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Synthesis of phthalocyanine derivatives by synergistic effect of catalysts over nanodimensional zeolites under solvent-free 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 over nanodimensional zeolites. 4-Nitro phthalonitrile synthesized from phthaimide in three steps. The newly prepared compounds have been characterized by IR, UV-Vis, ^{1}H NMR and MS spectra.

Keywords: Phthalocyanine, Nanodimensional zeolite, solvent-free, phthalonitrile.

1. INTRODUCTION

Phthalocyanines (Pcs) have macrocyclic 18π electron systems that are known to be the source of semiconductor characteristics, and are characterized by high thermal and reasonable chemical stability [1-2]. Phthalocyanines 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 which has been used, the encapsulation of transition metal complexes inside the cages and void spaces of nano-dimensional zeolite and zeolitic materials. The main advantages of using zeolites are environmentally benign and they can be reused and thermally stable. Protonated forms of zeolites have been found to be efficient catalysts in reactions [5-8]. In this study, we synthesized phthalocyanine derivatives by synergistic effect of catalysts over nanodimensional zeolites under solvent free conditions with environmentally benign and compared types of zeolites and catalysts [9-12].

2. EXPERIMENTAL

2.1 Reagents and Materials

General. 4-Nitro phthalimide, sulfuric and nitric acid, ammonium hydroxide, thionyl chloride, triflouro acetic acid and NaZSM-5, Naβ were chimically pure and were purchased from merck company. The UV-Vis spectra were measured on a Shimadzo UV 160A spectrometer. The ^{1}H NMR (500MHz) spectra were obtained with Bruker 400, 500 DRX-Avance NMR. The IR spectra were taken with a Shimadzo 470 spectrometer using KBr pellets. Melting points of crystalline dicyano compounds were measured with an Electrothermal melting point apparatus.

Mass spectra were recorded on a GC-MS Agilent Technologies QP-5973N MSD instrument.

2.2 Synthesis of 4-nitro phthalimide 1

To 25 mL of a mixture of concentrated sulfuric acid and nitric acid at 15 ^{o}C was added (0.027 mol, 4 g) phthalimide with stirring. The temperature was raised slowly to 35 ^{o}C and held for 1.5 h (Scheme 1). The product cooled to 0 ^{o}C and poured into 40 g of ice and collected by vacuum filtration. Yield: 70%, 3.88 g; mp: 195 ^{o}C; IR (KBr, υ/cm^{-1}): 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}.

2.3 Synthesis of 4-nitro phthalamide 2

To 10 mL of THF was added (0.005 mol, 1 g) of 4-nitro phthlimide **1** and the mixture was heated to 40 ^{o}C and 7 mL ammonium hydroxide was added to the solution with stirring for 2h (Scheme 1). The product collected by filtration. Yield: 75%, 0.78 g; mp: 197 ^{o}C; IR(KBr, υ/cm^{-1}): 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}; ^{1}H NMR (500 MHz, DMSO, ppm) δ: 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, NH$_2$, H$_f$) ppm.

2.4 Synthesis of 4-nitrophthalonitrile 3

To 7 mL of dry DMF at 0 ^{o}C and a CaCl$_2$ drying tube was slowly added 0.73mL of thionyl chloride and (0.0048 mol, 1 g) of 4-nitrophthalamide **2** in portion over a 10-min period. The reaction stirred for 3 h at room temperature (Scheme1). The reaction mixture was stirred into 20 mL ice and collected by vacuum filtration. Yield 90%, 0.75 g; mp: 142 ^{o}C; IR (KBr, υ/cm^{-1}): 3080 w, 2220 m, 1600 m, 1532 s, 1350 s, 865 s, 795 s, 740 s, cm^{-1} ; ^{1}HNMR (500 MHz, DMSO, ppm) δ: 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.

