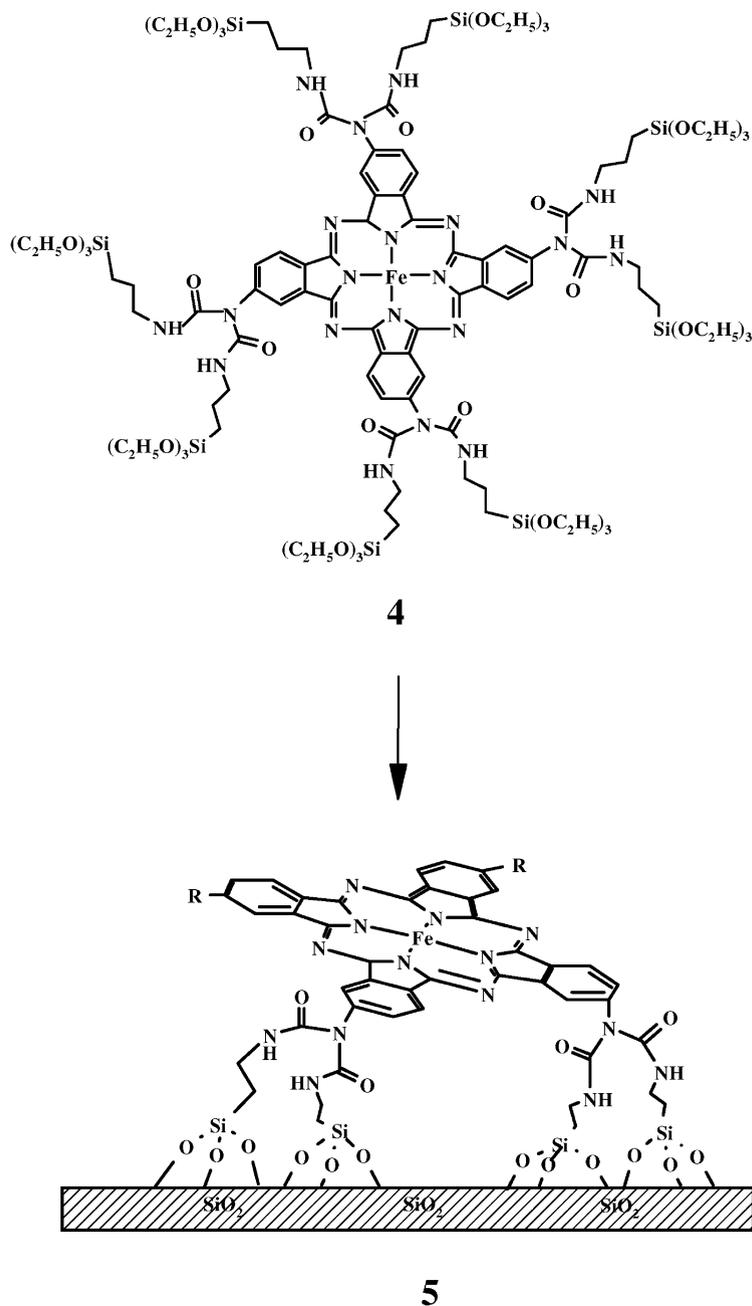
The catalytic properties of the phthalocyanine supported catalyst can be also tuned by changing of the structure of the complex and by the choice of the oxidant as illustrated below. Another important point is the preparation of new catalysts. The preparation of the supported catalysts usually needs an initial functionalization of the supports and complexes before the covalent attachment. Evidently, the preparation of complexes able to be covalently grafted directly onto silica support could be advantageous. We prepared a novel iron phthalocyanine complex **4** having eight triethoxysilyl units for covalent anchoring to the silica (Scheme 8) which was characterized by UV-VIS, ¹H NMR, IR and FAB MS methods [55]. At the first step, the iron complex of 2(3),9(10),16(17),23(24)-tetranitrophthalocyanine was prepared by classical template condensation of 4-nitrophthalic acid [13] followed by reduction with NaHS in DMF under argon to give iron 2(3),9(10),16(17),23(24)-tetraaminophthalocyanine. This complex was quite unstable under air. Consequently, a characterization (¹H NMR and UV-VIS) and further modification was carried out under argon. A novel iron phthalocyanine complex **4** was prepared by reacting of FePc(NH₂)₄ with 3-(triethoxysilyl)propyl isocyanate in dry DMF. We obtained a dark-green pasty solid very soluble in usual organic solvents. UV-VIS spectrum of **4** in acetone shows a concentration dependence: under high concentration the principal peak was at 638 nm along with shoulder at 696 nm while at low concentration the principal peak was at 696 nm along with a smaller peak at 638 nm. These concentration changes of UV-VIS spectra can be explain by aggregation phenomena in solution. There was no concentration dependence of

UV-VIS spectra in *p*-xylene, the principal peak being at 706 nm indicating that no aggregation occurs in apolar solvent.

