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# STUDIES ON THE TEMPLATE SYNTHESIS OF SOME PHTHALOCYANINES ON FERRITES SUPPORT AND THEIR CHARACTERIZATION USING MÖSSBAUER SPECTROSCOPY

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*A fost studiată sinteza unor compuşi de concepţie originală obtinuţi prin depunerea unor coloranţi ftalocianinici pe suport de ferită. Prepararea lor implică reacţii de tip template între ftalocianina de litiu sau liberă de metal cu diverse ferite. Compozitele sintetizate au fost analizate prin spectroscopie Mössbauer. Compuşii sintetizaţi au fost testaţi din punct de vedere al proprietăţilor catalitice în reacţia de oxidare a ciclohexanului cu aer.*

*The synthesis of some original compounds based on phthalocyanines deposed on various ferrites was studied. The preparation of the compounds consisted in the template type reaction between metal free phthalocyanine or lithium phthalocyanine and various ferrites. The characterization of the synthesized compounds was made using Mössbauer spectroscopy. The synthesized compounds were submitted to a catalytic test in the cyclohexane oxidation reaction with air.*

**Keywords:** metal free phthalocyanine, lithium phthalocyanine, ferrites, catalysts, Mössbauer spectroscopy

## 1. Introduction

The use of ferrites in technical applications was mostly related to the magnetic properties. In the recent years the studies regarding their uses as dehydrogenation catalyst in organic synthesis have been widely spread [1, 2].

Among the dehydrogenation reactions using ferrites as catalyst, the transformation of alcohols into carbonyl derivatives is very efficient processes [3]. Ferrites can be obtained by several methods: thermal dehydration ($1500^0$C) of a

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mixture of $Fe(OH)_3$ and $Fe(OH)_2$ or by hydrothermal method. The latest method consists in the heating goethite FeO(OH) at a temperature of $300^0$C and a pressure of 80-150 atm. [4].

Transition metal phthalocyanines are another category of catalysts for oxidation processes that can be performed in the presence of oxygen or air. Interesting catalytic processes are the oxidation of alcohols to carbonyl compounds [5] or the oxidation of the alkyl hydrosulfide to disulfides [6].

Selective oxidation of aromatic substrates using solid catalysts, preferably at near ambient conditions and using clean oxidants like $O_2$ or $H_2O_2$, is an interesting research area of growing importance in the recent years [7]. However, extensive studies have been reported on selective oxidation of organic compounds using as oxidants singlet oxygen sources, such as $H_2O_2$ and tert-butyl hydroperoxide (TBHP) [8]. Since the early work, only a few studies [9] have been reported on the activation of molecular oxygen by metal complexes (mostly of Fe with ligands such as porphyrins, phthalocyanines and salens).

The work dwells on the synthesis of potential catalysts, of original conception, based on phthalocyanines (metal free and lithium phthalocyanines) deposed on various ferrites.

$Ni/CoFe_2O_4$ and $Ni/ZnFe_2O_4$ obtained by hydrothermal processes were used as ferrites for the phthalocyanines catalysts.

The catalysts preparation procedure involves the following steps:
- synthesis of the metal free phthalocyanine;
- synthesis of lithium phthalocyanine;
- studies on the exchange reactions of these compounds and various ferrites.

The efficiency of the exchange reaction was tested by Mössbauer spectroscopy performed at the National Institute of Materials Physics of Bucharest.

## 2. Experimental

### 2.1 Reagents

All the reagents used for synthesis were of the highest purity commercially available. Phthalodinitrile (1,2-dicyanobenzene), sodium and lithium were purchased from Fluka. Moreover, all the solvents: 1-pentanol, N,N-dimethylformamide, N-methylpirrolidone, ethanol and methanol were of the highest purity grade (Aldrich). The ferrites were prepared by the National Institute of Materials Physics Bucharest.

### 2.2 Apparatus

The efficiency of the exchange reaction was tested on a Mössbauer spectrometer of AME-50 type. The IR spectra were recorded on a FT-IR Shimadzu FTIR 8900 spectrometer, in KBr pellets. The electronic spectra were recorded in N,N-dimethylformamide, using the JASCO V550 spectrometer. A

Varian 430-GC Gas cromatograph, equipped with a flame detector was used for the analysis of the oxidation products.