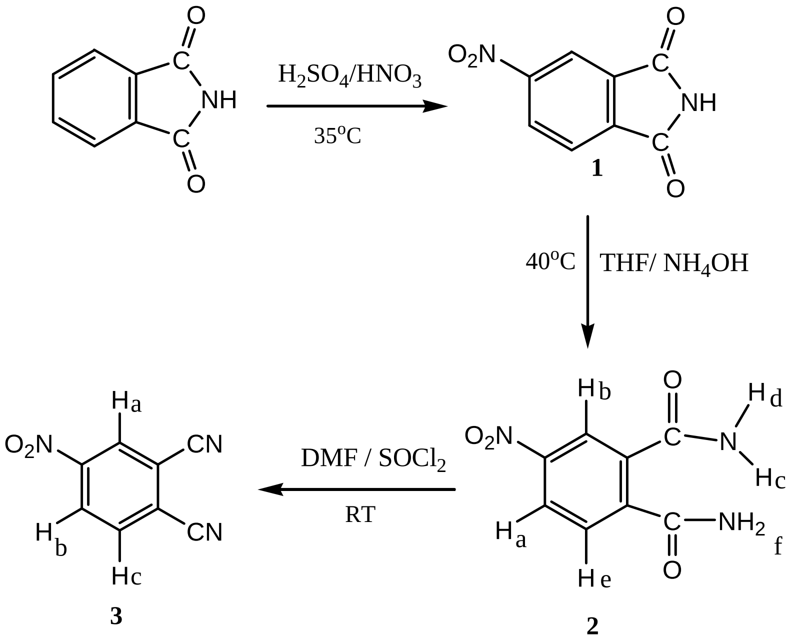


Fig. 1. Synthetic route of 4-nitro phthalonitrile 3

2.5 Preparation of nanodimensional Zeolites

The purchased sodium form of nanodimensional zeolites was calcined in air at 873 K for 5 h to decompose the organic templates. The resulting Na^+ ions was exchanged by NH_4^+ ions from a 1M NH_4NO_3 solution at 353 K for 10 h, using a liquid/solid ratio of 100 mL per gram of zeolite. Then, the nanodimensional 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 Hβ) (Table 1).

Table 1. Main structural characteristic of zeolites

Zeolite	Si/Al	Area (m^2g^{-1})	Particle size (um)
HZSM-5	40	420	1.0-3.0
Hβ	15	582	0.02-0.03

2.6 Synthesis of copper (II) phthalocyanine derivatives 4. A general procedure

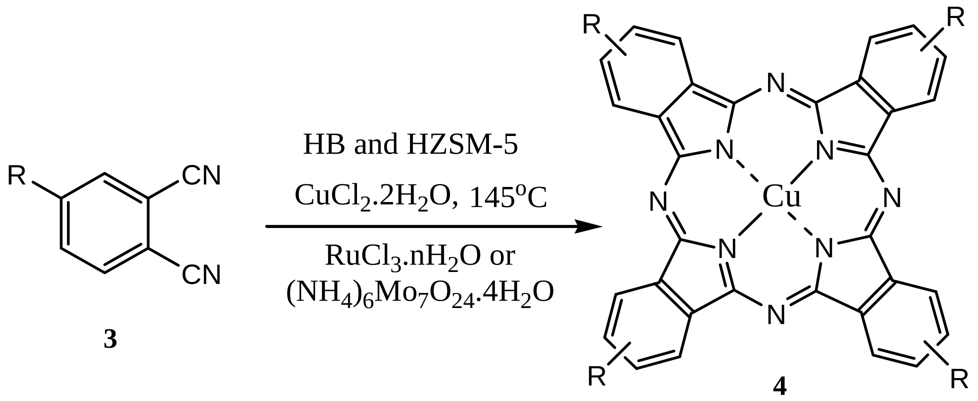
In this paper we synthesized phthalocyanine derivatives **4a-b** in the presence of ruthenium chloride ($RuCl_3$. nH_2O), ammonium molybdate ($(NH_4)_6$-$Mo_7O_{24}.4H_2O$) and $CuCl_2$-$.2H_2O$ catalysts over nanodimensional zeolites. We mixed 4 mmol of phthalonitrile derivatives, (1 mmol, 0.17 g) $CuCl_2$-$.2H_2O$ as first catalyst and 5 %W $(NH_4)_6MoO_{24}.4H_2O$ or $RuCl_3.nH_2O$ as a second catalysts using 10 %W Hβ or HZSM-5 nano-dimensional zeolites as third catalysts. The mixture heated with stirring to 130°C -145°C and solid washed with boiling water (Fig. 2) (Table 2). The dark blue solids were purred with dichloromethane and acetone. The solids were dissolved in DMSO and nanodimensional zeolites filtered. Solved products in DMSO were separated by distillation. Products were analyzed by IR, MS and UV-Vis spectra.

