



Synthesis of phthalocyanine derivatives by synergistic effect of two catalysts on zeolites under solvent conditions

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ABSTRACT

Copper (II) phthalocyanine and 2, 9, 16, 23 tetrakis nitro copper (II) phthalocyanine has been synthesized respectively from phthalonitrile and 4-nitro phthalonitrile under solvent-free condition using two different catalysts. 4-Nitro phthalonitrile synthesized from phthalimide in three steps. The reaction time of ruthenium chloride and HZSM-5 catalysts was very shorter than ammonium molybdate and H β catalysts. The yield while we used ruthenium chloride and HZSM-5 catalysts were very higher than another. The newly prepared compound has been characterized by IR, UV-Vis, ¹H-NMR and XRD spectra.

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Introduction

Pcs have macrocyclic 18 π electron systems that are known to be the source of semiconductor characteristics, and they are characterized by high thermal and reasonable chemical stability [1-2]. Pcs show interesting photophysical properties and both photo and dark semiconductivity, which makes them particularly interesting for use in more advanced technological applications, such as optical recording, non-linear optics, light emitting diodes, a basis for optical sensing, photodynamic therapy and gas sensors [3-4]. One of the goals of catalysis researchers in recent times has been the synthesis of inorganic compounds. One approach has been the encapsulation of transition metal complexes inside the cages and void spaces of zeolite and zeolitic materials the porous inorganic mantle zeolite. The right steric requirement for the metal complexes and imposing certain restrictions (based on size and shape) to the access of the active site by the substrate molecules [5-6]. Zeolites are crystalline microporous aluminosilicates. Their porous structure can accommodate a wide variety of cations which can readily be exchanged for other cations. They differ widely in their cations Si/Al ratios, pore shapes, sizes, and channel system. [7-14]

Experimental

Synthesis of 4-nitro phthalimide

To 25ml of a mixture of concentrated sulfuric acid and nitric acid at 15 °C was added 4g phthalimide with stirring. The temperature was raised slowly to 35 °C and held for 1.5h (Fig. 1). The product cooled to 0 °C and poured into 40 g of ice and collected by vacuum filtration. Yield (70%), mp: 195 °C. IR (KBr): 3200 s, 3050 w, 1730 s, 1620 w, 1600 w, 1540 s, 1462 m, 1400 m, 1345 s, 860 m, 795 s, 715 s, cm⁻¹

Synthesis of 4-nitro phthalamide

To 10ml of THF was added 1g of 4-nitro phthalimide and the mixture was heated to 40 °C with and 7ml ammonium hydroxide was added to the solution with stirring for 2h (Fig. 1). The product collected by filtration. Yield (75%), mp: 197 °C. IR

(KBr): 3400 s, 3300 m, 3100 w, 1665 s, 1605 m, 1525 s, 1475 m, 1400 w, 1345 s, 1125 m, 860 s, 790 s, 740 s cm⁻¹.

¹H-NMR (DMSO): 8.31 (dd, J=8.35Hz, J=2.3Hz, 1H, H_a), 8.28 (d, J=2.2, 1H, NH, H_b), 8.03 (s, 1H, NH, H_c), 7.97 (s, NH, 1H, H_d), 7.70 (d, J=8.33Hz, 1H, H_e), 7.60 (br.s, 2H, NH₂, H_f) ppm.

Synthesis of 4-nitrophthalonitrile

To 7ml of dry DMF at 0 °C and a CaCl₂ drying tube was slowly added 0.73ml of thionyl chloride and 1g of 4-nitro phthalamide as added in portion over a 10-min period. The reaction stirred for 3h at room temperature (Fig.1). The reaction mixture was stirred into 20ml ice and collected by vacuum filtration. Yield (90%), mp: 142 °C; IR (KBr): 3080 w, 2220 m, 1600 m, 1532 s, 1350 s, 865 s, 795 s, 740 s, cm⁻¹; ¹H-NMR (DMSO): 9.05 (d, J=2.4Hz, 1H, H_a), 8.69 (dd, J=8.8Hz, J=2.4Hz, 1H, H_b), 8.45 (d, J=8.8Hz, 1H, H_c) ppm.

Preparation of zeolites

The synthesized zeolites was calcined in air at 873 K for 5 h to decompose the organic templates. The resulting Na⁺ ions in the synthesized zeolite was exchanged by NH₄⁺ ions from a 1M NH₄NO₃ solution at 353 K for 10 h, using a liquid/solid ratio of 100 ml per gram of zeolite. Then, the zeolites were separated from the solution by filtering and were thoroughly washed. The exchange procedure was repeated three times to complete the Na⁺ ion exchange. Subsequently, the catalysts was dried overnight at 383 K and calcined in flowing dry air at 773 K for 5 h to produce the acidic form of the zeolites (HZSM-5 and H β).

