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Letter

Heterogeneous oxidation of aromatic compounds catalyzed by metallophthalocyanine functionalized silicas

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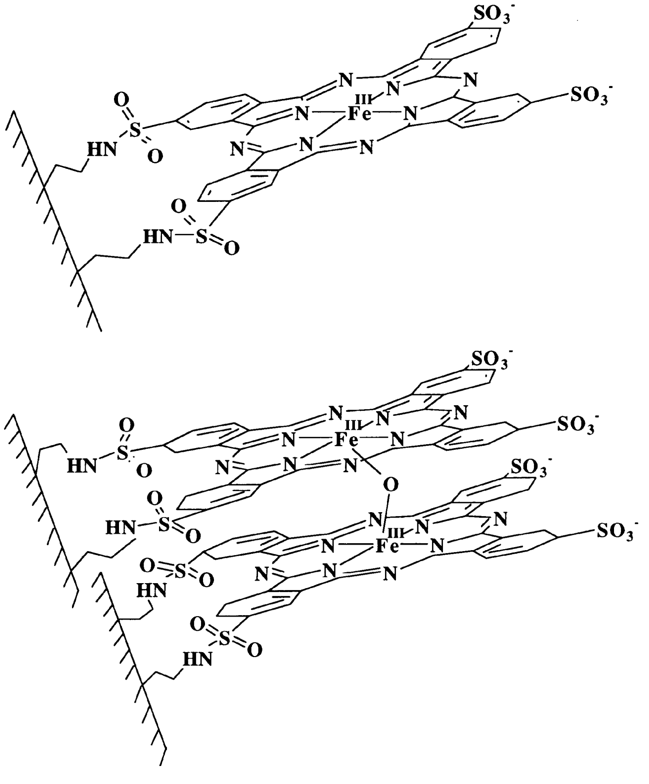
Controlled procedures for the covalent anchoring of iron tetrasulfophthalocyanine onto amino-modified silicas have been developed to fix the complex either in a monomer or dimer form. Usually considered as a catalytically inert form, dimeric μ-oxo iron tetrasulfophthalocyanine grafted onto amino-modified silica or MCM-41 is shown to be a selective catalyst for the oxidation of 2-methylnaphthalene to 2-methylnaphthaquinone (vitamin K_3) and of 2,3,6-trimethylphenol to trimethylbenzoquinone.

Catalytic methods involving environmentally friendly oxidants are needed to perform selective oxidation of alkylaromatics. For example, 2-methylnaphthoquinone (Vitamin K_3) is still prepared by stoichiometric oxidation of 2-methylnaphthalene (2MN) by CrO_3 in H_2SO_4, thus leading to severe environmental problems. As an alternative, several homogeneous catalytic methods have been developed.[1,2] Oxidation of aromatic compounds to quinones is a multistep reaction and the yields are rarely high because of coupling and over-oxidation reactions. Vitamin K_3 is obtained by 2MN oxidation with CrO_3–H_2SO_4 in 38–60% yields. A 46% yield of vitamin K_3 was reported in 2MN oxidation by the CH_3ReO_3–85% H_2O_2 system.[1] Recently, iron tetrasulfophthalocyanine (FePcS) has been shown to be an active catalyst in the oxidative degradation of chlorinated phenols[3] and in the homogeneous oxidation of condensed aromatics.[4] The fixation of active catalysts onto appropriate supports is highly desirable to provide a high catalyst stability as well as facile recovery and recycling. Another reason to immobilize homogeneous complexes is that homogeneous solutions of complexes often contain several species, for example, monomers and dimers, while only some species, usually monomeric ones, are catalytically active. For example, among the several monomer and dimer forms of FePcS in aqueous solutions, monomeric FePcS has been proposed to be the catalytically active complex in the oxidative degradation of trichlorophenol.[5] Consequently, by using appropriate methods one can prepare a heterogeneous catalyst supporting only the catalytically active form of the complex. We report here the controlled covalent anchoring of phthalocyanine complexes onto mesoporous MCM-41 silica (Scheme 1) and the catalytic properties of these hybrid materials in the oxidation of 2-methylnaphthalene and 2,3,6-trimethylphenol. Recently discovered mesoporous silicas having large ordered hexagonal channels with diameters from 15 to 100 Å (MCM-41) and high surface areas (above 700 m^2 g^{-1}) are promising supports for different types of catalysts.[6]



Scheme 1 Schematic representation of the monomeric and dimeric FePcS catalysts supported on silica.

