Synthesis of Iron Phthalocyanine Grafted onto SBA–15 through Single Siloxane Bond and its Application in Liquid–Phase Hydroxylation of Phenol

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Iron(III) phthalocyanine monosubstituted with trimethoxysilyl derivative was attached via covalent bonding onto SBA-15 support in order to obtain catalyst for activation of environmentally friendly oxidant – hydrogen peroxide. Catalyst prepared was tested in liquid-phase oxidation of phenol at 60°C. Covalently bonded complex exhibit higher activity than its unpendant analog.

Keywords: Phthalocyanine, iron(III) complex, SBA-15, catalysis, phenol, oxidation.

Introduction

For a long time, iron phthalocyanines are well known as efficient oxidation catalysts. However, the use of ungrafted *tert*-butyl-substituted iron phthalocyanine (^{t}BuPcFe) complexes is severely limited by the necessity of their isolation from the reaction mixtures after catalytic reactions. This drawback can be avoided by applying their immobilization upon the surface of inorganic supports such as silica gel, MCM-41 or SBA-15. Immobilization of ^{t}BuPcFe can be performed through simple adsorption[1] coordinative bonding with an anchoring group[2,3] and covalent bonding with surface silanol groups of the support.[4] Both free and heterogenized ^{t}BuPcFe complexes have been shown to be active in oxidation of cyclohexane,[5] phenol,[2] 2,3,6-trimethylphenol[4] and 2-methyl-1-naphthol.[6] The covalent attaching of Pc complex is also possible by siloxane bond if Pc has an (alkoxy)$_3$Si-containing substituent. In this case siloxane bond is formed between a silicon atom of Pc and oxygen atom of support surface. Iron(III) phthalocyanine complexes symmetrically substituted by (EtO)$_3$Si functional groups were described previously,[7] but monomeric derivatives seem to be more suitable for controlled immobilization that affords a stable heterogeneous catalyst with spatially separated active iron species.

Experimental

Synthesis

*2-(Trimethoxysilylpropoxymethylbenzyloxy)-9(10),16(17),23(24)-tri-tert-butylphthalocyanine ligand, **1b***. NaH was added to the solution of **1a**[8] (Scheme 1) (100 mg, 0.122 mmol) in DMF (5 ml) 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 %). *m/z* 985 $[MH]^+$, 862 $[M\text{-}C_3H_9O_3Si]^+$, 818 $[M\text{-}C_6H_{15}O_3Si]^+$, 802 $[M\text{-}C_6H_{15}O_4Si]$, 699 $[M\text{-}C_{14}H_{24}O_4Si]^+$. UV-vis ($CHCl_3$) λ_{max} nm: 349, 610, 680.

*2-(Trimethoxysilylpropoxymethylbenzyloxy)-9(10),16(17),23(24)-tri-tert-butylphthalocyanine Fe^{III}acac, **2***. DBU (0.2 ml) and Fe(acac)$_3$ (32 mg, 0.092 mmol) were added to the solution of **1b** (60 mg, 0.061 mmol) in *o*-DCB (10 ml), 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 CH_3OH to give 63 mg (91%). *m/z* 1188 $[M\text{-}acac\text{+}DHB]^+$, 906 $[M\text{-}acac\text{-}C_{14}H_{23}O_4Si\text{+}DHB]$.

SBA-15. The SBA-15 material was obtained by one-step synthesis method.[9] Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) (4 g) was added to 110 ml of H_2O and stirred at room temperature until the dissolution was complete. Then 12.4 ml of 0.1 M HCl and 0.01 g of NH_4F were added, and the mixture was heated to 40°C. TEOS (9.4 ml, 8.8 g) was added at vigorous stirring, then mixture was kept stirring for 72 h at 40°C. Solid precipitate was washed by centrifugation until p*H* 4-6. Then powder was dried at 90°C and calcined in mixture of N_2 (20-30 ml/min) and air (4-5 ml/min) for 24 h at 550°C.

