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 upendant 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 (^tBuPcFe) 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 ^tBuPcFe 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 ^tBuPcFe 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)₃Si-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)₃Si 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-C₃H₉O₃Si]⁺, 818 [M-C₆H₁₅O₃Si]⁺, 802 [M-C₆H₁₅O₄Si]⁺, 699 [M-C₁₄H₂₄O₄Si]⁺. UV-vis (CHCl₃) 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 CH₃OH to give 63 mg (91%). *m/z* 1188 [M-acac+DHB]⁺, 906 [M-acac-C₁₄H₂₃O₄Si+DHB].

SBA-15. The SBA-15 material was obtained by one-step synthesis method.^[9] Pluronic P123 (EO₂₀PO₇₀EO₂₀) (4 g) was added to 110 ml of H₂O and stirred at room temperature until the dissolution was complete. Then 12.4 ml of 0.1 M HCl and 0.01 g of NH₄F 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 pH 4-6. Then powder was dried at 90°C and calcined in mixture of N₂ (20-30 ml/min) and air (4-5 ml/min) for 24 h at 550°C.

^tBuPcFe-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 ^tBuPcFe 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 cata-

lyst and 10 ml of H₂O were placed into static reactor equipped with thermostat. Reaction mixture was heated to 60°C and then 2 ml of 25% H₂O₂ 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 TOF¹ 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**.

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.

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

Table 1. Phenol oxidation by H₂O₂ over unpendant and covalently bonded 'BuPcFe-complexes^a

Sample	PhOH conversion*, %	Catechol yield*, %	Hydroquinone yield*, %	TOF**, mol PhOH/[mol Fe × min]
unpendant 'BuPcFe	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 'BuPcFe-complexes don't exhibit the conversion of phenol.

¹ TOF – turn over frequency

of nitrogen was used for calculation of Fe within ¹BuPcFe attached amounts (see Experimental section). It is shown that 68% of ¹BuPcFe 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 ¹BuPcFe complex is not, in fact, homogeneous since ¹BuPcFe is insoluble in aqueous solution. In this case, hydroxylation seems to occur on the outer surface of ¹BuPcFe grains. In contrast, when ¹BuPcFe 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 ¹BuPcFe 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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