### 2.3 Procedure

*A. Synthesis of metal free phthalocyanine*

12.8 g (0.1 moles) phtalonitrile, 5.4 g (4 mL, 0.09 moles) formamide and 45 mL N-methylpirrolidone are added in a three neck bottom flask equipped with stirrer, thermometer and condenser and stirred for 15 minutes, at the room temperature. Small portions of the previously prepared sodium methoxyde (molar ratio phtalonitrile:sodium methoxide = 4:1) and the reaction mass are heated for 8 hours at $195^0$C under good stirring. The excess of methanol is distilled. The mixture is cooled at $120^0$C, filtered and the precipitate is washed with formamide, acetone and water. The product is demetallised by suspending it in 50 mL methanol and stirred at $50^0$C, and then refluxed for 4 hours. The product is filtered, washed with methanol and dried. The yield is 92%.

**Elemental analysis** (*calcd/found.)*: C%: 74.70/74.75, H%: 3.50/3.60, N%: 21.80/21.65.

**IR (KBr, cm$^{-1}$):** 700, 746, 754, 780, 870, 910, 1070, 1115, 1155, 1275, 1325, 1415, 1452, 1515, 1595, 1618, 2543, 2857, 3063, 3048, 3291

**UV-VIS spectra** ((DMF), $\lambda_{max}$(lg$\varepsilon_{max}$): 698 (5.10), 775 (1.760).

*B. Synthesis of lithium phthalocyanine*

5.6 g (0.8 moles) lithium are dissolved in 150 mL 1- pentanol in a three neck round bottom flask equipped with stirrer, thermometer and air condenser by heating them at $50^0$C for 2 hours. 20 g (0.156 moles) phtalonitrile are added and the color changed from beige to green. The reaction mass is then refluxed for 6-8 hours, cooled, filtered and washed with some ethyl alcohol. Lithium phthalocyanine is dried in an dessicator over anhydrous sodium hydroxide crystals. The yield is 85%.

**Elemental analysis** (*calcd/found.)*: C%: 73.01/73.15, H%: 2.64/2.77, N%: 21.29/21.20.

**IR (KBr, cm$^{-1}$):** 3103, 3078, 3042, 1654, 1590, 1572, 1508, 1484, 1446, 1296, 1248, 1228, 1206, 966, 908, 806, 770, 706, 562, 526, 474.

**UV-VIS spectra** ((DMF), $\lambda_{max}$(lg$\varepsilon_{max}$): 603(3.88), 662 (4.06).

*C. Deposition of metal free phthalocyanine on ferrites*

0.2 g (0.37 mmoles) metal free phthalocyanine are dissolved in 30 mL 1-pentanol (or N, N-dimethylformamide) into a three neck round bottom flask equipped with stirrer, thermometer and condenser. Then 3 g of ferrites are added and the mixture is refluxed for 4 hours. The precipitate is cooled, filtered, washed with acetone and dried in a dessicator.

*D. Deposition of lithium phthalocyanine on ferrites*

0.2 g (0.37 mmoles) lithium phthalocyanine are dissolved in 30 mL 1-pentanol (or N, N-dimethylformamide) into a three neck bottom flask having stirrer, thermometer and condenser. Then 3 g of ferrites are added and the mixture is refluxed for 4 hours in the water bath. The precipitate is cooled, filtered, washed with acetone and dried in a dessicator.

*E. Oxidation tests*

50 mL acetonitrile as a solvent, 25 g cyclohexane, 0.40 g of *tert*-butyl peroxide (promoter of the reaction), and 0.75 g of catalyst are loaded into the reactor. The air was bubbled at a rate of 1 L/minute at $70^0$C for 8 hours. After the reaction is finished the mixture is cooled at $20^0$C; a sample of the reaction mass is collected, the catalyst traces are removed by filtration and then analyzed by gas-chromatography using a flame-detector gas chromatograph.

## 3. Results and discussions

### A. Synthesis of metal free phthalocyanine

Generally, metal free phthalocyanine can be prepared in different ways:

- by heating phtalonitrile at $350\text{-}380^0$C separately or in the presence of ammonia, triethanolamine or another amines [10];
- by the cyclization of phtalonitrile in glycol mixture with aromatic compounds (containing 1,4-dihydroxy, mercapto or alkyl amino groups and halogen, alkyl or alkoxycarbonyl groups) and addition of inorganic bases [11];
- by heating phtalonitrile and butoxyethanole (containing traces of hydroquinone) and adding sodium hydroxide when metal free phthalocyanine is obtained in the β crystallization form [12].