2.6.1 Copper (II) phthalocyanine (4a)

IR (KBr, υ/cm^{-1}): 3040 w, 1647 m, 1600 m, 1475 w, 1322 s, 895 w, 750 m, 720 s cm^{-1} ; UV-Vis (DMSO) λ_{max} = 335 nm (S band) (logε = 0.766), 641 nm (Q band) (logε =0.380); Exact mass (M^+): calcd. For $C_{32}H_{16}CuN_8$, 576.08 found 576.08.

2.6.2 2, 9, 16, 23 Tetrakis nitro copper (II) phthalocyanine (4b)

IR (KBr, υ/cm^{-1}): 3100 w, 1680 m, 1610 m, 1520 s, 1335 s, 900 m, 845 s, 755 s cm^{-1}; UV-Vis (DMSO) λ_{max}= 630 nm (Q band) (logε = 0.346), 356 nm (S band) (logε = 0.428); Exact mass (M^+): calcd. For $C_{32}H_{12}CuO_8N_{12}$, 756.07 found 756.07.

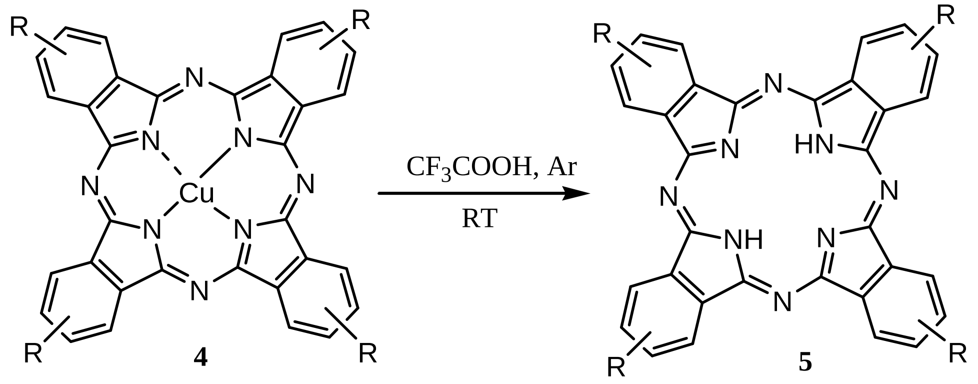


3a, 4a: R= H
3b, 4b: R= $-NO_2$

Fig. 2. Synthetic route of phthalocyanine derivatives **4a-b**

2.7 Synthesis of metal-free phthalocyanine derivatives (5). A general procedure

For synthesis of these products, the synthesized phthalocyanines (0.5 mmol) dissolved in minimum amount of triflouro acetic acid at room temperature with argon gas and stirred for 3h and then the product was poured into ice-water mixture and neutrilyzed with 25% ammonia solution. The solid was filtered by vacuum pomp and washed with water (Fig. 3).



4a, 4a: R= H
5b, 5b: R= $-NO_2$

Fig. 3. Synthetic route of metal-free phthalocyanine derivatives 5a-b

2.7.1 Metal-free phthalocyanine (5a)

Dark blue; yield: 82%, 0.21g; IR (KBr, υ/cm^{-1}): 3320 m, 3040 w,1647 m, 1600 m, 1475 w, 1322 s, 895 m, 750 m, 720 m cm^{-1}; UV-Vis (DMSO) λ_{Max}= 698 nm (Q_x band) (logε = 0.421), 668 nm (Q_y band) (logε = 0.402), 321 nm (S band) (logε=0.571); Exact mass (M^+): calcd. For $C_{32}H_{18}N_8$, 514.54 found 514.53.