The FAB spectrum of **4** using 3-nitrobenzyl alcohol as a matrix exhibits a peak at $m/z = 2426$ corresponding to the loss of one C₂H₅OH and three C₂H₅O fragments owing to a strong tendency of triethoxysilyl group to undergo such a fragmentation. A range of matrices including neutral nitrophenyl octyl ether has employed but no molecular peak was obtained. The presence of the traces of water during FAB experiment leading to hydrolysis of triethoxysilyl groups could be possible reason.

The ¹H NMR spectrum of **4** in DMSO-*d*₆ at room temperature shows two groups of signals: broad signals of aromatic protons of phthalocyanine at 7.90 ppm (H_a), 8.25 ppm (H_b'), 8.47 ppm (H_b) and signals of aliphatic protons of 3-(triethoxysilyl)propyl substituents at 2.45, 2.88 ppm (H₁), 1.34, 1.54 ppm (H₂), 0.48 ppm (H₃), 3.68 ppm (CH₂ of ethyl) and 1.09 ppm (CH₃ of ethyl). The triplet signal at 5.76 ppm with $J = 5.5$ Hz can be assigned to HN suggesting successful reaction of amino groups of phthalocyanine with isocyanate to give carbamate substituents. It should be noted that H₁ and H₂ of complex **4** shows two signals for each proton in difference with starting isocyanate suggesting their non-equivalence. The ratio between proton of NH and protons of 3-(triethoxysilyl)propyl substituents was correct 1:2:2:2:6:9. All these features indicate complete substitution and the absence of the excess of unreacted 3-(triethoxysilyl)propyl isocyanate in the product. The absence of the signal at 2275 cm⁻¹ due to isocyanate group in IR spectrum supports this conclusion. However, aromatic protons of phthalocyanine accounts 75% compared to aliphatic and imino protons. It can be explained by partial oxidation of Fe^{II} to Fe^{III} leading to broadening and/or shifting of the aromatic signals due to paramagnetism of Fe^{III}. Finally, obtained NMR data are in agreement with structure of **4**.

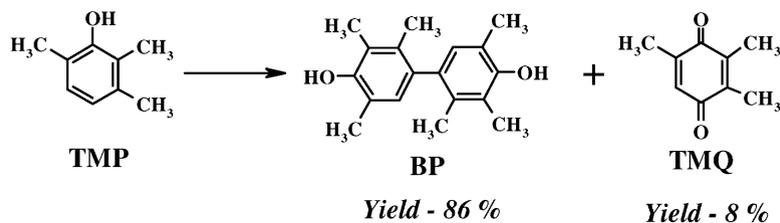
The covalent linkage of iron phthalocyanine **4** directly onto amorphous silica resulted in blue material FePc-SiO₂. The covalent anchoring was proven by the decrease of the silanol signal Q² (-91 ppm) and the appearance of a signal characteristic of (SiO)₃Si-CH₂ groups (-58 ppm) in the ²⁹Si CP MAS NMR spectrum. Interestingly, the silanol signal of Q³ (-100 ppm) was not decreased suggesting



Scheme 8. Structure of iron complex of **4** and schematic representation of the fixation of **4** onto silica support.

preferential grafting on to Q^2 sites. The diffuse reflectance UV–VIS spectrum of the solid shows band at 376, 730 and 932 nm. A large number of triethoxysilyl groups of **4** should facilitate a fixation of

phthalocyanine onto silica surface in parallel mode by several covalent bonds, up to eight in limit case. This should provide a material with isolated sites. Schematic representation of fixed **4** onto silica surface



Scheme 9. Oxidation of TMP.

is given in Scheme 8. The comparison of the DR UV–VIS spectrum of supported complex with UV–VIS spectrum of **4** in xylene suggests that complex is fixed in a monomer form.