The preparation of stable and pure crystalline forms is a difficult process [13] at industrial scale.

The new synthesis presented in this paper offers an easy and reproducible preparation route leading to high pure metal free phthalocyanine, which consists in the synthesis of sodium phthalocyanine followed by demetallation. In order to obtain mono- and di- sodium phthalocyanine, hydrogen donor reagents are used (amides, aliphatic amines or alcohols). Formamide was selected as hydrogen donor because it is also a high boiling point solvent.

Metal free phthalocyanine was characterized by elemental analysis, IR and electronic absorption spectra whose data confirm the proposed structure.

The band 3290-3295 $cm^{-1}$ in the IR spectra, corresponds to N-H bond and it can not be found in metal phthalocyanines. Three or four very intense bands are characteristic for metal free phthalocyanine in the 700-780 $cm^{-1}$ region.

The electronic absorption spectra show an intense peak at 698 nm and anotherone less intense but broader at 775 nm.

### B. Synthesis of lithium phthalocyanine

Lithium phthalocyanine shows paramagnetic electron signals, very sensitive to oxygen [8] among other semiconductive properties.

The synthesis of lithium phthalocyanine was performed according to the experimental part and consists in dissolving lithium in a high boiling point alcohol (1-pentanol, 1-heptanol) to obtain the alcoxyde, followed by its reaction with the phtalonitrile at a high temperature for several hours.

The alcohol acts also as a solvent. The lithium phthalocyanine was characterized by elemental analysis, IR and UV-VIS spectroscopy, and the analytical data confirm the proposed structures of the synthesized compounds.

### C. Deposition of the phthalocyanines on ferrites

The deposition of phthalocyanines on doped ferrites was made by a template type exchange reaction of metal free or lithium phthalocyanine and the corresponding ferrites.

The ferrites used for phthalocyanine-based catalyst, were Ni/$CoFe_2O_4$ and Ni/$ZnFe_2O_4$, synthesized by hydrothermal procedures.

1-pentanol and N, N-dimethylformamide were chosen as solvents.

The reaction takes place under reflux for 4 hours. The reaction mixture is cooled, filtered and the precipitate is washed with acetone and dried.

The characteristics of the initial structures and the reaction conditions for complexation are given in Table 1.

*Table 1*

**Experimental data regarding the deposition of phthalocyanines on ferrites at 180$^0$C and for 4 hours of reflux**

| **Code sample** | **Initial characteristics** | | **Reaction conditions for the complexation of ionic Fe** | |
|---|---|---|---|---|
| | Reagents | Iron content [mequiv. $Fe^{2+}$, $Fe^{3+}$ /100g] | ferrite/ phthalocyanine molar ratio | Yield (%) |
| **P1** | Ni/$CoFe_2O_4$ + metal free phthalocyanine | 76 | 2.28 /1.55 | 95 |
| **P2** | Ni/$CoFe_2O_4$ + lithium phthalocyanine | 70 | 2.28 /1.55 | 98 |
| **P3** | Ni/$ZnFe_2O_4$ + lithium phthalocyanine | 70 | 2.50 / 1.55 | 96 |

### D. Mössbauer spectrosopy

The reaction products were analyzed on the chemical phases that contain iron using Mössbauer spectroscopy. The analysis of the recorded Mössbauer spectra was made using specialized calculation and fitting software. The Mössbauer spectroscopy analytical data are given in Table 2 and the recorded Mössbauer spectra are given in Figures 1-3.

