ELSEVIER

Catalysis Today 57 (2000) 45–59

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Metallophthalocyanine functionalized silicas: catalysts for the selective oxidation of aromatic compounds

Alexander B. Sorokin *, Alain Tuel

Institut de Recherches sur la Catalyse, CNRS, 2, avenue A. Einstein, 69626 Villeurbanne Cedex, France

Abstract

Metallophthalocyanines of iron, manganese and cobalt have been successfully anchored onto the surface of mesoporous and amorphous silicas and used as catalysts in the liquid phase oxidation of 2-methylnaphthalene and 2,3,6-trimethylphenol with hydrogen peroxide and *t*-butylhydroperoxide. The iron tetrasulfophthalocyanine showed an activity from far superior to that of the other metallic complexes and to the corresponding homogeneous catalysts. The activity and selectivity depend on the nature of the solvent, oxidizing agent and the catalyst itself. In particular, iron tetrasulfophthalocyanine anchored in the dimeric form yielded catalyst much more active and selective that those containing monomeric species, which was unexpected since dimeric species are usually considered as inactive in homogeneous systems. The catalytic properties of these materials were compared with those of Ti containing silica-based molecular sieves. The latter were active in the oxidation of 2,3,6-trimethylphenol but not in that of 2-methylnaphthalene. Iron (III) peroxo species, formed by reaction of the peroxide with iron phthalocyanine were proposed to undergo a homolytic or heterolytic cleavage of O–O bond in case of the monomeric and dimeric complexes, respectively, to explain the difference in their catalytic properties. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; Heterogeneous oxidation; Supported catalyst; Phthalocyanine; Vitamin K_3

1. Introduction

The selective oxidation of aromatic compounds is still a challenge in chemical industry and catalytic researches. The aromatic compounds are currently oxidized by chromate and permanganate oxidants [1]. However, the use of these stoichiometric oxidants leads to severe environmental problems. For example, 2-methylnaphthoquinone is still prepared by stoichiometric oxidation of 2-methylnaphthalene (2MN) by CrO_3–H_2SO_4 system in 38–60% yields producing a lot of chromium containing toxic wastes. The development of catalytic methods involving "clean" oxidants to carry out selective oxidation of aromatics is thus of great practical interest. Several homogeneous catalytic methods including methyltrioxorhenium [2,3] and metalloporphyrin catalysts [4] have been developed for 2MN oxidation to obtain vitamin K_3 (VK_3). A 46% yield of VK_3 was reported in 2MN oxidation by the CH_3ReO_3–85% H_2O_2 system [3].

Metal complexes of phthalocyanines have been intensively studied as oxidation catalysts. The driving forces for the use of phthalocyanines are (i) the resemblance of their macrocyclic structure with that of porphyrins widely used by nature in the active sites of oxygenase enzymes; (ii) their rather cheap and facile preparation in a large scale; (iii) their chemical and thermal stability. The main drawback of phthalocyanines complexes from the point of view of the application in catalysis is their insolubility in the common organic solvents. This problem can be overcome

---

* Corresponding author. Fax: +33-04-72-44-53-99.
E-mail address: sorokin@catalyse.univ-lyon1.fr (A.B. Sorokin).

PII: S0920-5861(99)00312-0

either by the introduction of substituents at the periphery of the molecule to make phthalocyanines soluble and suitable for homogeneous catalysis or/and by dispersion and fixation of phthalocyanine complexes onto different supports to obtain heterogeneous catalysts. These phthalocyanine-based catalysts have been widely used in the oxidation of hydrocarbons, phenols and thiols (Merox process) [5,6,34,35]. Different methods can be used to immobilize the complexes onto inorganic supports. Metallophthalocyanines have been fixed onto zeolites [7] and zeolites embedded in polydimethylsiloxane membranes [8,36], activated carbon black [9], MCM-41-type molecular sieves [10] and by sol–gel processing [11]. The zeolite-based catalysts have shown to be active catalysts in the oxidation of alkanes [7,8,36] by *t*-butylhydroperoxide (TBHP). However, these materials are not suitable for oxidation of bulky substrates, such as 2MN. Immobilization of iron phthalocyanine onto MCM-41 by the physical adsorption provides the catalysts which undergo fast and irreversible deactivation during oxidation of alkanes by TBHP [10].

We have recently shown that iron tetrasulfophthalocyanine was active in oxidation of chlorinated phenols [6,35] and in the homogeneous oxidation of condensed aromatics [12]. An efficient catalytic homogeneous oxidation of naphthalene derivatives in the presence of metal phthalocyanines and tetraazaporphines complexes has been recently published [37,38]. So, a covalent anchoring of phthalocyanine complexes onto silicas seems to be a promising strategy to prepare heterogeneous catalysts for the oxidation of aromatic compounds [13].

The present paper reports on the application of hybrid heterogeneous materials prepared by the covalent anchoring of metallophthalocyanines onto mesoporous and amorphous silicas in the catalytic oxidation of 2-methylnaphthalene and 2,3,6-trimethylphenol. The activity of these new materials was compared to that of conventional oxidation catalysts like Ti-MCM-41 and Ti-beta zeolite.

2. Experimental

2.1. Instrumental

Solid state NMR spectra were acquired on a Bruker DSX 400 spectrometer operating at 79.4 (^{29}Si) and 100.6 (^{13}C) MHz. The diffuse reflectance UV–Vis spectra of solid catalysts were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. BET surface areas and pore size distributions of the materials were calculated from N_2 adsorption isotherms at 77 K using a Catasorb apparatus. The reaction products were identified and quantified by GC-MS (Fusons GC 8000, electron impact ionization at 70 eV, He carrier gas, 25 m × 0.25 mm capillary column), ^{1}H NMR (Bruker AM 250 MHz) and GC (Dany DE chromatograph equipped with a flame ionization detector and a 25 m × 0.25 mm capillary WCOT fused silica column with CP-Sil 8 CB stationary phase from Chrompack) methods.

2.2. Preparation of complexes and authentic compounds

All chemical used were of reagent grade. The iron, manganese and cobalt complexes of tetrasulfophthalocyanine were prepared according to the modified method of Weber and Busch [14,15] with yields of 68, 21 and 72%, respectively. The iron complex of hexachlorophthalocyanine was prepared with 13% yield according to [16,39]; UV–Vis (pyridine) λ_{max}(nm): 680, 626, 430, 356.

Authentic samples of 6-methyl-1,4-naphthoquinone (6MeQ) [17] and trimethyl-1,4-benzoquinone (TMQ) [18] were prepared according to published procedures.

Iron tetranitrophthalocyanine was prepared following the method published for the preparation of the copper complex [19]. 1.16 g of $FeSO_4 \cdot 1.5H_2O$, 5 g of 4-nitrophthalic acid, 610 mg of ammonium chloride, 68 mg of ammonium molybdate and 8.1 g of urea were ground together. Resulting mixture was added to 20 ml of nitrobenzene and heated slowly to 185°C for 1.5 h. The reaction mixture was heated at 185°C for additional 4.5 h. After cooling to room temperature the product was separated by filtration and washed with methanol until free from nitrobenzene. The crude product was purified by treatment with 70 ml of 1 M HCl saturated with NaCl. The resulting mixture was rapidly heated to boiling, cooled to room temperature and filtered. The solid was added to 70 ml of 1 M NaOH solution containing 25 g of NaCl and heated at 90°C for 6 h. The solid product was separated by filtration and the above treatment with HCl and NaOH was carried out one more time. Finally, the product was washed with H_2O until chloride-free. A black fine material was isolated by centrifugation, dried at 50°C overnight, than dried in vacuum at 100°C for 5 h. Yield - 4.18 g (88%). UV–Vis (pyridine): λ_{max}(nm): 682, 616_{sh}, 500, 450, 358_{sh}, 320. IR (KBr pellet): ν_{max}(cm^{-1}): 1511, 1317 (NO_2). Magnetic moment at room temperature — 1.80μ_B (low spin Fe^{III}). MS (FAB): *m/z* (%) 749 (100) [(M + 1)$^+$], 748 (86) [M$^+$]. Anal. Calc. for $C_{32}H_{12}N_{12}O_8FeCl\cdot H_2O$: C 47.93; H 1.76; N 20.96. Found: C 47.34; H 2.12; N 21.74.

