



Heterogenized Fe(III) phthalocyanine: Synthesis, characterization and application in liquid-phase oxidation of phenol

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ABSTRACT

Tetra-*tert*-butyl substituted FePc(acac) complexes were supported upon mesoporous molecular sieves MCM-41 and SBA-15 via adsorption and coordination bondings as well as by covalent grafting. Prepared materials were characterized by UV–vis, MALDI, N₂-BET, SEM, TEM, FTIR, ¹³C, ²⁹Si NMR and DSC–TG techniques. Supported FePcs exhibited high activity in liquid-phase oxidation of phenol with H₂O₂. The most resistant towards oxidative degradation were shown to be the covalently grafted FePc species.

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1. Introduction

There has been growing interest in the use of iron phthalocyanines (Pcs) as liquid-phase oxidation catalysts [1,2]. They are water-insoluble compounds and what is more important is that they provide fairly reversible redox cycles of iron atoms. Immobilization of FePcs on porous solids provides an easy way to separate a catalytic material from reaction products and thereby to reuse it. Application of high surface area matrices ensures the spatial separation of catalytic species that behave very similarly to the active centers in true molecular catalysis. In this respect, MCM-41 and SBA-15 mesoporous molecular sieves seem to present the most promising materials for using them as matrices because of their high surface, uniform pore size distribution and high thermal stability.

There are several ways to immobilize Pcs: simple physical adsorption [3], coordinative bonding to anchoring surface groups [4,5] and covalent bonding with surface silanol groups of a support [6]. The first two routes do not result in the chemical bonding and cannot prevent the Pc species from leaching whereas the third way provides rather strong Pc immobilization. Complexes can be covalently

grafted by forming the siloxane bonds between the reactive Pc molecules bearing (alkoxy)₃Si- containing functional substitutes and support surface OH groups. Earlier, FePcs symmetrically substituted with eight (EtO)₃Si- functional groups have been successfully grafted onto amorphous silica [7]. At the same time, the controlled immobilization of Pc through single siloxane bond could be also performed using monosubstituted derivatives.

The grafting of Pc via single bond provides some advantages due to the uniformity of active centers. Indeed, this way excludes different orientations of Pc molecules which may occur on using polysubstituted derivatives.

In this paper we report the synthesis and characterization of *tert*-butylphthalocyanine (¹PcFe) containing catalysts through the immobilization of ¹PcFe upon differently functionalized MCM-41 and SBA-15 sieves as catalysts for liquid-phase hydroxylation of phenol by hydrogen peroxide.

2. Experimental

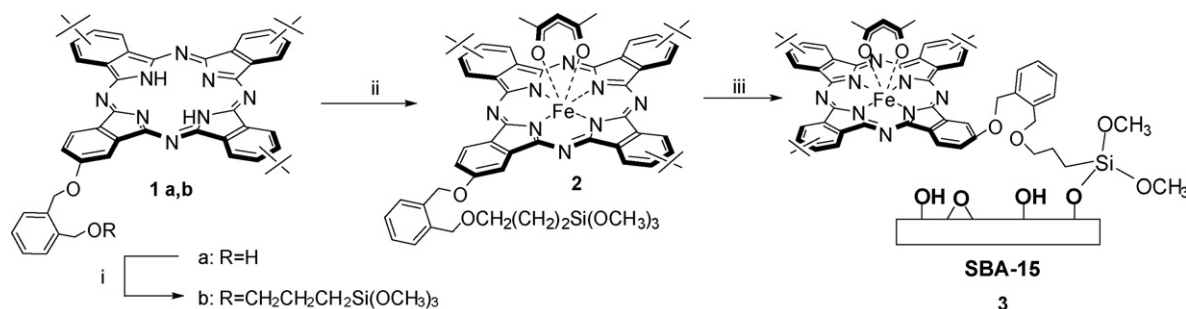
2.1. Syntheses

2.1.1. MCM-41 support

MCM-41 mesoporous molecular sieve was prepared using the following protocol [8]. The reaction mixture of molar composition 1 TEOS: 0.3 CTMABr:11 NH₃:60 EtOH:144 H₂O (TEOS = tetraorthoethoxysilane, CTMABr = cetyltrimethylammonium bromide) was stirred at RT for 2 h, then the amorphous

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Scheme 1. Synthesis of covalently bonded Fe(III) phthalocyanine **3**. (i) NaH/DMF, (CH₃O)₃SiCH₂CH₂CH₂Cl; (ii) DBU/*o*-DCB, Fe(acac)₃; (iii) SBA-15/toluene.

precipitate was separated, washed with water, dried and air-calcined at 550 °C.