MCM-41 was prepared as previously described[7] and modified with 3-aminopropyltriethoxysilane to obtain 0.5 mmol of NH_2 groups per gram of material. 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 $(SiO)_3Si{-}CH_2$ groups (-60 ppm) in the ^{29}Si MAS NMR spectrum. ^{13}C CP MAS NMR shows aminopropyl carbon signals at 5.5, 18.9 and 40.3 ppm. Textural characteristics of some solid materials are listed in Table 1. A decrease of specific surface area from 860 to 698 m^2 g^{-1} and average pore diameter from 40 to 36 Å as well as a decrease of the mesoporous volume from 1.30 to 1.04 cm^3 g^{-1} also indicates a successful modification of MCM-41.

Table 1 Textural parameters of the supports and supported catalysts

Material	Surface area/ m^2 g^{-1}	Pore diameter/ nm	Volume of pores[a]/ cm^3 g^{-1}
MCM-41	860	4.0	1.30
NH_2-MCM-41	698	3.6	1.04
m-FePcS@MCM-41	712	3.6	0.98
d-FePcS@MCM-41	601	3.9	0.91
m-FePcS@SiO_2	159	—	—
d-FePcS@SiO_2	173	—	—

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

FePcS was converted to iron tetrasulfochlorophthalocyanine, $FePc(SO_2Cl)_4$, by treatment with $SOCl_2$ or PCl_5. For covalent anchoring of $FePc(SO_2Cl)_4$ onto amino-modified MCM-41 two strategies were used in order to fix the phthalocyanine complex either as a monomer or as a dimer. We used UV-vis spectroscopy to identify these species. There is general agreement in the literature that the FePcS dimeric form in solution 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. 5). The UV-vis spectra obtained for FePcS adsorbed on either Pt or graphite were essentially identical to that of the solution.[8] This indicates that the interactions between the orbitals associated with the absorption bands are not involved to a large extent in the bonding of FePcS to the surface.[8] In the case of FePcS covalently grafted onto silica these considerations should be pertinent and physico-chemical properties, for example UV-vis spectra, of such grafted complexes should not differ much from those of the species in solution.

The dimeric material (d-FePcS@MCM-41) was prepared as follows. A solution of 300 mg of $FePc(SO_2Cl)_4$ in 35 mL of pyridine (Py) was added to a suspension of 3 g of amino-modified MCM-41 in 20 mL of Py under argon at 20 °C for 15 min. The resulting mixture was stirred under argon at 20 °C for 24 h. An intensely colored blue material was separated from the colorless solution by filtration and subsequently washed with water and acetone, followed by drying under vacuum at 80 °C for 24 h. The diffuse reflectance UV-vis spectrum of the solid shows bands at 352 and 636 nm corresponding to the spectrum of the dimeric species,[5] along with a small shoulder at 690 nm indicating that the material also contains a small amount of the monomeric species (Fig. 1).

For the preparation of a material containing the monomeric form of the complex (m-FePcS@MCM-41) the procedure was modified as follows. A solution of 52 mg of $FePc(SO_2Cl)_4$ in 20 mL of Py was stirred for 18 h to transform the major μ-oxo-dimeric species to a dipyridine complex of the monomer. Then this solution was slowly added to a suspension of 1.5 g of amino-modified MCM-41 in 12 mL of Py at 20 °C under Ar. The resulting mixture was stirred at 20 °C for 1.5 h, then at 80 °C for 24 h. A green material was separated by filtration and washed with acetone and water. Finally, the material was dried under vacuum at 80 °C for 24 h. The diffuse reflectance UV-vis spectrum shows bands at 360, 436 and 682 nm, indicating that FePcS has been fixed in the monomeric form (Fig. 1).