2.3. Preparation of supports

MCM-41, Ti-MCM-41 and aluminum-free Ti-beta zeolite were synthesized following reported procedures [20,21,22]. 3-aminopropyl modified MCM-41 (NH_2-MCM-41) was prepared as previously described [13].

3-chloropropyl-functionalized MCM-41 (Cl-MCM-41). 3-chloropropyltrimethoxysilane (1.09 ml, 4.5 mmol) was added to a suspension of 2.27 g of activated MCM-41 (200°C, vacuum, 20 h) in 25 ml of dry *m*-xylene. The mixture was stirred at 150°C under argon for 28 h. The material was separated by filtration, washed with acetone and dried in vacuum at 80°C for 9 h. BET surface: 729 m^2/g, mean pore diameter: 33 Å. ^{13}C CP-MAS-NMR (ppm): $=Si(OCH_2CH_3)–{}^{\alpha}CH_2–{}^{\beta}CH_2–{}^{\gamma}CH_2–Cl$: $^{\alpha}CH_2$: 9.3; $^{\beta}CH_2$: 26.3; $^{\gamma}CH_2$: 45.7. Attribution of signals was performed according to [23].

2.4. Preparation of supported catalysts

Monomer and dimer FePcS catalysts supported onto amino-modified MCM-41 and amorphous SiO_2 (m-FePcS@MCM-41, m-FePcS@SiO_2, d-FePcS@MCM-41, d-FePcS@SiO_2) were prepared as previously described [13].

Preparation of CoPcS@MCM-41. A solution of 100 mg of $CoPc(SO_2Cl)_4$in 20 ml of Py was stirred at 20°C for 7 h. This solution was added to a suspension of 1 g of amino-modified MCM-41 in 10 ml of Py within 30 min under argon. The resulting mixture was stirred at 80°C under argon for 22 h. A blue material was separated by filtration and washed with acetone, water and again with acetone until colorless washings. The material was dried under vacuum at 60°C for 14 h.

Preparation of MnPcS@MCM-41. A solution of 57 mg of $MnPc(SO_2Cl)_4$ in 20 ml of Py was stirred at 20°C for 22 h. This solution was slowly added to a suspension of 1 g of NH_2-MCM-41 in 10 ml of Py for 1.5 h under argon. The resulting mixture was stirred at 20°C for 3 h, then heated at 80°C for 24 h. A green material was isolated by filtration and washed with acetone and water. The material was dried under vacuum at 80°C for 24 h.

Preparation of iron tetraaminophthalocyanine and its fixation onto Cl-MCM-41. The reduction procedure was adapted from [24]. 94 mg of NaHS were added to the slurry of 75 mg of $FePc(NO_2)_4$ in 10 ml of dimethylformamide 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. The iron complex of tetraaminophthalocyanine was unstable in the presence of the air during work-up procedure. So, this complex was grafted onto Cl-MCM-41 without intermediate isolation according to two procedures.

1. The solid was dissolved in 20 ml of pyridine under argon and 1 g of Cl-MCM-41 was added. The reaction mixture was stirred at 100°C for 85 h under argon. The green material was isolated from cooled mixture by filtration and successively washed with acetone, water and ethanol. During washing procedure the color of the solid material gradually transformed to green-brown. The material was dried in vacuum at 70°C for 7 h.
2. Alternatively, the solid was dissolved in 20 ml of dimethylsulfoxide under argon, 1 g of Cl-MCM-41 was added and the resulting mixture was stirred for 1 h at 20°C. Then the mixture was stirred at 100°C for 26 h and cooled to room temperature. The green-gray solid was isolated by filtration, washed with ethanol and dried at 80°C in vacuum for 8 h.

Fixation of $FePcCl_{16}$ onto NH_2-MCM-41. A solution of 31 mg of $FePcCl_{16}$ in 20 ml of Py was stirred at 20°C for 7 h and slowly added to a suspension of 1 g of NH_2-MCM-41 in 10 ml of Py during 1 h under argon. The resulting mixture was stirred at 20°C for 1 h then refluxed for 24 h. A green material was separated by filtration, washed with acetone and dried in vacuum at 80°C for 15 h.

Typical procedure for 2-methylnaphthalene oxidation. A 25 ml flask was charged with 40 μmol of substrate in 2 ml of acetonitrile and 25–30 mg of supported catalyst, containing 1.6 μmol of metallophthalocyanine (4% catalyst/substrate ratio). 21 μl portions of 2.7 M TBHP solution in PhCl were added at reaction times of 0, 1, 2, 3 and 5 h and 31.5 μl at 7 h. Reactions were run for 24 h at 40°C under air. The course of the reaction was monitored by GC and substrate conversions and yields of VK_3 and 6-MeQ were determined using methylbenzoate as internal standard. The reaction products were identified and quantified by ^1H NMR and GC-MS methods. In this case the oxidation was performed in a 8 ml scale. After the reaction the solid catalyst was separated by filtration, washed with CH_2Cl_2 (2 × 3 ml). Organic phases were combined and the solvents were removed under vacuum. ^1H NMR ($CDCl_3$) [4]: 2-methylnaphthoquinone, δ 2.18 (d, 3H, CH_3), 6.83 (q, 1H, H_3), 7.68–7.75 (m, 2H, H_6 and H_7), 8.01–8.12 (m, 2H, H_5 and H_8); 6-methyl-1,4-naphthoquinone, δ 2.48 (s, 3H, CH_3), 6.93 (s, 2H, H_2 and H_3), 7.53 (dd, 1H, H_7), 7.86 (s, 1H, H_5), 7.96 (d, 1H, H_8). MS data (EI): 2-methyl-1,4-naphthoquinone, *m/z* (%) 172 (100) M^+, 144 (31) $(M\text{-}CO)^+$, 116 (33) $(M\text{-}2CO)^+$, 115 (78) $(M\text{-}2CO\text{-}H)^+$, 104 (68) $(M\text{-}COCHCCH_3)^+$, 76 (47) $(C_6H_4)^+$. 6-methyl-1,4-naphthoquinone, *m/z* (%) 172 (100) M^+, 144 (25) $(M\text{-}CO)^+$, 118 (51) $(M\text{-}C_2H_2)^+$, 116 (33) $(M\text{-}2CO)^+$, 115 (81) $(M\text{-}2CO\text{-}H)^+$, 90 (18) $(CH_3C_6H_3)^+$, 89 (66) $(C_7H_5)^+$. 2-naphthaldehyde, *m/z* (%) 156 (45) M^+, 155 (100) $(M\text{-}H)^+$, 127 (72) $(M\text{-}CHO)^+$, 126 (56) $(M\text{-}CHO\text{-}H)^+$. 2-naphthoic acid, *m/z* (%) 172 (100) M^+, 155 (50) $(M\text{-}OH)^+$, 127 (74) $(M\text{-}COOH)^+$. 2-methyl-2,3-epoxy-1,4-naphthoquinone, *m/z* (%) 188 (100) M^+, 173 (14) $(M\text{-}CH_3)^+$, 160 (20) $(M\text{-}CO)^+$, 158 (33) $(M\text{-}CH_2O)^+$, 132 (36) $(M\text{-}2CO)^+$, 131 (60) $(M\text{-}2CO\text{-}H)^+$, 115 (68) $(M\text{-}CH_3\text{-}2CO\text{-}2H)^+$, 76 (64) $(C_6H_4)^+$. 6-methyl-2,3-epoxy-1,4-naphthoquinone, *m/z* (%) 188 (25) M^+, 173 (100) $(M\text{-}CH_3)^+$, 160 (6) $(M\text{-}CO)^+$, 132 (9) $(M\text{-}2CO)^+$, 131 (22) $(M\text{-}2CO\text{-}H)^+$, 89 (81) $(C_7H_5)^+$. 4-methylphthalic anhydride, *m/z* (%) 162 (21) M^+, 118 (100) $(M\text{-}CO_2)^+$, 90 (42) $(M\text{-}CO_2\text{-}CO)^+$, 89 (90) $(M\text{-}CO_2\text{-}CO\text{-}H)^+$.