2.1.2. SBA-15 support

SBA-15 mesoporous molecular sieve was obtained by one-step synthetic procedure [9]. 4 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀) was added in 110 ml H₂O and stirred at RT until the dissolution was complete. Then 12.4 ml of 0.1 M HCl and 0.01 g of NH₄F were added, mixture was heated to 40 °C. 9.4 ml (8.8 g) of TEOS was added at vigorous stirring, then mixture was kept stirring for 72 h at 40 °C. Solid precipitate was washed by centrifugation until pH of 4–6. Then it was dried at 90 °C, calcined in the mixture of N₂ and air at 550 °C for 24 h

2.1.3. NH₂-MCM-41 support

The grafting of 3-APTES (3-aminopropyltriethoxysilane) onto MCM-41 was performed according to the method described in [10]. 1 g MCM-41 was dispersed in 50 ml of toluene followed by addition of 1 ml of 3-APTES. The mixture was refluxed for 6 h and every 1.5 h the ethanol formed was boiled away. The powder was washed with toluene and dried at 130 °C.

2.1.4. Fe^tPc(acac) sample

2,9(10),16(17),23(24)-tetra-*tert*-butylphthalocyanine iron(III)(acac) was prepared using the following procedures. To a solution of 2,9,16,23-tetra-*tert*-butylphthalocyanine ligand [11] (254 mg, 0.344 mmol) in *o*-dichlorobenzene (*o*-DCB) (10 ml), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.4 ml) and Fe(acac)₃ (180 mg, 0.514 mmol) were added followed by heating at 150 °C for 1.5 h (UV-vis and TLC control). After the reaction was completed, target complex was precipitated by adding CH₃OH to give 300 mg (98%) of target complex.

2.1.5. Fe^tPc(acac)/MCM-41 sample

The solution of Fe^tPc(acac) (120 mg) in methylene chloride was added to a thin uniform layer of MCM-41 (0.72 g) so as to cover all particles. Then the slurry was dried at 80 °C for 24 h which results in a dark green residue.

2.1.6. Fe^tPc(acac)/NH₂-MCM-41 sample

The procedure was the same as for Fe^tPc(acac)/MCM-41 except that NH₂-MCM-41 was used as the support. A dark blue residue was obtained.

2.1.7. Fe^tPc(acac)-Si(OMe)₃ sample

Synthesis of 2-(trimethoxysilylpropoxymethylbenzyloxy)-9(10),16(17),23(24)-tri-*tert*-butylphthalocyanine Fe(III)(acac) included two stages (Scheme 1)

i) Synthesis of 2-(trimethoxysilylpropoxymethylbenzyloxy)-9(10),16(17),23(24)-tri-*tert*-butylphthalocyanine ligand (**1b**). To the solution of **1a** [12] (100 mg, 0.122 mmol) in DMF

(5 ml), NaH was added followed by stirring for 1 h. Then 3-(chloropropyl)-trimethoxysilan (0.24 ml, 1.220 mmol) was added dropwise and the mixture was kept for 8 h (TLC control). After completion of the reaction, phthalocyanine compounds were precipitated by adding water followed by chromatographic isolation of target ligand **1b** to give 95 mg (79%).

ii) Synthesis of 2-(trimethoxysilylpropoxymethylbenzyloxy)-9(10),16(17),23(24)-tri-*tert*-butylphthalocyanine Fe(III)(acac) (**2**). To a solution of **1b** (60 mg, 0.061 mmol) in *o*-DCB (10 ml), DBU (0.2 ml) and Fe(acac)₃ (32 mg, 0.091 mmol) were added followed by heating at 150 °C for 1.5 h (UV-vis and TLC control). After completion of the reaction, target complex was precipitated by adding CH₃OH to give 63 mg (91%). MS (*m/e*): 1188 [M-acac+DHB]⁺, 906 [M-acac-C₁₄H₂₃O₄Si+DHB].

2.1.8. Fe^tPc(acac)-Si-SBA-15 catalyst

300 mg of SBA-15 was dispersed in 10 ml of toluene followed by addition of 59 mg of Fe^tPc(acac)-Si(OMe)₃. The mixture was refluxed for 24 h, then the powder was separated, washed with toluene and ethanol to remove the ungrafted Fe^tPc(acac)-Si(OMe)₃, then dried at 80 °C for 24 h. A pale green residue was obtained.

2.2. Characterization

Elemental analysis was performed using a Flash EA 1112 analyzer. Sample of catalyst was placed in a tin crucible and burnt in pure oxygen. Gas products were analyzed by GLC. Iron content was measured using AA analysis. A sample was treated by the mixture of concentrated HF, HNO₃ and HCl acids. Then the mixture was evaporated, and the residue was dissolved in HCl. This procedure was done twice followed by adding to analyzer.

The BET surface area, the pore volume, and the average pore diameter were calculated from the nitrogen adsorption isotherms at 77 K recorded on an automated porosimeter ASAP 2000N Micromeritics. Before determination, all samples except for NH₂-MCM-41 and Fe^tPc(acac)-Si-SBA-15 were evacuated at 350 °C and 10⁻³ mm Hg for 2 h.

FTIR spectra of the samples (KBr pellets) were recorded in the range of 400–4000 cm⁻¹ on a Nicolet Protege 460 E.S.P. Fourier-transform spectrometer. The recorded IR spectra were processed with the use of the OMNIC E.S.P. software package (Nicolet). The bands characteristic of the surface OH groups of the supports and grafted samples were recorded after evaluation.