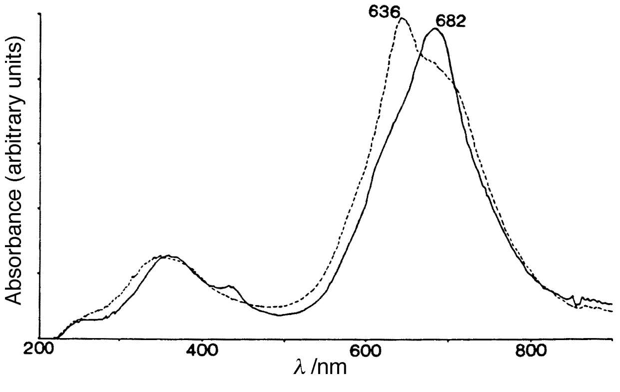


Fig. 1 The diffuse reflectance UV-vis spectra of solid m-FePcS@MCM-41 (solid line) and d-FePcS@MCM-41 (broken line).

The FePcS contents of the prepared materials were determined by iron analyses using an inductively coupled plasma-mass spectrometry method and were found to be 35.8 and 56.4 $\mu mol\ g^{-1}$ for m-FePcS@MCM-41 and d-FePcS@MCM-41, respectively. Textural characteristics of the catalysts are listed in Table 1. In order to check the influence of the porosity of the support, monomeric and dimeric FePcS were also grafted onto amino-modified non-porous SiO_2 (Aerosil 200, Degussa), according to the procedures mentioned above. The diffuse reflectance UV-vis spectra of m-FePcS@SiO_2 (59.0 $\mu mol\ g^{-1}$) and d-FePcS@SiO_2 (51.9 $\mu mol\ g^{-1}$) show bands at 370, 436, 680 nm and at 360, 644 (shoulder at 694 nm due to a small amount of monomer), respectively, indicating monomeric and dimeric states of anchored FePcS.

The supported catalysts have been tested in the oxidation of 2-methylnaphthalene (2MN) by *tert*-butylhydroperoxide (TBHP) and compared with the corresponding homogeneous oxidation in the presence of the tetrabutylammonium salt of FePcS. The main products of 2MN oxidation were 2-methylnaphthaquinone (vitamin K_3), 6-methylnaphthaquinone, products of the oxidation of the methyl group, as well as some unidentified products, presumably coupling products. The results of the oxidations are listed in Table 2. Homogeneous oxidation of 2MN gave only 11% vitamin K_3. Surprisingly, when monomeric catalysts supported either on MCM-41 or on SiO_2 were used, the conversions and selectivities were rather close to those of the homogeneous catalyst. Interestingly, dimer-based catalysts were more active and selective compared to homogeneous and supported monomeric catalysts (Table 2). The porosity of the support has no influence on the reaction rate and selectivity. The yield of vitamin K_3 after 7 h (run 7, Table 2) was 34% and the ratio between vitamin K_3 and 6-methylnaphthaquinone was 81 : 19, indicating that the catalytic system is quite selective in the oxidation of the methyl containing ring. The quinones are less oxidizable than 2MN: in 2 separate experiments under the same conditions their conversions after 24 h were 21% and 22% for vitamin K_3 and 6-methylnaphthaquinone, respectively. Consequently, the high selectivity towards vitamin K_3 is due to initial selective oxidation of 2MN, not to preferential over-oxidation of 6-methylnaphthaquinone. At the end of the reaction trace amounts of the products of the epoxidation of vitamin K_3 and 6-methylnaphthaquinone were detected and identified by GC-MS. We obtained a slower reaction rate and a lower selectivity when the oxidation of 2MN was performed

Table 2 Catalytic oxidation of 2-methylnaphthalene by Bu^tOOH at 40 °C

		Conversion/%				
Run	Catalyst	5 h	24 h	Yield of quinones[a] (%)	Selectivity in vitamin K_3[a] (%)	vit. K_3/6-MeQ ratio
1	Homogeneous FePcS	36	64	17	11	68/32
2	m-FePcS@MCM-41	37	61	13	10	74/26
3	m-FePcS@SiO_2	32	58	14	11	77/23
4	d-FePcS@MCM-41	54	81	35	24	67/33
5	d-FePcS@MCM-41[b]	46	80	46	34	75/25
6	d-FePcS@SiO_2	53	78	35	24	70/30
7	d-FePcS@SiO_2[b]	55	90	43	34[c]	81/19

[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.

under Ar. 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 $1e^-$ oxidations, when intermediate radicals can be trapped by O_2 to produce quinones.[4]