A maximal content of complex **4** per gram of material can be estimated from dimensions of **4** and specific surface of silica (183 m²/g). One can assume that the size of **4** is about 5 nm × 5 nm. Consequently, a maximal content of complex **1** per gram of SiO₂ is estimated to be 12.2 μmol. This estimation is in excellent agreement with experimental data of 12.5 μmol found by inductively coupled plasma-mass spectrometry. Therefore, we believe that **4** is fixed parallel to silica surface thus occupying practically all accessible surface and providing isolated FePc sites.

We tested this new supported catalyst **5** in the oxidation of olefins and phenols. Catalytic oxidation of phenol is an important subject in the preparation of fine chemicals giving quinones or/and products of coupling of the aromatic moieties. The selective preparation of biaryl compounds is also a demanding goal since the biaryl axis is the central building block in a large number of natural products and pharmaceuticals [56]. The main problem is to perform an oxidation leading selectively either to quinones or to coupling products while avoiding side reactions.

Molecular oxygen is the most environmentally and economically significant oxidant. The supported catalyst **5** was evaluated in the oxidation of TMP by molecular oxygen in the presence of isobutyraldehyde. Reaction was carried out by using 160 μmol of TMP in 8 ml of acetonitrile with catalyst containing 1.6 μmol of **4** under a 1 bar atmosphere of oxygen. After induction period the conversion of 94% was achieved within 24 h. The main reaction products were identified by NMR and GC–MS methods to be 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol (86% yield) and trimethyl-1,4-benzoquinone (8% yield) (Scheme 9). It should be noted that this catalytic system is complementary to the previous catalytic systems based on supported FePcS (TBHP) which selectively oxidize phenol to quinones. Thus, one can modulate selectivity of the phenol oxidation by just the choice of supported phthalocyanine catalyst and oxidant.

In order to check the catalytic performance of the new supported catalyst we decided to oxidize olefins by dioxygen in the presence of isobutyric aldehyde. All olefins studied were oxidized to epoxides with quite good selectivities. Representative examples obtained using a catalyst:substrate:isobutyraldehyde ratio of 1:265:530 are collected in Table 4. The yields

Table 4
Oxidation of olefins by molecular oxygen catalyzed by FePc-SiO₂ supported catalyst in acetonitrile

Substrate	Conversion (%)	Reaction time (h)	Product(s) (yields ^a , %)
Cyclooctene	96	7	Cyclooctene oxide (90)
Cyclohexene	91	9	Cyclohexene oxide (78) 2-Cyclohexen-1-ol (1) 2-Cyclohexen-1-one (7)
Styrene	99	5	Styrene oxide (74) Benzaldehyde (18)

^a Based on initial amount of substrate.

of cyclooctene oxide, cyclohexene oxide and styrene oxide were 90, 78 and 74%, respectively, turnover number being as high as 240 cycles per phthalocyanine fixed.

3. Experimental

3.1. Instrumental

NMR spectra of solids were acquired on a Bruker DSX 400 spectrometer operating at 79.4 MHz (^{29}Si). The diffuse reflectance UV–VIS spectra of solid catalysts were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. The reaction products were identified and quantified by GC–MS (Hewlett-Packard 5973/6890 system; electron impact ionization at 70 eV, He carrier gas, 30 m \times 0.25 mm crosslinked 5% PH ME siloxane (0.25 μm coating) capillary column, HP-5MS) and CG (Dany ED chromatograph equipped with a flame ionization detector and a 25 m \times 0.25 mm capillary WCOT fused silica column with CP-Sil 8 CB stationary phase from chromatopack) methods. The iron phthalocyanine contents of the prepared materials were determined by iron analyses using an inductively coupled plasma-mass spectrometry method.

3.2. Materials

All chemical used were of reagent grade. Acetonitrile (99%) was purchased from Acros and used as received. The iron complex of tetrasulfophthalocyanine (FePcS) was prepared according to the modified method of Weber and Busch [57,58]. FePcS was converted to tetrachlorosulfonylphthalocyanine FePc(SO₂Cl)₄ by treatment with SOCl₂ MPPH was synthesized from 2-methyl-1-phenyl-2-propyl bromide [59] according to [46,60]. Thianthrene 5-oxide, 5,5- and 5,10-dioxides and 5,5,10-trioxides were synthesized and analyzed as described [51,52].