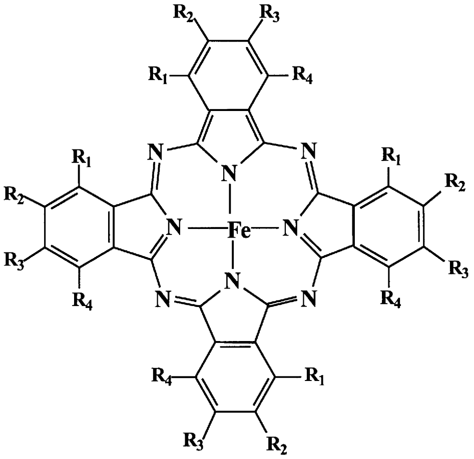
Typical procedure for 2,3,6-trimethylphenol oxidation. A 100 ml flask was charged with 160 μl of TMP in 8 ml of 1,2-dichloroethane and 25–30 mg of solid catalyst, containing 1.6 μmol of metallophthalocyanine (1% catalyst/substrate ratio). A 2.7 M TBHP solution in PhCl was added in 84 μl portions at reaction times of 0, 0.5, 1, and 1.5 h. Reactions were run for 2 h at 30°C under air.

3. Results

3.1. Preparation of metal complexes and modification of supports

Metal complexes of phthalocyanines were prepared according to published procedures [14–16,19,39]. Taking into account that the catalytic activity of the complex depends on the phthalocyanine structure, e.g. electron-donating or electron-withdrawing substituents at the periphery of the phthalocyanine molecule as well as the metal, we decided to prepare the iron complexes of three different phthalocyanine ligands: tetrasulfophthalocyanine (FePcS, **1a**), tetraaminophthalocyanine ($FePc(NH_2)_4$, **2a**) and hexachlorophthalocyanine ($FePcCl_{16}$, **3a**) (Fig. 1). To check the influence of the metal we have also prepared the manganese (MnPcS, **1b**) and cobalt (CoPcS, **1c**) complexes of tetrasulfophthalocyanine.

Recently discovered mesoporous silicas having large ordered hexagonal channels with diameter from 15 to 100 Å (MCM-41) and high surface area (above 700 m^2/g) are promising supports for different types of catalysts (for recent reviews on applications of MCM-41-based catalysts see Ref. [25,40–43]). MCM-41 was prepared as previously described [20] using $C_{16}H_{33}NH_2$ neutral primary amine as a template. Alternatively, we have also used an amorphous silica in order to evaluate the role of the support on the catalytic properties. Both mesoporous and amorphous silica have been modified with 3-aminopropyltriethoxysilane or with 3-chloropropyltrimethoxysilane to obtain 0.5 and 1.9 mmol of NH_2 and Cl sites per gram of materials, respectively. The modification was proven by the decrease of the silanol signals Q^2 (−91 ppm) and Q^3 (−100 ppm) and the appearance of a signal characteristic of $(SiO)_3Si\text{–}CH_3$ groups (−60 ppm) in the ^{29}Si MAS NMR spectrum. ^{13}C CP MAS NMR of NH_2-MCM-41 shows aminopropyl carbon signals at 5.5, 18.9 and 40.3 ppm. ^{13}C CP MAS NMR of Cl-MCM-41 shows chloropropyl carbon signals at 9.3, 26.3 and 45.7 ppm.



1 - $R_1, R_2, R_4 = H ; R_3 = SO_3^-$
2 - $R_1, R_2, R_4 = H ; R_3 = NH_2$
3 - $R_1, R_2, R_3, R_4 = Cl$

a - Fe
b - Mn
c - Co
d - Cr

Fig. 1. Structure of metal complexes of phthalocyanines.

Textural characteristics of initial and modified supports are listed in Table 1. A decrease of specific surface area and average pore diameter as well as a decrease of the mesoporous volume upon modification also indicates a successful covalent linkage of organic groups to the silica surface. The values of the BET parameter, C_{BET}, decreases from starting MCM-41 to modified material, suggesting a decrease in the average polarity of the surface as a result of the grafting of organic functionalities [42].

Iron, manganese and cobalt complexes of tetrasulfophthalocyanine were converted to corresponding tetrasulfochlorophthalocyanine complexes $MPc(SO_2Cl)_4$ by treatment with $SOCl_2$ or PCl_5.

3.2. Covalent linkage of complexes onto supports and characterization of the hybrid materials

The controlled covalent linkage of $FePc(SO_2Cl)_4$ onto amino-modified silica has been described in our previous communication [13]. Depending on the experimental conditions it was possible to fix FePcS on the surface either in a monomer or in a dimer form (Fig. 2). UV–Vis spectroscopy is a suitable method to identify these species since it is well established that the FePcS dimeric form shows an absorption maximum near 630–635 nm whereas the monomer form exhibits a peak in the region of 680 nm (for a discussion on the state of FePcS in solution and in the solid state see Ref. [15]). The diffuse reflectance UV–Vis spectra of the m-FePcS@MCM-41 and d-FePcS@MCM-41 are shown in Fig. 3. The spectrum of d-FePcS@MCM-41 catalyst shows bands at 352 and 636 nm corresponding to the spectrum of the dimeric species, along with a small shoulder at 690 nm indicating that the material also contains a small amount of the monomeric species. The spectrum of m-FePcS@MCM-41 shows maxima at 360, 436 and 682 nm, corresponding to a monomer form.

The CoPcS@MCM-41 and MnPcS@MCM-41 materials have been prepared by the method similar to

Table 1
Textural parameters of the supports

Material	Surface area ($m^2 g^{-1}$)	Pore diameter (Å)	Volume of pores[a] ($cm^3 g^{-1}$)	C_{BET}
MCM-41	860	40	1.30	132
NH_2-MCM-41	698	36	1.04	53
Cl-MCM-41	729	33	0.92	40

[a] Cumulative volume of pores with diameters between 25 and 45 Å.