A beneficial effect of supporting FePcS on a silica support was even more significant in the oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,6-trimethylbenzoquinone (TMQ), an important intermediate for preparation of vitamin E. 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 achieved. Again, with homogeneous and monomeric supported catalysts the yields of TMQ were rather low, ranging from 21 to 47% (Table 3). A significant enhancement of selectivity was observed with dimeric catalyst immobilized on SiO_2, the yield of TMQ being 77%. However, dimeric catalyst fixed on MCM-41 shows an even lower selectivity than homogeneous or monomeric heterogeneous catalysts. The reason for such a low selectivity for d-FePcS@MCM-41 in the TMP oxidation can be explained by the formation of 2,2′,3,3′,6,6′-hexamethyl-4,4′-biphenol (BP) along with TMQ in the course of the TMP oxidation. This biphenol was shown to be an intermediate in the oxidation of TMP in the presence of molybdovanadophosphoric heteropoly acids and was further oxidized to TMQ.[9] Indeed, ^1H NMR analysis of the reaction mixture shows 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 corresponding quinone) should be diffusionally restricted, while the further oxidation of BP should be more favored with dimeric FePcS fixed onto non-porous SiO_2, 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 SiO_2. This example illustrates the importance not only of the state of the catalytic complex, but also of the texture of the support.

To test for leaching we filtered the catalyst after 30 min reaction (57% conversion) and allowed the filtrate to react further. No further reaction was detected, indicating no leaching of the complex into solution. Additionally, a UV-vis spectrum of this recovered filtrate did not show any peaks in the 600–700 nm region, indicating that possible leaching of FePcS was below the detection limits (less than 0.02% from FePcS fixed).

The stability of the d-FePcS@SiO_2 catalyst was checked by carrying out recycling experiments as follows. After completion of the TMP oxidation under the conditions of run 5, Table 3, the solution was carefully removed by decantation. New portions of substrate and oxidant were added to the recovered catalyst (no regeneration procedure) to perform a second oxidation. A similar procedure was repeated once more. The catalytic activity of the recovered solid material remained unchanged: 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. This suggests that during the catalytic reaction the selective dimeric catalyst was gradually transformed to the less selective monomeric catalyst, resulting in a decrease of TMQ yield.

Table 3 Catalytic oxidation of 2,3,6-trimethylphenol by Bu^tOOH 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

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

It should be noted that the catalysts containing μ-oxo-dimeric species show superior activity and selectivity in both 2MN and TMP oxidations compared to catalysts containing the monomeric species. Usually, μ-oxo-dimers are considered as catalytically inactive forms. This work presents an example where a dimeric iron phthalocyanine catalyst is more active and selective than the monomeric one. Surface confinement is further needed to favor the most selective dimeric form and to prevent deactivation through monomer formation. Further studies to characterize the state of complexes on the silica surface and to stabilize a μ-oxo-dimer of FePcS on the surface of the support are in progress.

Experimental

All NMR spectra of solids 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), ^1H NMR (Bruker AM 250 MHz) and GC (Dani 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.

All chemicals used were of reagent grade. The iron complex of tetrasulfophthalocyanine was prepared according to the method of Weber and Busch.[10] Authentic samples of 6-methyl-1,4-naphthaquinone[11] and trimethyl-1,4-benzoquinone[12] were prepared according to published procedures.

General method for the modification of silica

3-Aminopropyltriethoxysilane (0.52 mL, 2.22 mmol) was added to a suspension of 4.46 g of activated MCM-41 or non-porous silica (200 °C, vacuum, 22 h) in 40 mL of dry *m*-xylene. The mixture was refluxed under Ar for 15 h. The material was separated by filtration, washed with acetone and dried at 80 °C under vacuum.

Procedure for 2-methylnaphthalene oxidation

A 25 mL reaction 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 FePcS (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 reactions was monitored by GC.

Procedure for 2,3,6-trimethylphenol oxidation

A 100 mL reaction flask was charged with 160 μmol of TMP in 8 mL of 1,2-dichloroethane and 25–30 mg of solid catalyst, containing 1.6 μmol of FePcS (1% catalyst/substrate ratio). A 2.7 M solution of TBHP in chlorobenzene was added in 84 μL portions at reaction times of 0, 0.5, 1 and 1.5 h. The reaction was run for 2 h at 30 °C under air.

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