DSC-TG curves were registered in air in the regime of a linear 10 °C/min temperature increase in the range of 20–1000 °C. The recording and processing of the data were performed using Universal Analysis software package.

The morphology of the particles was determined on a JEM-2000FXII electron microscope in the SEM mode. TEM images were collected using LEO912 AB OMEGA electron microscope.

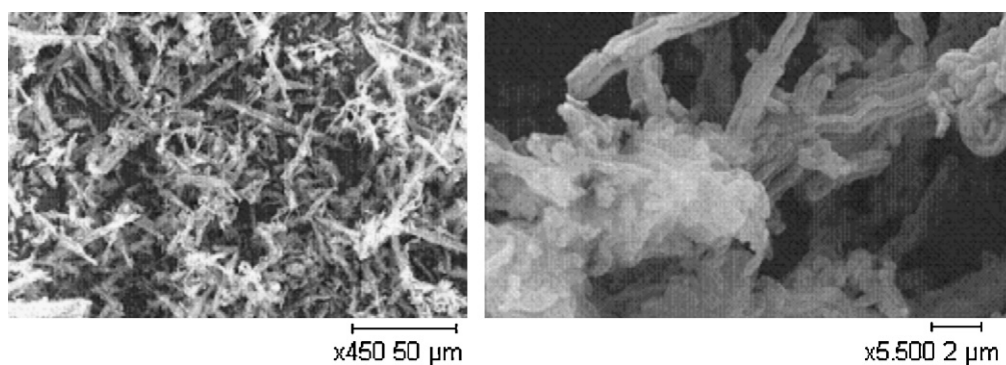


Fig. 1. SEM microphotographies for SBA-15 material.

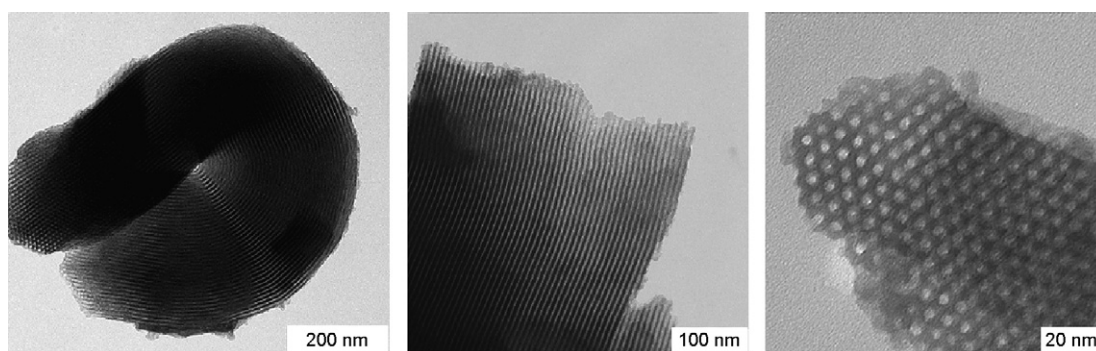


Fig. 2. TEM microphotographies for SBA-15 material.

Table 1
Characteristics of free supports and immobilized Fe^lPc(acac).

Sample	Fe, wt.%		S _{BET} , m ² /g	Pore volume, cm ³ /g	Av. pore diameter, Å
	AAA	CHNS			
MCM-41	–	–	1010	0.68	27
NH ₂ -MCM-41	–	–	760	0.28	18
SBA-15	–	–	820	0.84	65
Fe ^l Pc(acac)/MCM-41	0.80	0.93	n/a	n/a	n/a
Fe ^l Pc(acac)/NH ₂ -MCM-41	0.84	0.95	n/a	n/a	n/a
Fe ^l Pc(acac)-Si-SBA-15	0.57	0.55	500	0.62	65

Mass spectra of phthalocyanines (MALDI-TOF) were registered on Autoflex II using 2,5-dihydroxybenzoic acid as a matrix.

NMR spectra of solid phase samples were collected on Bruker Avance-II 400 with 9.4T magnetic field corresponding with the working frequency ²⁹Si = 79.49 MHz. The spectra were processed with TopSpin 2.1 software (Bruker). ²⁹Si NMR spectra were collected for air dry samples using magical angle (54.7 °C) rotation, 5 kHz frequency and a 7 mm ZrO₂ rotor. As an external reference Si(CH₃)₄ was used, the collection of spectra was performed using one impulse consecution (90 °C-impulse) ²⁹Si and an impulse consecution with polarization transition to silica (cross-polarization ¹H-²⁹Si) and a suppression of a spin-spin interaction. In the first case there were 128–512 scans and the time between impulses was 60 s. In the second case there were 2048 scans and the time was 5 s while the time of polarization transition was 2 ms.

2.3. Catalytic tests

The hydroxylation of phenol was performed in a static system at atmospheric pressure. Experiments were performed as follows. Water (10 ml), phenol (1 g) and catalyst (10 mg) were placed into a 30-ml flask and heated up to at 60 °C. Then 2 ml of 25% H₂O₂ was

added with vigorous stirring. Samples of 1 ml were periodically taken for analyses from the reaction mixture. Reaction products were analyzed using GC (30 m × 0.22 mm capillary SE-30 column). The reaction catalysts were separated, washed with hot water (~80 °C), dried in air and then tested in the second cycle.