Iron complex of phthalocyanine **4** was prepared as described [55].

3.2.1. Iron complex of

2(3),9(10),16(17),23(24)-tetraaminophthalocyanine

The reduction procedure was adapted from [61]. NaHS (200 mg, 3.6 mmol) was added to the slurry

of FePc(NO₂)₄ (197 mg, 0.26 mmol) in 12 ml of dry DMF under argon. The resulting mixture was stirred at 100 °C for 5 h under argon, cooled to room temperature and the solvent was removed in vacuum. To remove inorganic salts the material was washed under argon by two portions of 5 ml oxygen-free water. The product was dried in vacuum overnight leaving a dark-green solid sensitive to the oxygen of atmosphere (turned to brown color in a few minutes). Yield of FePc(NH₂)₄ was 80%. δH (250 MHz, DMSO-*d*₆) 5.69, 6.05 (s, 2H), 7.04, 7.20 (s, 1H), 8.18, 8.31 (s, 1H), 8.58, 8.78 (s, 1H). λ_{max} (DMF): 305, 350sh, 714 nm.

3.2.2. Iron complex 2(3),9(10),16(17),23(24)-tetra[1,5-di(3-triethoxysilyl-propyl)biuryl]-phthalocyanine (**4**)

A solution of 3-(triethoxysilyl)propyl isocyanate (1.12 ml, 4.3 mmol) in 5 ml of dry DMF was dropwise added to the solution of FePc(NH₂)₄ (270 mg, 0.43 mmol) in 15 ml of dry DMF under argon. The reaction mixture was heated at 80 °C for 6 h. Then the solvent and excess of isocyanate was removed under vacuum. The absence of the band at 2275 cm⁻¹ (isocyanate group) in IR spectrum and correct integral values in ¹H NMR spectrum indicate the complete remove of 3-(triethoxysilyl)propyl isocyanate excess. Then the product was dried at 40 °C in vacuum overnight. The product **4** was obtained as a dark-green pasty solid in 75% yield (841 mg). To avoid possible hydrolysis of the triethoxysilyl groups during further purification, e.g. by chromatography, the material was directly used for the preparation of supported catalyst. δH (250 MHz, DMSO-*d*₆) 0.48 (m, br, 4H, H₃), 1.09 (t, *J* = 7.0 Hz, 18H, CH₃), 1.34, 1.54 (br, 4H, H₂), 2.45, 2.88 (br, 4H, H₁), 3.68 (q, *J* = 7.0 Hz, 12H, CH₂), 5.76 (t, *J* = 5.5 Hz, 2H, NH), 7.90 (br, 1H, H_a), 8.25 (br, 1H, H_b), 8.47 (br, 1H, H_b). ν_{max} (Nujol)/cm⁻¹ 3340, 1695, 1629, 1336, 1314, 1295, 1167, 958, 792, 762. *m/z* (FAB⁺) isotopic cluster at (M–C₂H₅OH–3C₂H₅O)⁺ 2426. λ_{max} (DMF): 342, 604sh, 668 nm.

3-Aminopropyl modified amorphous SiO₂ (NH₂-SiO₂) was prepared and characterized by BET, ¹³C CP-MAS-NMR and chemical analysis as previously described [13,29]. BET surface: 169 m²/g, C_{BET} = 42. NH₂ content: 0.52 mmol/g (chemical analysis).

3.2.3. Preparation of supported catalysts

Dimer FePcS catalyst supported onto amino-modified amorphous SiO₂ (d-FePcS-SiO₂) was prepared and characterized by diffuse reflectance UV–VIS spectroscopy and chemical analysis as previously described [13,29].

3.2.4. Preparation of FePc(SO₂XRX)-SiO₂ modified supported catalysts **1a**, **1b**, **2b**

Three materials were prepared using 50 μmol of the spacer (*N,N'*-diethylethylenediamine, *N,N'*-diethyl-1,3-propanediamine or 1,3-propanediol) per gram of FePc(SO₂Cl)₄-SiO₂. A solution of 8 μl of *N,N'*-diethyl-1,3-propanediamine in 5.5 ml of THF was added very slowly at 60 °C to a suspension of 1 g of FePc(SO₂Cl)₄-SiO₂ in 5 ml of THF under argon. The resulting mixture was stirred at 75 °C under argon for 16.5 h. Blue-green materials were separated by filtration and washed three times with distilled water, ethanol and acetone. The materials were dried under vacuum at 50 °C for 24 h.