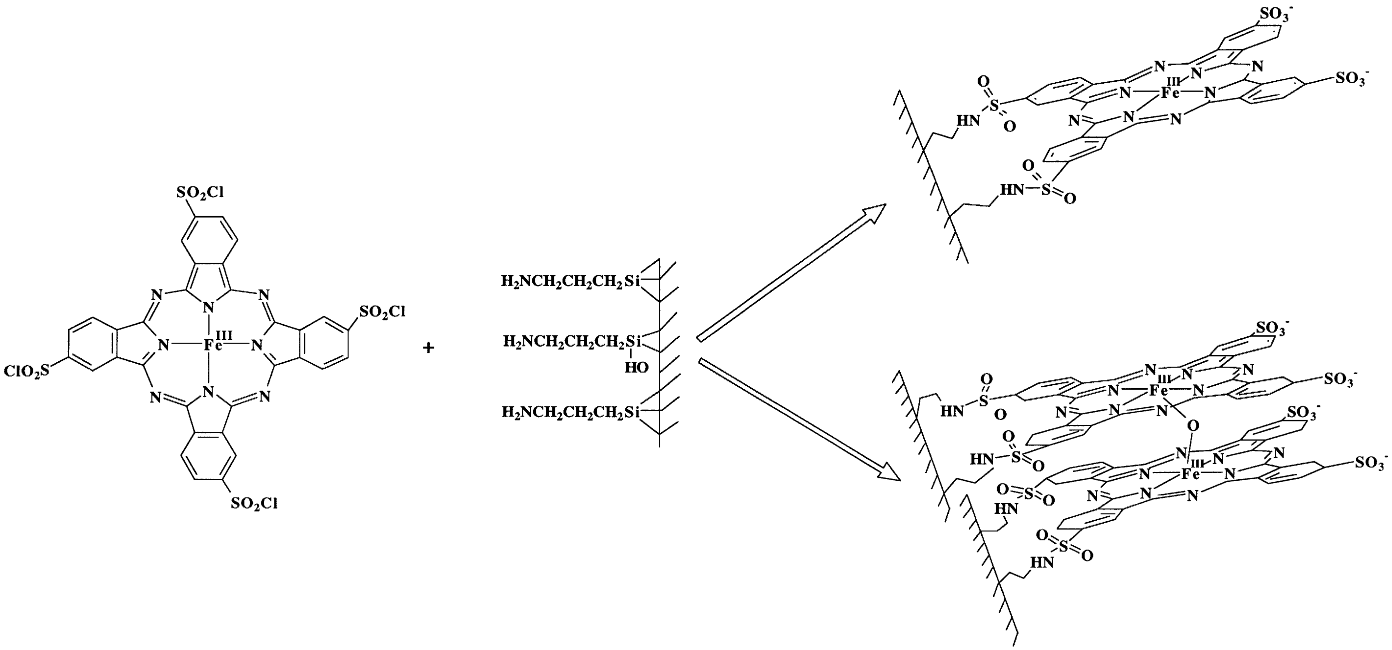


Fig. 2. Synthesis and schematic representation of the monomeric and dimeric FePcS catalysts supported on silica.

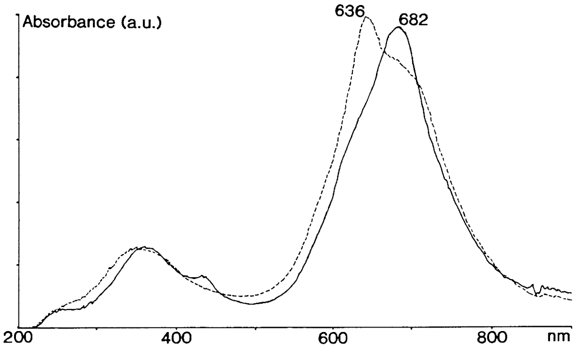


Fig. 3. Diffuse reflectance UV–Vis spectra of solid m-FePcS@MCM-41 (solid line) and d-FePcS@MCM-41 (broken line).

that used for the preparation of m-FePcS@MCM-41 (see Section 2). The diffuse reflectance UV–Vis spectra of the CoPcS@MCM-41 shows bands at 340 and 670 nm corresponding to the spectrum of the monomeric species along with a small shoulder at 620 nm due to a small amount of the dimeric species [26,44,45]. UV–Vis spectrum of MnPcS@MCM-41 shows bands at 378, 516 and 726 nm suggesting that MnPcS has also been fixed in the monomer form [27,46].

$FePcCl_{16}$@MCM-41 material was prepared by nucleophilic substitution of activated chlorine substituents of $FePcCl_{16}$ with the amine function of NH_2-MCM-41 support. $FePc(NH_2)_4$ has been prepared by reduction of $FePc(NO_2)_4$ with NaHS in DMF and directly grafted onto Cl-MCM-41 without isolation (Fig. 4). The diffuse reflectance UV–Vis spectra of both materials indicated the presence of phthalocyanines, but it was difficult to conclude whether $FePc(NH_2)_4$ and $FePcCl_{16}$ were grafted as a monomer or a dimer owing to the lack of UV–Vis data for these species.

The metal complex contents in the prepared materials were determined by metal analyzes using an inductively coupled plasma-mass spectrometry and were in the range of 16–60 μmol of complex per 1 g of material (Table 2). The supported catalysts have also been characterized by N_2 physisorption method. Nitrogen sorption isotherm analysis indicated that all MCM-41-based materials retained their mesoporous morphology after grafting of metallophthalocyanines. The isotherms of the grafted MCM-41 materials exhibit the type IV isotherm characteristic of the uniform pore size. The surface areas and mesoporous volumes further decreased after anchoring of phthalocyanine molecules. The higher values of BET parameter of metallophthalocyanine-modified silicas as compared to those of NH_2-MCM-41 and Cl-MCM-41 suggest an increase in the average polarity of the surface as a result of the grafting of phthalocyanines containing polar substituents on the periphery of the molecules.

3.3. Catalytic oxidation of 2-methylnaphthalene

The supported catalysts containing different metallophthalocyanines have been tested in the oxidation of 2MN by *t*-butylhydroperoxide (TBHP). The efficiency of the oxidation was shown to be sharply dependent on the solvent used. The conversions of 2MN were rather low when using CH_2Cl_2 and ethanol. The selectivity and conversion of 2MN oxidation catalyzed by d-FePcS@MCM-41 increased in the following order: isobutyric acid < acetone < 1,2-dichloroethane < acetonitrile. Oxidations in the presence of d-FePcS@MCM-41 catalyst were carried out at 20, 40 and 70°C. The conversions were 47, 54 and 62% after 5 h and 69, 81 and 82% after 24 h at 20, 40 and 70°C, respectively, while the yields of 2-methylnaphthoquinone were 21, 24, 23% (24 h) indicating no significant dependence of the efficiency of 2MN oxidation on temperature. Then, the further experiments on the 2MN oxidation in presence of different catalysts were conducted in MeCN at 40°C.

Apart from the practical importance, the oxidation of 2-MN is interesting from a selectivity point of view since oxidation can occur either on the methyl group or on the aromatic rings (Scheme 1). Moreover, aromatic oxidation provides two quinones: 2-methylnaphthoquinone and 6-methylnaphthoquinone (6MeQ), the former being the product of interest, VK_3. Consequently, an ideal catalyst should preferentially perform an aromatic oxidation in the methyl containing ring to provide a maximal yield of VK_3.