3. Results and discussion

3.1. MCM-41, NH₂-MCM-41 and SBA-15 supports

SEM image of as-synthesized MCM-41 material showed this support to consist of 0.25–1.0 μm uniform microspheres. For SBA-15 sieve, SEM reveals the amorphous needle-shaped microstructures (Fig. 1). As seen, these needles are uniform and isolated from each other that could facilitate easy access for entering reagent molecules.

The uniform pore sizes of SBA-15 can be directly evidenced by TEM images (Fig. 2). On the other hand, the use of P123 as a template leads to a worm-like channeled phase with 2D hexagonally ordered structure.

Textural characteristics for all supports are summarized in Table 1. Surface area of MCM-41 as determined by N₂-BET method was of 1010 m²/g, and average pore diameter was estimated as

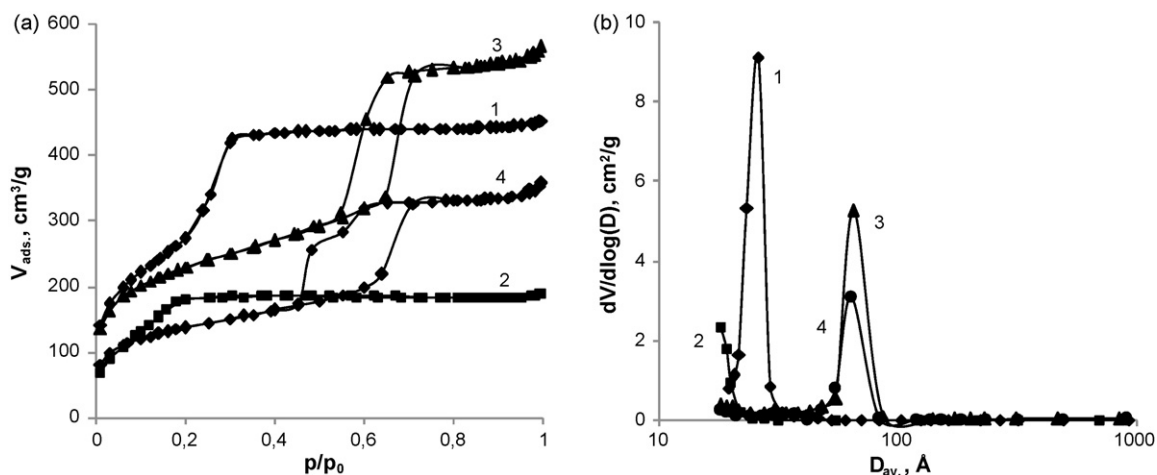


Fig. 3. N_2 adsorption isotherms (a) and pore size distribution (b) for MCM-41 (1), NH_2 -MCM-41 (2), SBA-15 (3) and $Fe^I Pc(acac)$ -Si-SBA-15 (4).

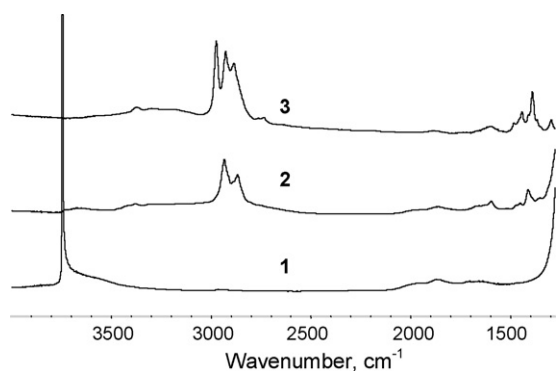


Fig. 4. FTIR spectra for samples (1) MCM-41; (2) NH_2 -MCM-41; (3) 3-APTES. ^{29}Si (A) and ^{13}C (B) NMR spectra of grafted 3-APTES.

c.a. 3 nm. After grafting 3-APTES modifier, both specific surface and pore volume of MCM-41 significantly decreased. This can be considered as the evidence (though indirect) for the occurrence of the grafting, since the peaks at pore size distribution curves keep their shapes and change only in absolute values (Fig. 3).

FTIR spectra presented in Fig. 4 provide strong evidence of 3-APTES grafting onto the matrix surface. After reaction of 3-APTES modifier with the surface OH groups, their band at 3740 cm^{-1} disappear while the bands characteristic for the modifier appear. Complete disappearance of 3740 cm^{-1} band implies that molecules of modifiers cover all support surface and fully reacted with

its OH groups. As to the grafted 3-APTES, 3373 and 3296 cm^{-1} bands can be attributed to the asymmetrical and symmetrical NH stretching vibrations in NH_2 groups, and 1596 cm^{-1} bands can be ascribed to its deforming oscillations [13]. Bands in the range of 2800 – 3000 cm^{-1} are related to both propyl and ethoxy groups of 3-APTES: 2882 cm^{-1} (CH_3 sym. stretch.), 2929 cm^{-1} (CH_2 asym. stretch.), 2976 cm^{-1} (CH_3 asym. stretch.) [14,15].