Synthesis of copper (II) phthalocyanine and 2,9,16,23 tetrakis nitro copper (II) phthalocyanine

In this paper we synthesized phthalocyanine derivatives in the presence of RuCl₃.nH₂O, (NH₄)₆Mo₇O₂₄.4H₂O and CuCl₂.2H₂O catalysts using zeolites. In experimental we mixed 4mmol 4-nitro phthalonitrile, 1mmol CuCl₂.2H₂O as first catalyst and 5%W (NH₄)₆Mo₇O₂₄.4H₂O or RuCl₃.nH₂O as a second catalysts using 10%W H β or HZSM-5 zeolites as third catalysts. The mixture heated with stirring to 130-145 °C and

solid washed with boiling water (Fig. 2). The dark blue solids were purified with dichloromethane and acetone. The solids were dissolved in DMSO and zeolites filtered. Solved products in DMSO separated by distillation. Products analyzed by IR, XRD and UV-Vis spectra.

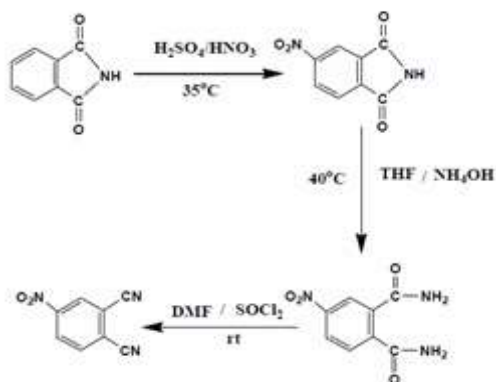


Fig. 1. Synthesis of 4-nitro phthalonitrile

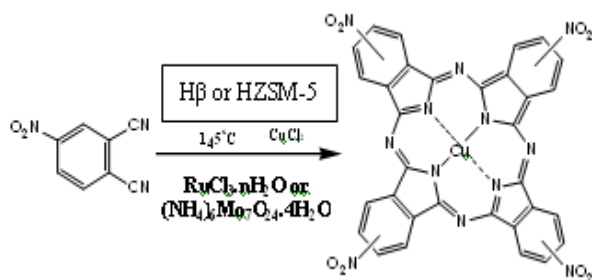


Fig2. Synthesis of 2,9,16,23 tetrakis nitro copper phthalocyanine

Synthesis of phthalocyanine and 2,9,16,23 tetrakis nitro phthalocyanine without metal

For synthesis of these products the synthesized phthalocyanines dissolved in minimum amount of trifluoro acetic acid at room temperature with argon gas and stirred for 3h. Then the product poured into ice-water mixture and nitrilyzed with 25% ammonia solution. The solid was filtered by vacuum pump and washed with water.

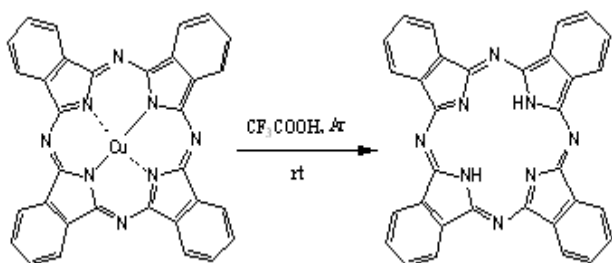


Fig. 3. Synthesis of phthalocyanine

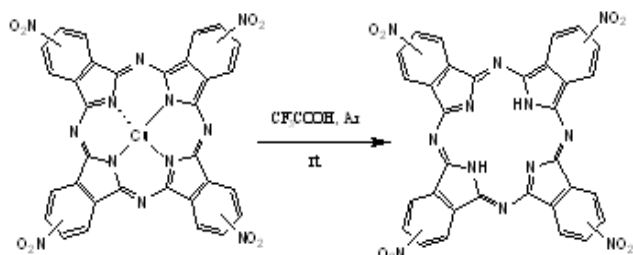


Fig. 4. Synthesis of 2,9,16,23 tetrakis phthalocyanine

Result and discussion

The synthesis time of 2,9,16,23 tetrakis nitro copper (II) phthalocyanine in the presence of ruthenium chloride and HZCM-5 catalysts was very shorter than ammonium molybdate and H β zeolite. Moreover, its yield was very higher than another (Table 2). These products were identified by IR, UV-Vis, and XRD. The peak at 620–690 nm (Q-band) attributed to the π - π^* transition and the peak at 330–380 nm (S-band). IR spectra: elimination of peak of nitrile group in (2230 cm^{-1}), appearance of peak of C=N in (1640 cm^{-1}) and C=C in (1600 cm^{-1}). UV-Vis (DMSO) $\lambda_{\text{max}} = 335\text{ nm}$ ($\log\epsilon=0.766$), 641 nm ($\log\epsilon=0.380$). (copper (II) phthalocyanine)