The data on 2MN oxidation in the presence of different metallophthalocyanine MCM-41 supported catalysts are listed in Table 3. d-FePcS@MCM-41 and m-FePcS@MCM-41 catalysts are the most active ones in terms of conversion, providing 81 and 61% con-

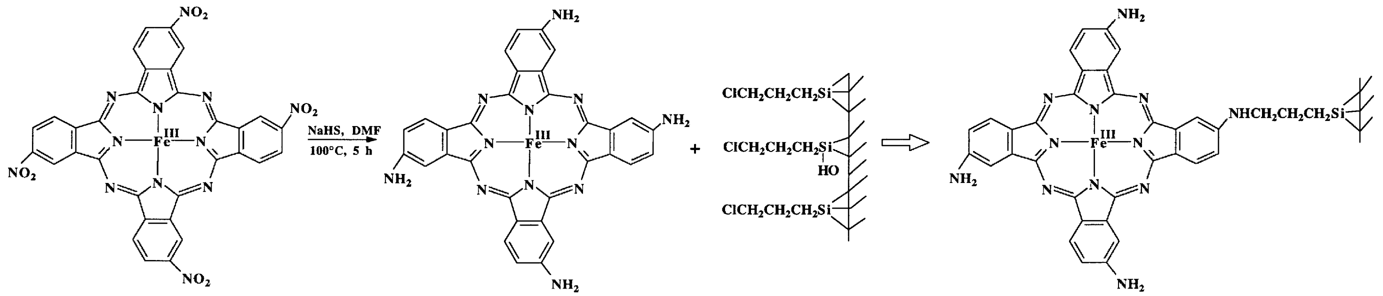
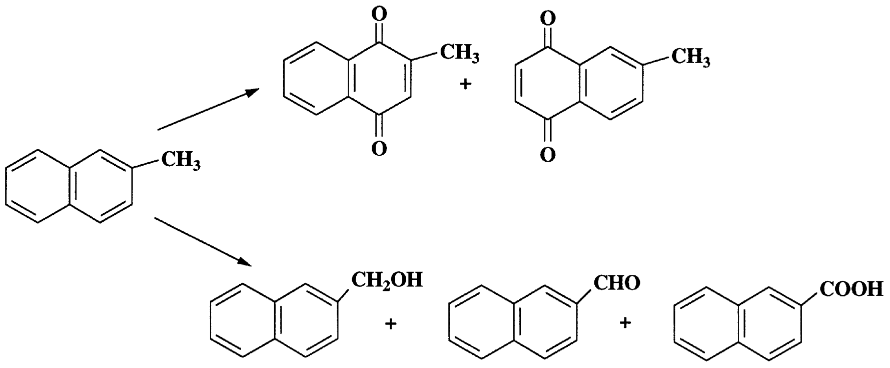


Fig. 4. Preparation of $FePc(NH_2)_4$@MCM-41 catalyst.

Table 2
Characterization of supported catalysts

Catalyst	Surface (m^2/g)	C_{BET}	Volume of pores[a] ($cm^3\,g^{-1}$)	Pore diameter (Å)	Complex content (μmol/g)	UV–Vis (λ, nm)
d-FePcS@MCM[b]	601	55	0.91	39	56.4	360, 640, 690$_{sh}$
d-FePcS@MCM[c]	604	42	0.40	33	34.9	352, 636, 690$_{sh}$
m-FePcS@MCM	712	70	0.98	35.5	32.2	360, 436$_{sh}$, 682
FePcCl$_{16}$@MCM	725	67	0.98	35	16.1	376, 437, 630, 691
FePcNH$_2$@MCM[d]	708	50	0.97	34	17.9	356, 404, 712$_{bd}$
FePcNH$_2$@MCM[e]	742	50	0.98	37	21.4	394, 732
CoPcS@MCM	630	76	0.65	44	49.2	340, 608$_{sh}$, 670
MnPcS@MCM	724	89	0.99	37	30.9	378, 516, 726
m-FePcS@SiO$_2$	159	43	–	–	59.0	360, 644, 694$_{sh}$
d-FePcS@SiO$_2$	173	102	–	–	51.9	370, 436, 680

[a] Cumulative volume of pores with diameters between 25 and 45 Å.
[b] Material prepared at 20°C.
[c] Material prepared at 80°C.
[d] Protocol 1, in pyridine.
[e] Protocol 2, in DMSO.



Scheme 1. Possible routes of 2-methylnaphthalene oxidation.

Table 3
Oxidation of 2MN by TBHP catalyzed by metallophthalocyanine supported catalysts (n.d. — not determined)

Run	Catalyst	Conversion (%)		Yields[a] (%)			VK_3/6MeQ ratio (mol/mol)
		5 h	24 h	VK_3	6MeQ	Naphthoic acid	
1	d-FePcS@MCM	54	81	24	11	15	67:33
2	d-FePcS@MCM[b]	46	80	34	12	n.d.	75:25
3	m-FePcS@MCM	37	61	10	3	n.d.	74:26
4	m-FePcS@SiO$_2$	32	58	11	3	n.d.	77:23
5	Homogeneous FePcS	36	64	11	6	n.d.	68:32
6	d-FePcS@SiO$_2$	53	78	24	11	n.d.	70:30
7	d-FePcS@SiO$_2$[b]	55	90	34[c]	9[c]	n.d.	81:19
8	FePcCl$_{16}$@MCM	20	40	12	6	24	68:32
9	FePcNH$_2$@MCM	32	45	32	13	–	75:25
10	MnPcS@MCM	26	49	14	6	14	71:29
11	CoPcS@MCM	9	16	tr.	–	–	–

[a] Based on converted substrate, after 24 h.
[b] Reaction carried out with 20 μmol of substrate and 2 μmol of catalyst.
[c] After 7 h.

versions after 24 h, respectively (runs 1–3, Table 3). Other iron containing catalysts having hexachloro- and tetraaminophthalocyanine ligands are shown to be less active, resulting in 40–45% conversions (runs 8 and 9, Table 3). MnPcS@MCM-41 catalyst exhibits a similar catalytic activity, while CoPcS@MCM-41 is the less active catalyst.

The main products of 2MN oxidation were 2-methylnaphthoquinone (VK_3), 6-methylnaphthoquinone (6MeQ), products of the oxidation of the methyl group, 2-naphthaldehyde and naphthoic acid, as well as some unidentified products, presumably coupling products. All these products were identified using GC-MS and ^1H NMR methods and the authentic compounds, when it was possible. Additionally, small amounts of some over-oxidation products, including VK_3 2,3-epoxide, 6-methyl-2,3-epoxy-1,4-naphthoquinone and 4-methylphthalic anhydride, have been identified by GC-MS.

The product selectivity depends on the catalyst structure. $FePc(NH_2)_4$@MCM-41 was the most selective catalyst to obtain VK_3. However, a quite fast bleaching of this catalyst took place during reaction resulting only in 45% conversion. d-FePcS@MCM-41 catalyst exhibits preferential aromatic ring oxidation: 35% yield of quinones vs 15% yield of naphthoic acid. Mn-based catalyst shows a similar activity in aromatic and aliphatic chain oxidation, while $FePcCl_{16}$@MCM-41 is most active in the oxidation of methyl group providing naphthoic acid as a principal product.

Concerning the regioselectivity of the aromatic ring oxidation, all catalysts tested preferentially oxidize the methyl-containing ring, the VK_3/6MeQ molar ratio being between 70:30 and 80:20.