Nitrogen wt.% was found to be of 3.1% that gives 2.2 mmol/g of grafted 3-APTES. Total concentration of OH groups was calculated from TG data providing the dehydroxylation of surface accounts for the weight loss in the range of 200 – 1200°C . For MCM-41 this value was 3.5 mmol/g or 2.1 OH groups/ nm^2 which is close to the surface concentration of 3-APTES. Generally, for MCM-41 material OH concentration was shown to be in the range of 1.5–2.5 groups/ nm^2 [16]. Given the measurement errors as well as the assumption mentioned above, this can be considered only as a rough estimate.

The direct information on the interplay between grafting agents and support surface can be gathered from ^{29}Si NMR spectra (Fig. 5A).

The chemical shift at -109 ppm is of highest intensity and is characteristic for framework silica. The shoulder at -102 ppm is related to silica atoms with terminal silanol groups. The peak at -66 ppm can be attributed to the silica atoms of 3-APTES linked by three bonds with the support. This value is -65 ppm in [17] and -69 ppm in [18]. Peak at -60 ppm refers to the silica linked by two bonds with the surface (-61 ppm in [18]). The propyl fragment of 3-APTES gives three peaks in ^{13}C NMR spectra (Fig. 5B) attributed to the first (9 ppm), second (26 ppm) and third (44 ppm) carbon atom counting from silica [17].

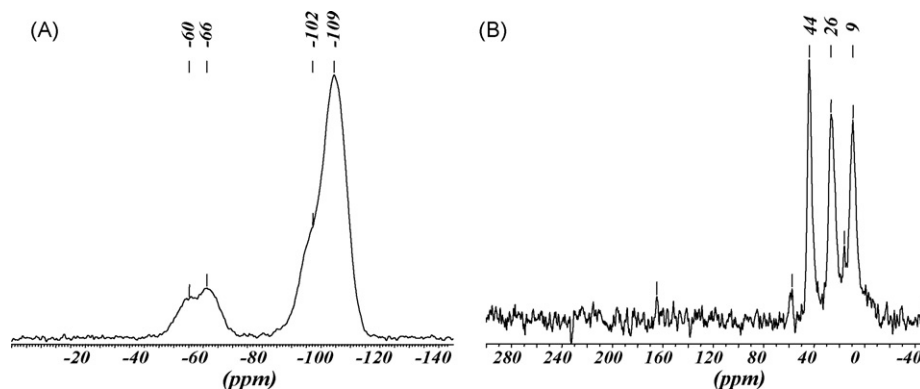


Fig. 5. ^{29}Si (A) and ^{13}C (B) NMR spectra of grafted 3-APTES.

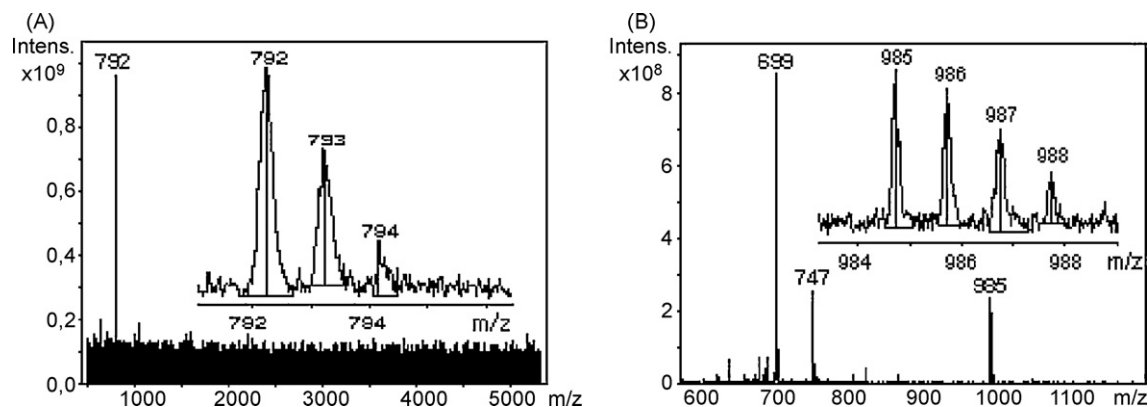


Fig. 6. MALDI-TOF mass spectra for Fe⁺Pc(acac) (A) and H₂⁺Pc-Si(OMe)₃ (B).

Composition and textural characteristics of both sieve supports and Fe⁺Pc(acac) containing samples are given in Table 1. Substantial increase in the average pore size of molecular sieve matrix on going from MCM-41 to SBA-15 is due to the fact that the use of polymer template P123 instead of CTMABr leads to a structure with quite different morphologies and textures [19,20].