2.7.2. 2,9,16 ,23Tetrakis nitro phthalocyanine (5b)

Dark blue; yield: 87%, 0.30 g; IR(KBr, υ/cm^{-1}): 3325 s, 3100 w, 1680 m, 1610 s,1520 s, 1335 s, 900 m, 845 m, 755 cm^{-1}; UV-Vis (DMSO) λ_{Max}= 668 nm(Q_x band) (logε = 0.439), 619 nm (Q_y band) (logε = 0.451), 348 nm (S band) (logε = 0.536); Exact mass (M^+): calcd. For $C_{32}H_{14}O_8N_{12}$, 694.52 found 694.53.

3. RESULTS AND DISCUSSION

The synthesis time of copper (II) phthalocyanine derivatives in the presence of ruthenium chloride ($RuCl_3.nH_2O$) as Lewis acid and HZSM-5 catalysts was very shorter than ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_20$) and Hβ nano-dimensional zeolite. Moreover, its yield was very higher than another (Table 2). The low activity of Hβ, a small pore bi-directional zeolite, is probably related to diffuseional limitations of the pores and geometrical constraints for the formation of the intermediates inside the pores and large area of Hβ zeolite that decrease intermediates availability for the reaction (Table 1). The peak at 620–690 nm (Q-band) attributed to the π–π* transition and the peak at 330–380 nm (S-band) attributed to the n- π* (**4a-b**). In IR spectra, peak elimination of nitrile group in (2230 cm^{-1}) and appearance of peak of C=N identified the synthesis of products. In UV-Vis spectra of these compounds (D_4h symmetry) which was observed two strong absorbance at 620-690 nm (Q band) and 330-380 nm (S band), the Q band attributed to electronic transition from HOMO to LUMO and S band from HOMO-1 to LUMO **4a-b** (Fig. 4). In metal-free UV-Vis spectra of these compounds (D_2h symmetry) three absorbance at (Q_x band), (Q_y band) and (S band) was observed. UV-Vis absorption spectra of the metal-free phthalocyanines **5** exhibited the split of Q band, which is a characteristic of metal-free phthalocyanines. The peak at Q_x band attributed to electronic transition from HOMO to LUMO and Q_y band from HOMO to LUMO+1. The S band attributed to electronic transition from HOMO-1 to LUMO **5a-b** (Fig. 4).

Table 2. Synthesis of copper (II) phthalocyanine derivatives **4a-b** over nanodimensional zeolites

Entry	Precursor (4mmol)	Catalysts	Zeolite	Time (min)	Yield (%)	Colour	Mp (^oC)
4a	3a, (0.51 g)	$RuCl_3.nH_2O$ and $CuCl_2.2H_2O$	HZSM-5	35	90, 0.5 g	blue dark	upper 350
4a	3a, (0.51 g)	$(NH_4)_6Mo_{24}.4H_2O$ and $CuCl_2.2H_2O$	Hβ	60	75, 0.43 g	blue dark	upper 350
4b	3b, (0.69 g)	$RuCl_3.nH_2O$ and $CuCl_2.2H_2O$	HZSM-5	20	95, 0.72 g	blue dark	upper 350
4b	3b, (0.69 g)	$(NH_4)_6Mo_{24}.4H_2O$ and $CuCl_2.2H_2O$	Hβ	50	80, 0.60 g	blue dark	upper 350