Taking into account the highest activity and the reasonable selectivity in VK_3 formation of iron tetrasulfophthalocyanine-based catalysts, these materials have been chosen for a more detailed study of 2MN oxidation. The dimer and monomer forms of FePcS have been immobilized onto amorphous silica and the catalytic activities of both mesoporous and amorphous silica supported catalysts were compared with the corresponding homogeneous oxidation in the presence of the tetrabutylammonium salt of FePcS. Homogeneous oxidation of 2MN gave only 11% VK_3. When monomeric catalysts supported on either MCM-41 or SiO_2 were used, conversions and selectivities were rather close to those of the homogeneous catalyst. Surprisingly, dimer-based catalysts were more active and selective compared to homogeneous and monomeric supported catalysts (Table 3). The porosity of the support has no influence on the reaction rate and selectivity. The yield of VK_3 after 7 h was 34% and the ratio between VK_3 and 6MeQ was 81:19 (run 7, Table 3), indicating that the catalytic system is quite selective in the oxidation of the methyl containing ring. The stability of both quinones under reaction conditions has been evaluated in two separate experiments. Under the same conditions the conversions after 24 h were 21 and 22% for VK_3 and 6MeQ, respectively, indicating that they were less oxidizable than 2MN. Consequently, the high selectivity towards VK_3 is due to initial selective oxidation of 2MN, not to preferential over-oxidation of 6MeQ compared to VK_3. This result was also confirmed by looking at product selectivities in course of reaction. The VK_3/6MeQ ration was found to be independent on reaction time.

We obtained a slower reaction rate and a lower selectivity when the oxidation of 2MN was performed under argon. Consequently, O_2 takes part in the reaction pathway leading to quinones. This result is in accordance with a previously proposed mechanism for the oxidation of polycyclic aromatics via successive 1 e^- oxidations, when intermediate radicals can be trapped by O_2 to produce quinone.

Alternatively, we checked the influence of small additives of acid or base on the catalytic properties of the system. The 2MN conversions and VK_3 selectivity dropped when 2MN oxidation catalyzed by d-FePcS@MCM-41 was performed in the presence of the small amounts of acetic acid or pyridine (10–125 fold excesses to FePcS).

3.4. Catalytic oxidation of 2,3,6-trimethylphenol

A beneficial effect of supporting dimeric FePcS on a silica support was even more significant in the oxidation of 2,3,6-trimethylphenol (TMP) to trimethyl-1,4-benzoquinone (TMQ), an important intermediate for the preparation of vitamin E. The efficiency of the oxidation depended on the solvent used. The TMP conversion and yield of TMQ increased in the order: acetic acid $<$ acetonitrile $<$ 1,2-dichloroethane. Interestingly, acetonitrile was the best solvent for 2MN oxidation, while 1,2-dichloroethane was more suitable for TMP oxidation. When using 1,2-dichloroethane the oxidation of TMP was quite rapid, the conversions being quasi-complete after 2 h. In the absence of catalyst under otherwise identical conditions less than 10% conversion was detected after 2 h. Again, with homogeneous and monomeric FePcS supported catalyst the yields of TMQ were rather low, ranging from 21 to 47% (Table 4). A significant enhancement of selectivity was observed with dimeric catalyst immobilized onto amorphous SiO_2 for which 77–80% yields of TMQ have been obtained (runs 5 and 6, Table 4). By contrast, dimeric FePcS catalyst fixed on MCM-41 shows an even lower selectivity than homogeneous or monomeric heterogeneous catalysts (run 4, Table 4). The reason for such a low selectivity for d-FePcS@MCM-41 in the oxidation of TMP can be explained by the simultaneous formation of 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol (BP) along with TMQ. This product was shown to be an intermediate in the oxidation of TMP in the presence of molybdovanadophosphoric heteropoly acids, which was further oxidized to TMQ [28]. Indeed, ^{1}H NMR analysis of the reaction mixture revealed the presence of BP along with TMQ (signals of benzene ring protons at 6.63 and 6.49 ppm). In the case of d-FePcS@MCM-41 mediated oxidation, the reaction of this large dimeric catalyst immobilized inside the mesopores of MCM-41 with such a bulky substrate as BP (or the corresponding quinone) should be diffusionally restricted, while the further oxidation of BP should be more favored with dimeric FePcS fixed onto amorphous non-porous silica, resulting in a high selectivity for this catalyst to produce TMQ. The difference in density of the active sites on the surface between d-FePcS@MCM-41 (0.09 μmol/m^2) and d-FePcS@SiO_2 (0.3 μmol/m^2) could also be responsible for a high selectivity of the catalyst immobilized on non-porous silica. This example illustrates the importance not only of the state of the catalytic complex, but also of the texture of the support on the catalytic properties of the catalyst.

Table 4
Catalytic oxidation of 2,3,6-trimethylphenol by TBHP in 1,2-dichloroethane at 30°C

Run	Catalyst	Conversion after 2 h (%)	Yield of quinone[a] (%)
1	Homogeneous FePcS	96	47
2	m-FePcS@MCM-41	98	21
3	m-FePcS@SiO_2	95	42
4	d-FePcS@MCM-41	98	24
5	d-FePcS@SiO_2	96	77
6	d-FePcS@SiO_2[b]	96	80
7	MnPcS@MCM-41	96	40
8	MnPcS@SiO_2	65	22
9	MnPcS@SiO_2[c]	94	47
10	d-FePcS@MCM-41[d]	96	16

[a] Based on converted substrate.

[b] Reaction performed with 40 μmol of substrate and 1.6 μmol of catalyst, other conditions being the same.

[c] Reaction time 19 h.

[d] Reaction was run at 20°C in acetonitrile.

3.5. Stability and recycling of supported catalyst

The stability of the supported heterogeneous catalyst under reaction conditions means (i) no leaching of the active species into solution and (ii) no degradation of active form of the catalyst during reaction providing stable and recyclable heterogeneous catalyst. The leaching of the metal ions or complexes is often the problem in the case of transition metal substituted molecular sieves and transition metal complexes immobilized by electrostatic interaction [29]. To test for leaching we filtered the catalyst after 30 min reaction (57% conversion was achieved at this stage) and allowed the filtrate to react further. No further reaction was detected, suggesting no leaching of the complex into solution. Additionally, a UV–Vis spectrum of the recovered filtrate did not show any adsorption peaks in the 600–700 nm region, indicating that possible leaching of FePcS was below the detection limit (less than 0.02% from FePcS fixed).

The stability of the d-FePcS@SiO_2 catalyst was studied in repetitive TMP oxidation reactions under conditions of run 5, Table 4. After completion of the first TMP oxidation the solution was carefully removed by decantation. New portions of substrate stock solution and oxidant were added to the recovered catalyst (no regeneration procedure was applied) to perform a second oxidation. The same procedure was repeated once more. The catalytic activity of the recovered solid material remained uncharged:

Table 5
Oxidation of TMP in the presence of Ti catalysts in acetonitrile

Run	Catalyst	Oxidant (temperature)	Conversion (reaction time)	Yield of TMQ (%)
1	Ti-MCM-41	H_2O_2 (30°C)	98% (24 h)	91
2	Ti-MCM-41	H_2O_2 (70°C)	98% (4 h)	86
3	Ti-beta	H_2O_2 (70°C)	99% (4 h)	93
4	Ti-MCM-41	TBHP (70°C)	65% (23 h)	32

96, 97 and 93% conversions in the 1st, 2nd and 3rd run, respectively, while the yield of TMQ gradually diminished: 77, 59 and 51%. After the 3rd run, the catalyst was recovered, washed with acetone and dried. The UV–Vis spectrum showed a rather sharp band at 688 nm indicating monomeric FePcS as the major species, along with a small shoulder at 648 nm due to residual dimeric FePcS. The yield of TMQ in m-FePcS@SiO_2 mediated oxidation of TMP was 42% (run 3, Table 4). Thus we can conclude that during the catalytic reactions the selective dimeric catalyst was gradually transformed to the less selective monomeric species, resulting in a decrease in TMQ yield.