Taking into account the molecular size of Fe⁺Pc(acac) with large derivative, large pore SBA-15 matrix seems to be more preferable for covalent bonding rather than MCM-41 material. Noteworthy, uniform pore size distribution does not change after Fe⁺Pc(acac)-Si(OMe)₃ grafting but there is a decrease of the total pore volume. Since diameter of pores remains constant it could be explained by partial blocking of pores by bulk phthalocyanine molecules. On the other hand, the size of a single Fe⁺Pc(acac)-Si(OMe)₃ complex is much smaller than the pore diameter of the support. So, the blocking of pores most likely may occur by Fe⁺Pc(acac) aggregations, which is well known even in diluted solutions. Significant decrease of BET surface from 820 to 500 m²/g may also be connected with the pore blocking. At the same time, most of Fe⁺Pc(acac) molecules are very probable to reside within the support mesopores. In fact, the total amount of grafted complexes could not be grafted onto the outer surface (~10 m²/g), so that it makes possible to consider Fe⁺Pc(acac) species as located mainly within the matrix pores.

3.2. Fe⁺Pc(acac)-containing catalysts

Structure of prepared Fe⁺Pc(acac) complexes was evidenced by means of MALDI-TOF technique (Fig. 6). Fe⁺Pc(acac) complex gives 792 m/z peak which is characteristic for molecular ion with cleaved

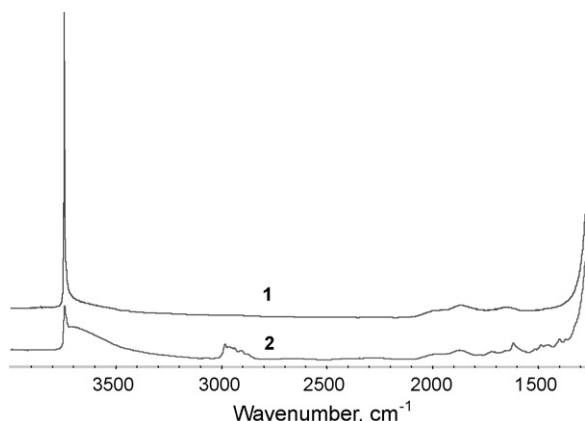


Fig. 7. FTIR spectra for SBA-15 (1) and Fe⁺Pc(acac)-Si-SBA-15 (2).

acac ligand [M-acac]⁺. For Fe⁺Pc(acac)-Si(OMe)₃ complex the spectrum of metal-free precursor (Scheme 1b) is shown as an example (Fig. 6B). 985 m/z peak is attributed to [MH]⁺ molecular peak and all of the characteristic fragment ion peaks are also detected: 862 [M-C₃H₉O₃Si]⁺, 818 [M-C₆H₁₅O₃Si]⁺, 802 [M-C₆H₁₅O₄Si]⁺, 699 [M-C₁₄H₂₄O₄Si]⁺.

UV-vis spectra of Fe⁺Pc(acac)-Si(OMe)₃ showed the band at 672 nm which can be attributed to monomeric form of phthalocyanine with vibrational satellite at 616 nm.

For Fe⁺Pc(acac)-Si-SBA-15 sample, it was shown by means of FTIR (Fig. 7) that Fe⁺Pc(acac) molecules are chemically bonded to SBA-15 surface. On the spectrum for the grafted sample the band for the terminal silanol group (3740 cm⁻¹) has significantly decreased. Though, in comparison with grafted 3-APTES sample it was not completely disappeared because the amount of Fe⁺Pc(acac)-Si(OMe)₃ present in reaction mixture was not enough to react with all surface OH groups of SBA-15. The bands in the range of 2800–3000 cm⁻¹ can be attributed to the oscillations of CH₂ and CH₃ groups.

The amount of grafted Fe⁺Pc(acac)-Si(OMe)₃ was evaluated by means of CHNS elemental analysis. 1.1 wt.% of N corresponds to 0.145 mmol/g of iron phthalocyanine grafted or 68 mol.% of initially added complex. Nitrogen wt.% was also used for calculation of iron content (Table 1). The values estimated by such a way are just slightly different from those determined by AAA.

For all Fe⁺Pc(acac) containing samples, UV-vis reflectance spectra exhibit three peaks characteristic of phthalocyanine complexes (Fig. 8). Bands in the range of 680–710 nm can be attributed to monomeric form of Pcs, while absorbance in the range of 550–660 nm indicates the presence of their aggregates. Soret bands at 340–350 nm are well typical for both porphyrin and analogous structures. Assumption on the aggregation is also supported by the red shift of bands in comparison with that of free complexes [21]. It is to note that freshly prepared Fe⁺Pc(acac) and Fe⁺Pc(acac)-Si(OMe)₃ are monomeric which was shown by means of MALDI-TOF. However, their concentration on the support surface could lead to the aggregation. In solid state individual Fe⁺Pc(acac) is already aggregated as the intensity of a band at 643 nm is much higher than that of monomeric form. Chemical immobilization of Fe⁺Pc(acac) makes them mainly monomerized but nevertheless some portion of a complex remains aggregated. This aggregation effect may be resulted from the formation of μ-oxo complexes which can be revealed using the FTIR techniques as the absorbance at 833 cm⁻¹ is commonly attributed to the Fe-O-Fe deformation mode [22]. In our case the identification of this band is rather complicated by very strong absorbance at 800 cm⁻¹ characteristic of symmetric Si-O-Si oscillations [23]. However, the formation of μ-oxo complexes is hardly possible because a catalyst preparation was performed in anhydrous solvents.