In UV-Vis spectra of this compound (D_{4h} symmetry) was observed two strong absorbance at 641 nm (Q band) and 335 nm (S band). The peak at 641 nm attributed to electronic transition from HOMO to LUMO and peak at 335 nm from HOMO-1 to LUMO.

UV-Vis (DMSO) $\lambda_{\text{Max}} = 698\text{ nm}$ ($\log\epsilon=0.421$), 668 nm ($\log\epsilon=0.402$), 321 nm ($\log\epsilon=0.571$) (phthalocyanine without metal). In UV-Vis spectra of this compound (D_{2h} symmetry) was observed three absorbance at 698 nm (Q_x band), 668 nm (Q_y band) and 321 nm (S band). UV-Vis absorption spectra of the metal-free phthalocyanines exhibited the split Q band, which is characteristic of metal-free phthalocyanines. The peak at 698 nm attributed to electronic transition from HOMO to LUMO and peak at 668 nm from HOMO to LUMO+1. The peak at 321 nm attributed to electronic transition from HOMO-1 to LUMO.

UV-Vis (DMSO) $\lambda_{\text{max}} = 630\text{ nm}$ ($\log\epsilon=0.346$), 356 nm ($\log\epsilon=0.428$) (2,9,16,23 tetrakis nitro copper (II) phthalocyanine)

In UV-Vis spectra of this compound (D_{4h} symmetry) was observed two strong absorbance at 630 nm (Q band) and 356 nm (S band). The peak at 630 nm attributed to electronic transition from HOMO to LUMO and peak at 356 nm from HOMO-1 to LUMO.

UV-Vis (DMSO) $\lambda_{\text{Max}} = 668\text{ nm}$ ($\log\epsilon=0.439$), 619 nm ($\log\epsilon=0.451$), 348 nm ($\log\epsilon=0.536$) (2,9,16,23 tetrakis nitro phthalocyanine)

In UV-Vis spectra of this compound (D_{2h} symmetry) was observed three absorbance at 668 nm (Q_x band), 619 nm (Q_y band) and 348 nm (S band). UV-Vis absorption spectra of the metal-free phthalocyanines exhibited the split Q band, which is characteristic of metal-free phthalocyanines. The peak at 668 nm attributed to electronic transition from HOMO to LUMO and peak at 619 nm from HOMO to LUMO+1. The peak at 348 nm attributed to electronic transition from HOMO-1 to LUMO.

Conclusion

The low activity of H β , a small pore bidirectional zeolite, is probably related to diffusional limitations of the pores and geometrical constraints for the formation of the intermediates inside the pores (table1). If catalyst decay is related to a strong adsorption of reactant or products, and since adsorption is an exothermic process, we have to expect that when the reaction temperature is increased, the adsorption constant, and therefore the amount of reactants and products adsorbed, should decrease, decreasing the catalyst decay.

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Table 1. Main structural characteristic of zeolites

Zeolite	Si/Al	Area (m ² g ⁻¹)	Crystallite size (um)
ZSM-5	40	420	1.0-3.0
β	15	582	0.02-0.03

Table2. Time, colour and yield of reactions

substrate	catalysts	zeolite	Reaction time	yield	Colour of product	Melting point
phthalonitrile	RuCl ₃ .nH ₂ o and CuCl ₂ .2H ₂ O	HZSM-5	35min	90%	Blue dark	Upper 350 °C
phthalonitrile	(NH ₄) ₆ Mo ₂₄ .4H ₂ O and CuCl ₂ .2H ₂ O	Hβ	40min	75%	Blue dark	Upper 350 °C
4-nitro phthalonitrile	RuCl ₃ .nH ₂ o and CuCl ₂ .2H ₂ O	HZSM-5	20min	95%	Blue dark	Upper 350 °C
4-nitro phthalonitrile	(NH ₄) ₆ Mo ₂₄ .4H ₂ O and CuCl ₂ .2H ₂ O	Hβ	30min	80%	Blue dark	Upper 350 °C