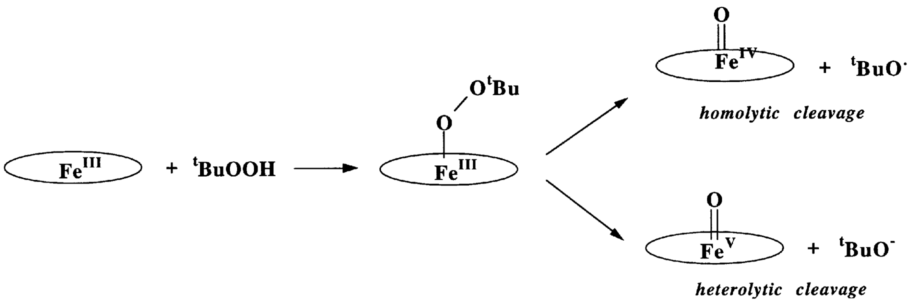
3.6. Comparison of metallophthalocyanine supported catalysts with Ti-MCM-41 and Ti-beta

Ti-MCM-41 and Ti-beta titanium containing catalysts have also been tested in the oxidation of 2MN and TMP by H_2O_2 and TBHP. Indeed, these catalysts were reported to be active in aromatic ring oxidation in the presence of both oxidizing agents. In particular, Ti-MCM-41 catalyzes the oxidation of 2,6-di-*t*-butylphenol to the corresponding quinone with high activity and selectivity [30]. By contrast to metallophthalocyanine supported catalysts Ti-MCM-41 and Ti-beta were completely inactive in the oxidation of 2MN by H_2O_2 or TBHP, while both Ti containing materials were very active in the oxidation of TMP (Table 5). Higher conversion and selectivity in TMQ formation were obtained when using H_2O_2 as an oxidant rather than TBHP. The reaction was rather slow at 30°C (reaction time — 24 h), but at 70°C the maximal conversion and TMQ yield were achieved after 4 h. These data clearly show the superiority of metallophthalocyanine supported catalysts as compared to Ti-substituted materials in the oxidation of aromatic hydrocarbons like 2-methylnaphthalene.

4. Discussion

We have prepared metallophthalocyanine complexes covalently anchored onto mesoporous or amorphous silica and tested them in the catalytic oxidation of the aromatic compounds. A dimeric FePcS supported catalyst revealed promising catalytic properties in the heterogeneous oxidation of 2-methylnaphthalene and 2,3,6-trimethylphenol to the corresponding quinones.

Generally, μ-oxo-dimeric species are considered as catalytically inert forms. This work presents an example where a dimeric iron phthalocyanine catalyst is more active and selective than the monomeric one in the oxidation of 2-methylnaphthalene and 2,3,6-trimethylphenol. The reason for the better catalytic properties of the dimer supported catalyst is not yet well understood. In the homogeneous oxidation of trichlorophenol by FePcS/H_2O_2 system a nucleophilic $PcSFe^{III}–OO^-$ complex was proposed to be the active species [6,31]. 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/H_2O_2 [31]. An electrophilic $PcSFe^{IV}=O$ complex (one redox equivalent above the Fe^{III} state) was proposed to be the active species involved in the FePcS mediated homogeneous oxidation of condensed aromatic compounds by H_2O_2 [12]. When using ^tBuOOH as an oxidant one can suggest the formation of $PcSFe^{III}–OO^tBu$ complex on the first step. In general, peroxides can react with iron porphyrin complexes via homolytic or heterolytic cleavage of the O–O bond to form $LFe^{IV}=O$ or $LFe^{V}=O$ species (L — porphyrin ligand), respectively [32]. It is reasonable to assume that iron phthalocyanine would be able to react with ^tBuOOH in the same way to give $PcSFe^{IV}=O$ or $PcSFe^{V}=O$ according to Scheme 2.



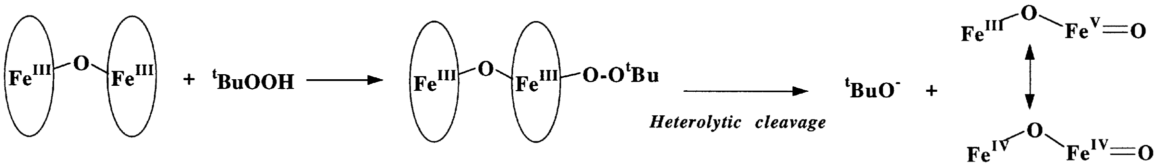
Scheme 2. Proposed mechanism of the formation of active species from monomeric form of FePcS and TBHP.

It has been concluded that the higher oxidation states of the central transition metal ions are more readily accessible in the porphyrin series than in the phthalocyanine series [33]. In other words, phthalocyanine ligand tends to stabilize the lower oxidation states of metal compared to porphyrin one. This implies that high oxidation states metallophthalocyanines should be stronger oxidizing agents than their porphyrin analogues in the same oxidation state. In porphyrin series the kind of the cleavage of O–O bond (homolytic vs heterolytic) is determined by the structures of porphyrin ligand and peroxide and the presence of axial ligand, which favors a heterolytic O–O bond cleavage [32].

Taking into account above considerations, one can suggest, that in the case of PcSFe^{III}–OO^{t}Bu peroxo complex, *homolytic* cleavage of O–O bond to give PcSFe^{IV}=O and ^{t}BuO$^\cdot$ should be favored to heterolytic pathway to produce PcSFe^{V}=O, since Fe^{V} oxidation state is less accessible in phthalocyanine complex than in porphyrin one. This proposal is in accordance with previously proposed PcSFe^{IV}=O as the active species in FePcS/H_2O_2 mediated oxidation of condensed aromatics [12].

In the course of the homolytic cleavage of O–O bond of PcSFe^{III}–OO^{t}Bu, the ^{t}BuO$^\cdot$ radical produced could be involved in the chain oxidation side reactions resulting in the decrease of the overall selectivity of 2MN and TMP oxidations. In the case of dimeric FePcS complex with peroxide a *heterolytic* cleavage of O–O bond with parallel formation of ^{t}BuO$^-$ rather than a radical should be much more favorable than in the case of monomeric FePcS due to the possibility of the delocalization of the charge on two iron atoms of the dimer (Scheme 3). 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.

Recycling experiments indicated that during the catalytic reaction the selective dimeric catalyst was gradually transformed to the less selective monomeric



Scheme 3. Proposed mechanism of the formation of active species from dimeric form of FePcS and TBHP.

catalyst. Therefore, further studies are needed to characterize the state of the complexes on the silica surface and to stabilize a μ-oxo-dimer of FePcS on the surface of the support.