*^{t}BuPcFe-Si-SBA-15, **3***. SBA-15 (300 mg) dried at 180°C overnight was dispersed in 10 ml of toluene followed by addition of 59 mg of **2**. The mixture was refluxed for 24 h, the powder was separated, washed with toluene and ethanol to remove the unbonded **2**, then dried at 80°C for 24 h. The pale green residue was obtained. Elemental analysis data (%): N 1.1, Fe 0.55. The content of ^{t}BuPcFe was calculated – 0.145 mmol/g showing 68% of phthalocyanine to be bound.

Characterization

Elemental analysis was performed using Flash EA 1112 analyzer. Sample of catalyst was placed in a tin crucible and burnt in pure oxygen followed by gas products being analyzed by GLC.

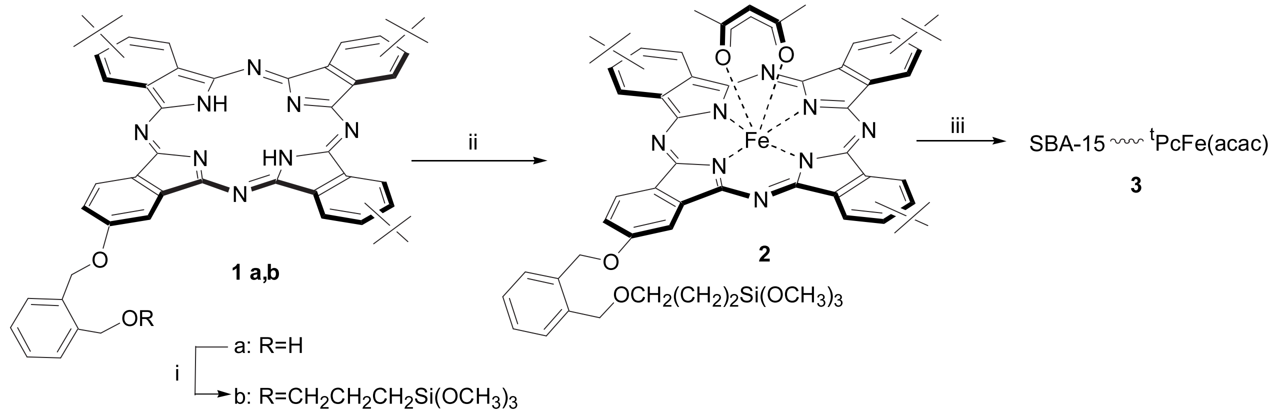
The catalytic activity was evaluated in liquid-phase oxidation of phenol by hydrogen peroxide: 1 g of phenol, 10 mg of catalyst and 10 ml of H_2O were placed into static reactor equipped with thermostat. Reaction mixture was heated to 60°C and then 2 ml of 25% H_2O_2 was added. Samples of reaction mixture were collected, products were extracted with 1-butanol and analyzed using GLC with 30 m x 0.22 mm capillary SE-30 column and a FID. Activity of catalysts was expressed in TOF[1] values calculated from experimental curves of phenol conversion *vs.* reaction time.

Results and Discussion

Initially, structure of phthalocyanine **1a**[8] was modified by nucleophilic reaction (Scheme 1, i). Further, iron(III) insertion led to complex **2** with acetylacetonate (acac) ligand as an axial substituent. The last compound was attached onto SBA-15 surface to give covalently bonded Fe^{III} phthalocyanine **3**.

The structures of compounds **1b** and **2** were proved by mass spectrometry data. In the mass spectrum (MALDI-TOF) of phthalocyanine **1b** molecular ion peak (*m/z* 985) and all of the characteristic fragment ion peaks were detected. In addition, fragmentation is observed by consecutive breakdown of the peripheral substituent. As an example Figure 1 shows the mass spectrum of ligand **1b**. We have found for molecular ion peak of complex **2** to be replaced by secondary ion peak formed through substitution of acac by DHB matrix. Also compounds **1a** and **2** were characterized by electron absorption spectra showing typical pattern for phthalocyanine ligand and their metallocomplex, correspondingly.

The bonding of **2** onto SBA-15 surface was evidenced by means of “CHNS”-elemental analysis. The total amount



Scheme 1. Synthesis of covalently bonded Fe^{III} phthalocyanine **3**. *i* - NaH/DMF, $(CH_3O)_3SiCH_2CH_2CH_2Cl$; *ii* - DBU/*o*-DCB, $Fe(acac)_3$; *iii* - SBA-15/toluene.