3.2.5. Preparation of supported catalyst **5**

A suspension of 122 mg (47 μmol) of **4** and 2.03 g of amorphous silica (dried at 200 °C for 24 h prior to use) in dry xylene was heated at 80 °C for 6 h. The blue solid was isolated by filtration and washed with acetone and ethanol until colorless washings. The material was dried under vacuum at 60 °C for 16 h. Found: Fe, 0.07%, corresponding to 12.5 μmol/g. Nitrogen sorption isotherm analysis indicated a specific surface of 183 m²/g, slightly less than that of starting SiO₂ material (200 m²/g). Diffuse reflectance UV–VIS, λ_{max}: 376, 730, 932 nm.

3.3. Catalytic tests

3.3.1. Typical procedure for 2MN oxidation by TBHP

A 25 ml flask was charged with 40 μmol of 2MN in 2 ml of acetonitrile and 30–35 mg of supported catalyst containing 1.6 μmol of iron phthalocyanine (4% catalyst/substrate ratio). An amount of 14 μl of 3.7 M TBHP solution in PhCl was added to the mixture at reaction times of 0, 1, 2, 3 and 5 h, and 18.5 μl after 7 h. The reaction was run for 24 h at 40 °C under air.

3.3.2. Typical procedure for TMP oxidation by TBHP

A 100 ml flask was charged with 160 μmol of TMP in 8 ml of 1,2-dichloroethane and 30–35 mg of

supported catalyst containing 1.6 μmol of iron phthalocyanine (1% catalyst/substrate ratio). An amount of 59.7 μl of 3.7 M TBHP solution in PhCl was added to the mixture at reaction times of 0, 0.5, 1 and 1.5 h. The reaction was run for 2 h at 30 °C under air. The courses of reactions were monitored by GC and substrate conversions and product yields were determined using methylbenzoate as internal standard.

3.3.3. Typical procedure for aerobic TMP oxidation

A 250 ml flask was charged with 160 μmol of TMP in 8 ml of acetonitrile and 128 mg of solid catalyst, containing 1.6 μmol of iron phthalocyanine (1:100 catalyst/substrate ratio). Two portions of 320 μmol of isobutyraldehyde were added at reaction times of 0 and 2 h. Reactions were run for 24 h at 60 °C under air. The courses of reactions were monitored by GC and substrate conversions and trimethyl-1,4-benzoquinone (TMQ) yields were determined using methylbenzoate as external standard. Product yields were determined by ¹H NMR as follows. The reaction mixture was filtered and solid catalyst was washed with diethyl ether (3 × 3 ml). After evaporation of the combined organic phases, the solid residue was dissolved in deuterated chloroform for NMR analysis. We added 10 μl of dichloromethane (0.156 mmol) as an internal standard. The quantities of the oxidation products were determined by NMR from intensities of signals of aromatic protons of TMQ and 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol (BP) at δ 6.50 and 6.70 ppm, respectively. 2,2',3,3',5,5'-Hexamethyl-4,4'-biphenol, MS data (EI): *m/z* (%) 270 (100) M⁺, 255 (29) (M-CH₃)⁺, 240 (57) (M-2CH₃)⁺, 225 (11) (M-3CH₃)⁺; ¹H NMR (CDCl₃) δ 1.93 (s, 6H, CH₃), 2.19 (s, 6H, CH₃), 2.22 (s, 6H, CH₃), 6.70 (s, 2H, aromatic H₆).

3.3.4. Typical procedure for aerobic olefin oxidation

A 250 ml flask was charged with 100 μmol of olefin in 4 ml of acetonitrile and 30 mg of solid catalyst, containing 0.38 μmol of iron phthalocyanine (1:265 catalyst/substrate ratio). Two portions of 200 μmol of isobutyraldehyde were added at reaction times of 0 and 3 h. The courses of reactions were monitored by GC and substrate conversions and product yields were determined using *o*-dichlorobenzene (cyclohexene and styrene oxidation) and cyclooctane (*cis*-cyclooctene oxidation) as internal standards.