5. Conclusion

Iron, manganese and cobalt phthalocyanine complexes have been anchored onto the surface of mesoporous and amorphous silicas. Anchoring was performed by modifying silica with 3-aminopropyltriethoxysilane followed by reaction with tetrasulfochlorophthalocyanine complexes. For mesoporous materials, the modification resulted in a decrease of surface area, mean pore diameter as well as BET constant, indicating a decrease in the average surface polarity due to the grafting of organic functionalities. By an appropriate choice of reaction conditions, iron complexes have been grafted either in the monomeric or in the dimer form, as evidenced by UV–Vis spectroscopy. Both Co- and Mn-based complexes showed a poor activity in oxidation of aromatic substrates. By contrast, Fe-based catalysts were active and selective in the oxidation of 2-methylnaphthalene and 2,3,6-trimethylphenol with TBHP. Oxidation of 2MN gave essentially 2-methyl-1,4-naphthoquinone (VK_3) and 6-methyl-1,4-naphthoquinone with a strong excess in VK_3. Ti-substituted silica-based catalysts were inactive in this reaction, whatever the nature of the oxidizing agent. Nevertheless, excellent results were obtained in oxidation of 2,3,6-trimethylphenol to the corresponding quinone over Ti-containing materials with aqueous H_2O_2 as oxidizing agent. Iron tetrasulfophthalocyanine grafted on silica was also very active in the oxidation of 2,3,6-trimethylphenol to the corresponding quinone with TBHP. Higher activities were obtained over amorphous catalyst, suggesting a diffusion limitation of the large organic molecules within the porous system of the mesoporous containing catalyst. For both reactions, the dimeric form of the FePcS supported complex was found to be more active and selective than the monomeric one, that was quite unexpected since dimeric species have often been considered as inactive in homogeneous catalysis. However, it was observed that the dimeric species were gradually transformed into the monomeric species during recycling experiments, suggesting a rearrangement of complexes on the surface in course of the reaction. Attempts to stabilize the dimeric form of the complex under reaction conditions are in progress.

References

[1] M. Hudlicky, Oxidation in organic chemistry, ACS Monograph, Vol. 186, Washington, DC, 1990.
[2] W. Adam, W.A. Herrmann, J. Lin, C.R. Saha-Möller, R.W. Fisher, J.D.G. Correia, Angew. Chem. Int. Ed. Engl. 33 (1994) 2475.
[3] W.A. Herrmann, J.J. Haider, R.W. Fisher, J. Mol. Catal. A: Chem. 138 (1999) 115.
[4] R. Song, A. Sorokin, J. Bernadou, B. Meunier, J. Org. Chem. 62 (1997) 673.
[5] M.J. Chen, J.W. Rathke, in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, Vol. 4, VCH, New York, 1996, pp. 187–198.
[6] A. Sorokin, J.-L. Séris, B. Meunier, Science 268 (1995) 1163.
[7] K.J. Balkus Jr., M. Eissa, R. Levado, J. Amer. Chem. Soc. 117 (1995) 10753.
[8] R.F. Parton, I.F.J. Vankelecom, M.J.A. Casselman, C.P. Bezoukhanova, J.B. Uytterhoeven, P.A. Jacobs, Nature 370 (1994) 541.
[9] R.F. Parton, P.E. Neys, P.A. Jacobs, R.C. Sosa, P.G. Rouxhet, J. Catal. 164 (1996) 341.
[10] S. Ernst, R. Gläser, M. Selle, Stud. Surf. Sci. Catal. 105 (1997) 1021.
[11] U. Schubert, A. Lorenz, N. Kundo, T. Stuchinskaya, L. Gogina, A. Salanov, V. Zaikovskii, V. Maizlish, G.P. Shaposhnikov, Chem. Ber. 130 (1997) 1585.
[12] A. Sorokin, B. Meunier, Eur. J. Inorg. Chem. (1998) 1269.
[13] A. Sorokin, A. Tuel, New J. Chem. 23 (1999) 473.
[14] J.H. Weber, D.H. Busch, Inorg. Chem. 4 (1965) 469.
[15] A. Hadasch, A. Sorokin, A. Rabion, B. Meunier, New J. Chem. 22 (1998) 45.
[16] J. Metz, O. Schneider, M. Hanack, Inorg. Chem. 23 (1984) 1065.
[17] A.N. Grinev, V.N. Ermakova, A.P. Terent'ev, Zh. Obshch. Khim. 29 (1959) 90.
[18] M. Shimizu, H. Orita, T. Hayakawa, K. Takehira, Tetrahedron Lett. 30 (1989) 471.
[19] B.N. Achar, G.M. Fohlen, J.A. Parker, J. Keshavayya, Polyhedron 6 (1987) 1463.
[20] A. Tuel, S. Gontier, Chem. Mater. 8 (1996) 114.
[21] A. Corma, M.T. Navarro, J. Perez-Parienté, J. Chem. Soc., Chem. Commun. (1994) 147.
[22] R.J. Davis, Z. Liu, J.E. Tabora, W.S. Wieland, Catal. Lett. 34 (1995) 101.
[23] M. Laspéras, T. Llorett, L. Chaves, I. Rodriguez, A. Cauvel, D. Brunel, Stud. Surf. Sci. Catal. 108 (1997) 75.
[24] Y. Orihashi, M. Nishikawa, H. Ohno, E. Tsuchida, H. Matsuda, H. Nakanishi, M. Kato, Bull. Chem. Soc. Jpn. 60 (1987) 3731.
[25] A. Corma, Chem. Rev. 97 (1997) 2373.

[26] E.W. Abel, J.M. Pratt, R. Wherlan, J. Chem. Soc., Dalton Trans. (1976) 509.

[27] A.B.P. Lever, J.P. Wilshire, S.K. Quan, Inorg. Chem. 20 (1981) 761.

[28] O.A. Kholdeeva, A.V. Golovin, R.I. Maksimovskaia, I.V. Kozhevnikov, J. Mol. Catal. 75 (1992) 235.

[29] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485.

[30] W. Zhang, M. Fröba, J. Wang, P.T. Tanev, J. Wong, T.J. Pinnavaia, J. Amer. Chem. Soc. 118 (1996) 9164.

[31] B. Meunier, A. Sorokin, Acc. Chem. Res. 30 (1997) 470.

[32] B. Meunier, Chem. Rev. 92 (1992) 1411.

[33] A.B.P. Lever, E.R. Milaeva, G. Speier, in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, Vol. 3, VCH, New York, 1993, pp. 1–69.

[34] K.J. Balkus Jr., in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, Vol. 4, VCH, New York, 1996, pp. 285–305.

[35] A. Sorokin, B. Meunier, Chem. Eur. J. 2 (1996) 1308.

[36] R.F. Parton, I.F.J. Venkelecom, D. Tas, K.B.M. Janssen, P.-P. Knops-Gerrits, P.A. Jacobs, J. Mol. Catal. A: Chem. 113 (1996) 283.

[37] S.V. Barkanova, V.M. Derkacheva, O.V. Dolotova, V.D. Li, V.M. Negrimovski, O.L. Kaliya, E.A. Luk’yanets, Tetrahedron Lett. 37 (1996) 1637.

[38] S.V. Barkanova, O.L. Kaliya, J. Porphyrins Phthalocyanines 3 (1999) 180.

[39] M.N. Golovin, P. Seymour, K. Jayaraj, Y. Fu, A.B.P. Lever, Inorg. Chem. 29 (1990) 1719.

[40] T. Maschmeyer, J.M. Thomas, A.F. Masters, in: C.R.A. Catlow, A. Cheetham (Eds.), New Trends in Material Chemistry, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997, pp. 461–494.

[41] J.H. Clark, D.J. Macquarrie, Chem. Commun. (1998) 853.

[42] D. Brunel, N. Bellocq, P. Sutra, A. Cauvel, M. Laspéras, P. Moreau, F. Di Renzo, A. Galarneau, F. Fajula, Coord. Chem. Rev. 178–180 (1998) 1085.

[43] D. Brunel, Microporous Mater. 27 (1999) 329.

[44] A. Skorobogaty, T.D. Smith, J. Mol. Catal. 16 (1982) 137.

[45] Y.-C. Yang, J.R. Ward, R.P. Seiders, Inorg. Chem. 24 (1985) 1765.

[46] C. Ercolani, B. Floris, in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, Vol. 2, VCH, New York, 1993, pp. 1–41.