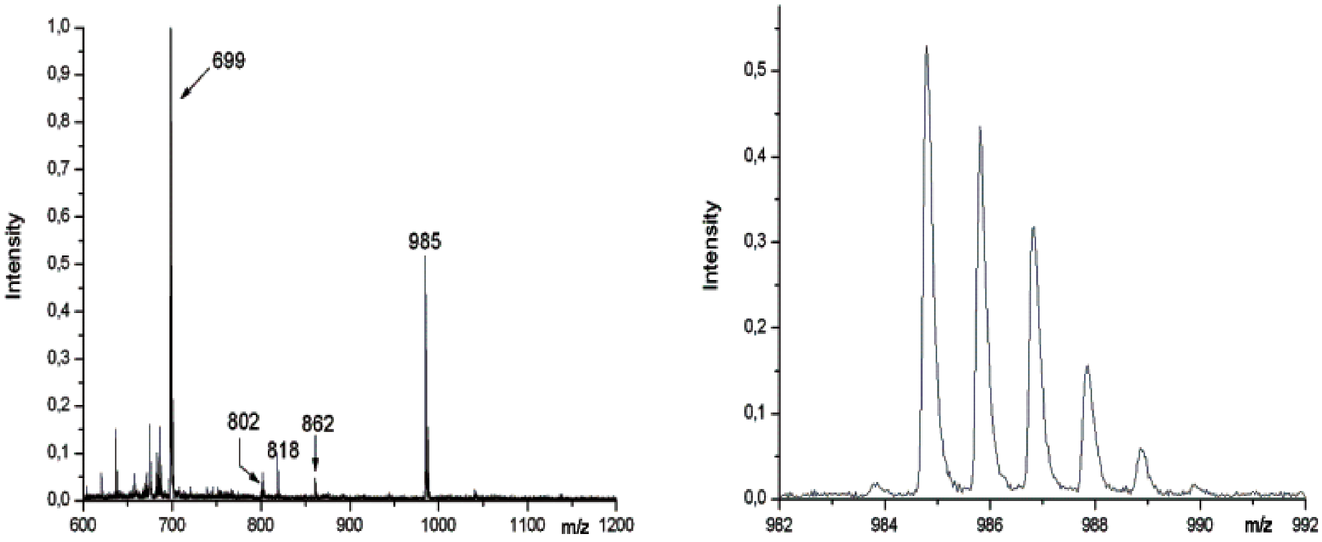


Figure 1. Mass spectrum and molecular ion peak of phthalocyanine **1b**.

Table 1. Phenol oxidation by H_2O_2 over unpendant and covalently bonded ^tBuPcFe-complexes[a]

Sample	PhOH conversion*, %	Catechol yield*, %	Hydroquinone yield*, %	TOF**, mol PhOH/[mol Fe × min]
unpendant ^tBuPcFe	26	8	1	25
3	33	12	0	60

* After 2 h since reaction started
** At 5% conversion of PhOH
[a] SBA-15 support without ^tBuPcFe-complexes don’t exhibit the conversion of phenol.

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[1] TOF – turn over frequency

of nitrogen was used for calculation of Fe within ^{t}BuPcFe attached amounts (see Experimental section). It is shown that 68% of ^{t}BuPcFe was condensed with surface silanol groups and thus bonded. The results of catalytic tests are summarized in Table 1. The catalysis of phenol hydroxylation by unpendant ^{t}BuPcFe complex is not, in fact, homogeneous since ^{t}BuPcFe is insoluble in aqueous solution. In this case, hydroxylation seems to occur on the outer surface of ^{t}BuPcFe grains. In contrast, when ^{t}BuPcFe is covalently bonded to the support surface the TOF value increases by 140%. In both cases, significant amounts of side products were found, supposedly, polymerized benzoquinone which could be formed directly from phenol.[10]

Conclusions

Unsymmetrically-substituted ^{t}BuPcFe complex containing $(MeO)_3Si$ functional group was prepared and attached onto the surface of SBA-15 mesoporous molecular sieve. The catalysts with chemically bonded iron phthalocyanine as prepared by such a way were shown to exhibit higher activity in liquid phase hydroxylation of phenol than unpendant iron phthalocyanine.

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