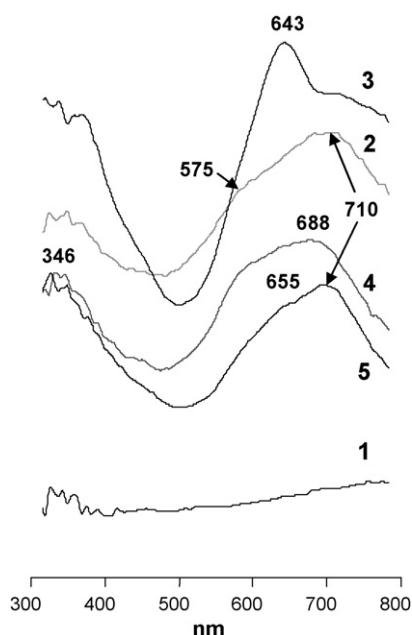


Fig. 8. UV-vis spectra for catalysts containing Fe^IPc(acac) (1) MCM-41; (2) Fe^IPc(acac); (3) Fe^IPc(acac)/MCM-41; (4) Fe^IPc(acac)/NH₂-MCM-41; (5) Fe^IPc(acac)-Si-SBA-15.

Experimental kinetic curves of phenol conversion and the calculated TOF values are presented in Fig. 9. It is to note, the blank experiments showed the MCM-41 and SBA-15 supports were completely inactive in oxidation reaction.

Free Fe^IPc(acac) complex is insoluble in aqueous media, so that in this case the catalytic process could be unambiguously defined as heterogeneous or, more exactly, as microheterogeneous one. In fact, the phenol hydroxylation seems to occur on the outer surface of finely dispersed particles of Fe^IPc(acac) but the catalytic activity as calculated per unit mass is rather small due to low total surface of such grains.

The adsorption of Fe^IPc(acac) on MCM-41 leads to dramatic increase in activity. Even though the part of Fe^IPc(acac) presents on the outer surface of support in less active aggregated form, Fe^IPc(acac)/MCM-41 sample is the most active.

Unexpectedly, Fe^IPc(acac) complexes stabilized upon MCM-41 by coordination with surface amino groups exhibit very poor activity. On the contrary, the anchoring Fe^IPc(acac) species via covalent bonding results in appreciable increase of activity. These features of immobilized Fe^IPc(acac) are most probably due to specific environment of central Fe atom in Pc molecules as it is illustrated in Fig. 10.

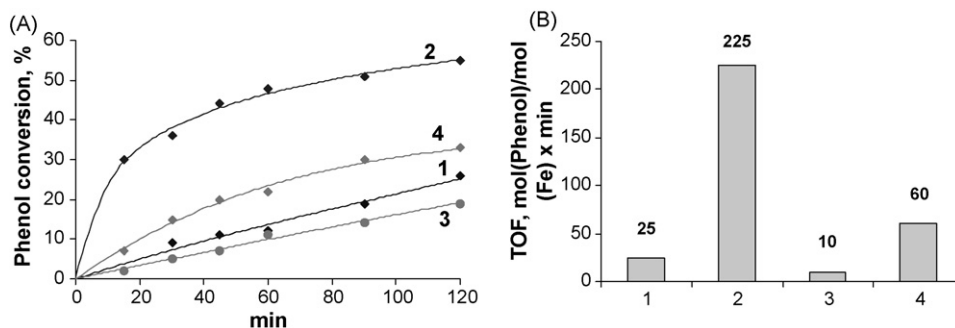


Fig. 9. Oxidation of phenol over Fe^IPc(acac) containing catalysts. (A) Curves of phenol conversion; (B) TOF values for samples (1) Fe^IPc(acac); (2) Fe^IPc(acac)/MCM-41; (3) Fe^IPc(acac)/NH₂-MCM-41; (4) Fe^IPc(acac)-Si-SBA-15 (1 g phenol, 10 ml H₂O, 2 ml 25% H₂O₂, 10 mg cat. or corresponding amount of Fe^IPc(acac), 60 °C).

As it has been shown in [24], the Pc molecules adsorbed upon a matrix surface has on-edge orientation even at low coverages. If this is the case, the 6th axial coordination position is well accessible for entering substrate molecules. In contrast, on immobilizing Fe(III)Pc by coordination such an extra ligation is excluded since this position is occupied by nitrogen atom of NH₂-anchor group.