4. Conclusion

A chemical modification of FePcS covalently grafted onto amino-modified silica was achieved with different diamine and diol spacers in order to stabilize a dimeric structure of the complex, more active and selective in aromatic oxidation, through the covalent binding of two adjacent grafted phthalocyanine molecules. The catalyst **1b** modified with *N,N'*-diethyl-1,3-propanediamine was most selective in the oxidation of TMP to corresponding quinone (87% yield) while *N,N'*-diethylethylenediamine modified catalyst **1a** was most selective in the more demanding oxidation of 2MN to VK₃ (45% yield). Thus, catalytic properties of supported catalysts can be tuned by appropriate modification of the catalytic sites. The results obtained support our idea that stabilization of the dimeric structure of supported FePcS complexes by covalent linking of two adjacent phthalocyanine molecules through an appropriate spacer is a promising strategy to prepare selective heterogeneous catalysts. However, only part of FePcS molecules could be initially fixed in the configuration favorable to following stabilization of dimer by covalent link with diamine spacer. Obviously, the further study is needed to optimize and characterize these supramolecular supported catalysts and to understand key factors governing the catalytic activity of new dimeric catalysts. The preparation of dimer cofacial phthalocyanines followed by anchoring of these characterized individual dimers onto silica could be interesting possibility to obtain tailor-made catalysts. The work in this direction is in progress in our laboratory.

Fe(III) peroxo species formed by the reaction of the peroxide with FePcS are proposed to undergo a homolytic or heterolytic cleavage of O–O bond in the case of the monomeric and dimeric complexes, respectively, to explain the difference in their catalytic properties. Since phthalocyanine ligand tends to stabilize the lower states of central metal compared to porphyrin, one can suggest, that in the case of monomeric PcSFe^{III}–OOBu complex, *homolytic* cleavage of O–O bond to give PcSFe^{IV}=O and BuO· should be favored to heterolytic pathway to produce PcSFe^V=O. This proposal is in accordance with previously proposed PcSFe^{IV}=O as the active species in FePcS/H₂O₂ mediated oxidation of condensed aromatics [12].

In the case of dimeric FePcS complex with peroxide a *heterolytic* cleavage of O–O bond with parallel formation of BuO[–] rather than a radical should be much more favorable than in the case of monomeric FePcS due to possibility of the delocalization of the charge on two iron atom of the μ -oxo dimer.

Indeed, the experiments with MPPH mechanistic probe for the heterolytic versus homolytic O–O bond cleavage support this hypothesis: homolytic cleavage is more abundant in the presence of monomeric FePcS supported catalyst compared to dimer FePcS supported catalyst.

Consequently, a higher selectivity of the dimer FePcS catalyst could be explained by the formation of the active species without concomitant formation of radical species leading to side reactions resulting in the decrease of the selectivity of the oxidations. The difference in the intrinsic reactivity of the proposed PcSFe^{IV}=O and PcSFe^{IV}–O–Fe^{IV}(PcS)=O species could also be responsible for a difference in the selectivity of 2MN and TMP oxidation mediated by monomer and dimer FePcS catalyst.

Thianthrene probe indicated that both active species derived from monomeric and dimeric supported complexes are neither typical electrophilic nor typical nucleophilic oxygen transfer agents. However, dimeric FePcS active species possesses a stronger electrophilic character as compared to monomeric FePcS active species.

Finally, we demonstrated that the appropriate design of phthalocyanine supported catalyst and the choice of the oxidant allows to change a selectivity of aromatic oxidation. A novel iron phthalocyanine complex **4** having eight triethoxysilyl residues was directly grafted onto silica. The new supported catalyst showed a promising catalytic activity using molecular oxygen in combination with isobutyraldehyde in epoxidation of olefins and oxidation of TMP to the coupling product, 2,2',3,3',5,5'-hexamethyl-4,4'-biphenol, providing a 86% yield. It should be also noted that this catalytic system is complementary to the previous catalytic system based on supported FePcS (*t*-butylhydroperoxide) that selectively oxidizes phenols to quinones. Developed catalytic methods present interesting synthetic possibilities for the selective synthesis of quinones or biaryl compounds whose preparation is a demanding goal in the chemistry of pharmaceuticals.

Acknowledgements

The present work was supported by Fonds National de la Science (ACI Blanche-99 from the French Ministry of Education, Research and Technology, Grant no. 4107). CP is indebted to the French Ministry of Education, Research and Technology for a doctoral fellowship.

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