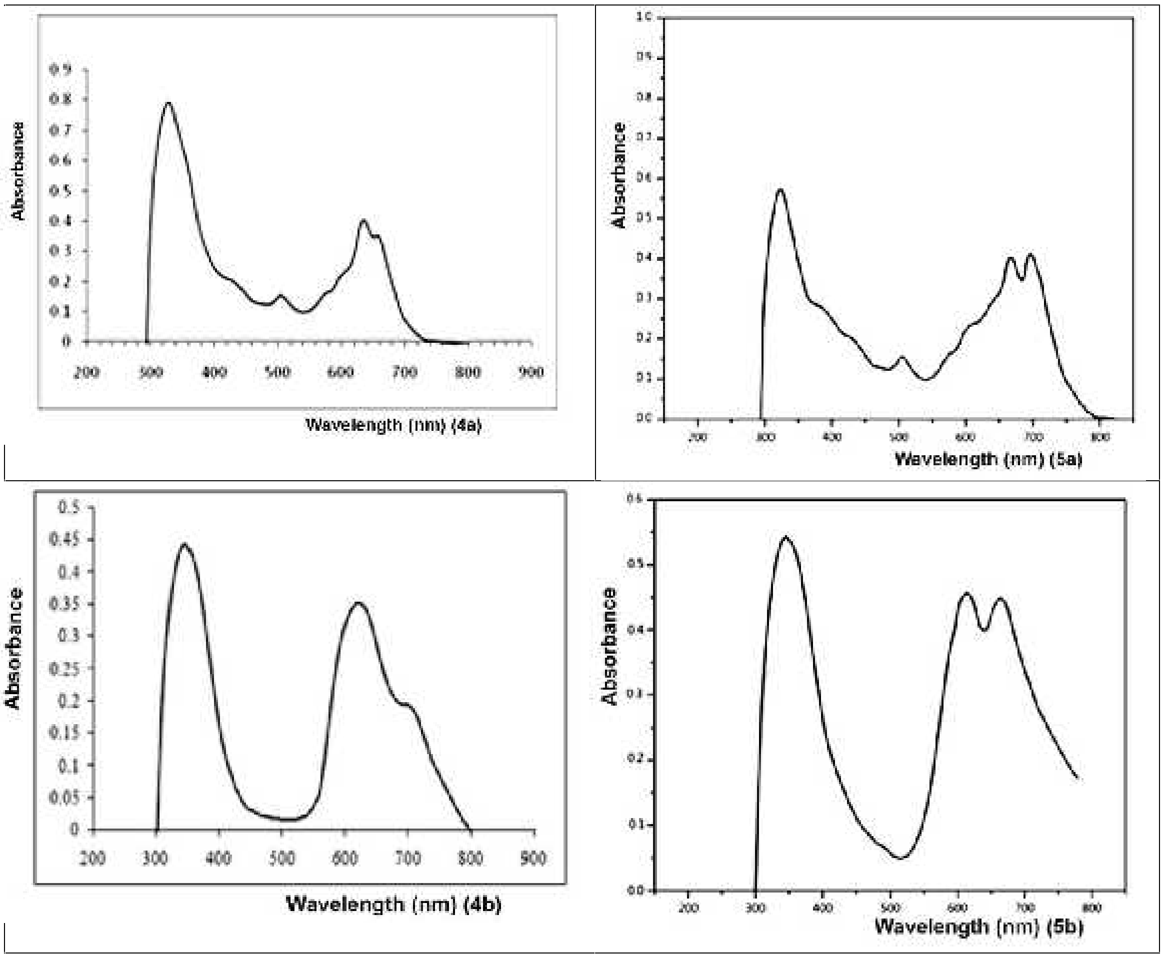


Fig. 4. Uv-Vis spectra of compounds 4a-b and 5a-b in DMSO

4. CONCLUSION

The low activity of Hβ, a small pore bidirectional nanodimensional zeolite, is probably related to diffusional limitations of the pores and geometrical constraints for the formation of the intermediates inside the pores (Table 1). If catalyst decay is related to a strong adsorption of reactant or products, we have to expect that when the reaction temperature is increased; the adsorption constant, and therefore the amount of reactants and adsorbed products should be decreased, decreasing the catalyst decay.

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سنتز مشتقات فتالوسیانین توسط تاثیر هم کوشی کاتالیزورها روی زئولیت‌های نانو ساختار تحت شرایط بدون حلال

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چکیده:

مس (II) فتالوسیانین و ۲، ۹، ۱۶، ۲۳ ترا کیس نیترو مس (II) فتالوسیانین به ترتیب از فتالونیتریل و ۴- نیترو فتالونیتریل تحت شرایط بدون حلال با دو کاتالیزور مختلف بر روی زئولیت های نانو ساختار سنتز شدند. ۴- نیترو فتالونیتریل از فتاایمید در سه مرحله سنتز شد. ترکیبات تهیه شده جدید توسط تکنیک‌های IR، UV-Vis، ^{1}H NMR و مشخصه یابی شدند.

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