Again, the 6th axial position remains unoccupied when the covalent bonding of Fe^IPc(acac) via siloxane groups occur (see Fig. 10), and this results in increase of activity. However, Fe^IPc(acac)-Si-SBA-15 sample exhibits noticeably lower activity than the catalyst with on-edge oriented Fe^IPc(acac) complexes though both samples display free axial coordination positions. Probably, this effect is due to rather long and flexible spacers through which Fe^IPc(acac) species are anchored onto the surface. On the one hand, these spacers are strongly believed to minimize the influence of support walls on the FePc complexes and thus to ensure their equal efficiency, regardless of whether they are located on internal or outer surface. On the other hand, this makes it possible that two neighboring Fe(III)Pcs form μ -oxo complex-like dimers. Such dimers expose no free extra coordination sites and thereby are inactive. At the same time, these Fe(III)Pc dimers have been shown to be more active than monomeric FePcs in oxidation of 2,3,6-trimethylphenol oxidation [6] and allylic oxidation of cyclohexene [25].

Data on activity of the catalysts tested in phenol oxidation and their selectivity to dihydroxylation products are summarized in Table 2.

First, as it is seen from these data, the sum of catechol and hydroquinone yields is substantially lower than the total phenol conversion. It would be suggested that this difference may originate from the very fast polymerization of benzoquinone as a primary product of phenol oxidation to the black tar. However, the formation of benzoquinone on phenol monohydroxylation has been reported [5] to be suppressed in the presence of any N-containing compounds, e.g., Pc complexes, and also in acidic media.

Further, there is no substantial difference in product distribution between the catalysts studied. At the beginning of reaction, phenol seems to be oxidized in parallel to catechol and benzoquinone which was well documented for homogeneous systems in [26].

Though the initial activities of all Fe^IPc(acac) containing materials were high enough, they exhibit no activity on their reusing after separation from reaction products obtained in the first oxidation experiment. This loss in activity is commonly believed to be resulted from the oxidative degradation of both free and heterogenized FePc complexes which occurs not only with H₂O₂ but also with a mild oxidant as *tert*-butylhydroperoxide [27]. So that, UV-vis spectra of the recovered Fe-containing catalysts showed no adsorption bands characteristic of Pc core. Noteworthy, the Fe(III) ions of these complexes do not seem to be the key factor of their

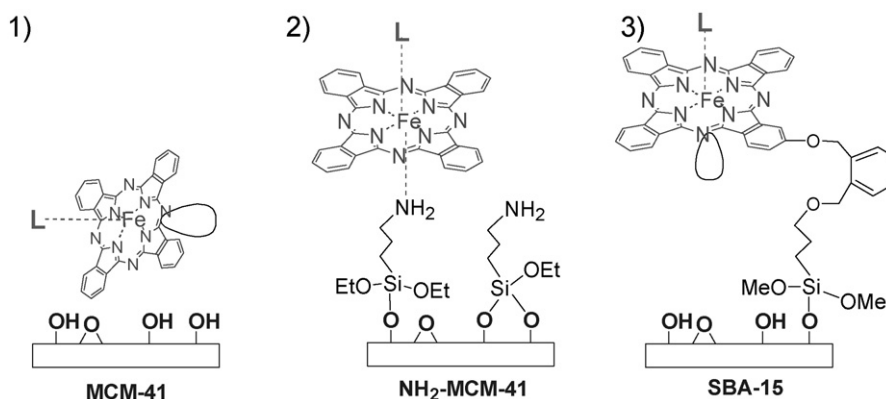


Fig. 10. Location of FePcs on the support (1) Fe¹Pc(acac)/MCM-41; (2) Fe¹Pc(acac)/NH₂-MCM-41; (3) Fe¹Pc(acac)-Si-SBA-15 (L = acac ligand, *tert*-butyl substituents of Pc are omitted for clarity).

Table 2

Total phenol conversion and yields of dihydroxylation products on Fe¹Pc(acac) containing catalysts.

Catalyst and reaction time	Fe ¹ Pc(acac)		Fe ¹ Pc(acac)/MCM-41		Fe ¹ Pc(acac)/NH ₂ -MCM-41		Fe ¹ Pc(acac)-Si-SBA-15	
	15 min	120 min	15 min	120 min	15 min	120 min	15 min	120 min
Phenol conversion, %	9	26	30	55	2	19	7	33
Catechol yield, %	0	8	13	23	1	5	0	12
Hydroquinone yield, %	0	1	3	9	0	0	0	0

autoxidation. In fact, we found Zn-containing polymerized Pc complex to be stable toward H₂O₂. The synthesized Pc compounds that were used for catalyst preparations bear electron-donor substituents and on being heterogenized show poor stability towards oxidation by H₂O₂.

One may expect that in contrast to these complexes with electron-donor groups, FePcs with electron-acceptor substituents would be more oxidation resistant [28] and thereby more stable under the conditions of oxidation by hydrogen peroxide. However this possibility requires further investigations.

4. Conclusions

Fe(III)¹Pc(acac) adsorbed upon MCM-41 and covalently grafted onto SBA-15 show high activity in phenol oxidation because of easy accessibility of unoccupied axial position of Fe(III) atom in the phthalocyanine molecule. It is not the case when Fe¹Pc(acac) forms the coordination bond with the grafted NH₂ groups which results in low activity. All Fe¹Pc(acac) containing catalysts were shown to undergo fast oxidative degradation by hydrogen peroxide.

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