*Table 2*

**Mössbauer spectra parameters**

| Sample | $H_{hf}^{*}$ (T) | IS** (mm/s) | QS** (mm/s) |
|---|---|---|---|
| **$Fe^{2+}$phthalocyanine** | - | 0.31 | 2.39 |
| **P1** | 48.1 | 0.44 | 0.05 |
|  | 48.4 | 0.21 | 0.08 |
| **P2** | 46.9 | 0.53 | 0.04 |
|  | 49.0 | 0.23 | 0.07 |
| **P3** | - | 0.30 | 0.66 |
|  | - | 0.33 | 1.13 |
| **Error** | ±0.3 | ±0.01 | ±0.02 |

| Sample | Relative area (%) | Identified iron phases |
|---|---|---|
| **$Fe^{2+}$phthalocyanine** | 100.0 | **$Fe^{2+}$ (low spin state, $Fe^{II}Pc$)** |
| **P1** | 33.5 | **Octa** |
|  | 30.0 | **Tetra** |
| **P2** | 27.0 | **Octa** |
|  | 41.7 | **Tetra** |
| **P3** | 74.8 | **$Fe^{3+}$** |
|  | 25.2 | **$Fe^{2+}$** |
| **Error** | ±0.4 |  |

* $H_{hf}$ –hyperfine magnetic splitting

**IS, the isomer shifting is given in relation to α-Fe

**QS, quadrupole splitting

Commercial Fe(II) phthalocyanine (Aldrich) is used as standard.

The tetrahedral and octahedral magnetic sites of magnetite were identified in the Mössbauer spectra of ferrite Ni/$CoFe_2O_4$ treated with metal free phhthalocyanine (Figure 2a) or lithium phthalocyanine (Figure 2b) according to the hyperfine field and the isomer shifting. The great width of the lines correspond to octahedral sites and is generated by the presence of $Co^{2+}$ and $Ni^{2+}$ in the spinally structure. None of the two samples shows radical differences-as new iron phases-in the limits of the method sensibility. The effects of the treatment which could lead to the modification of the surface might be relieved by conversion electron Mössbauer spectroscopy. In the case of P3 sample, both ionic species $Fe^{3+}$ and $Fe^{2+}$ are present in a 3/1 ratio, as shown by the relative area of the characteristic sites.

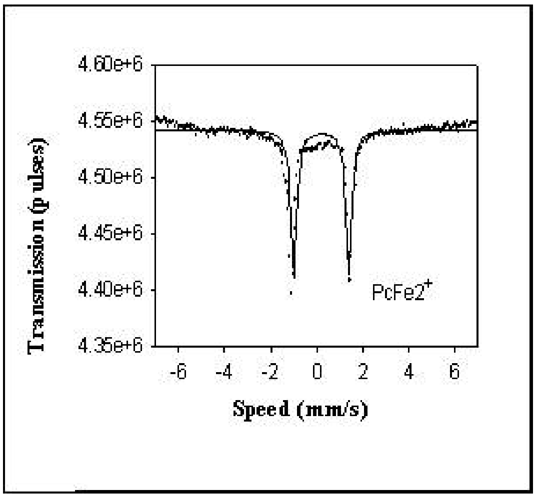


Fig. 1 Mössbauer spectrum of $Fe^{2+}$ phthalocyanine

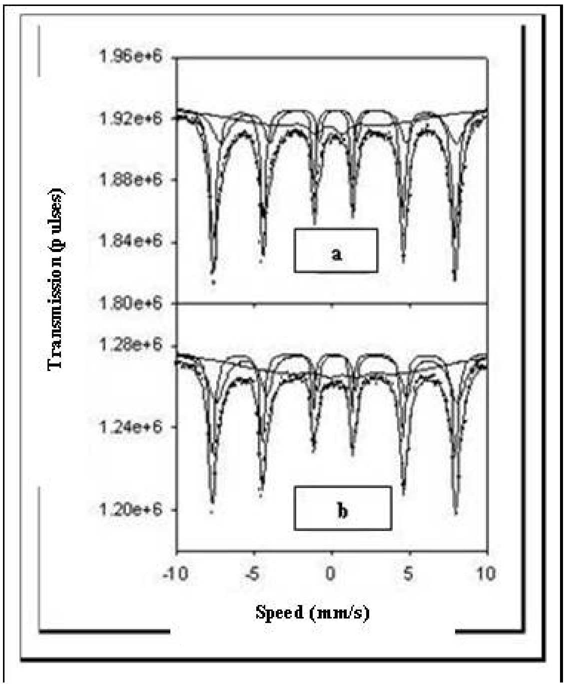


Fig. 2 Mössbauer spectra of sample P1 (a) and P2 (b)

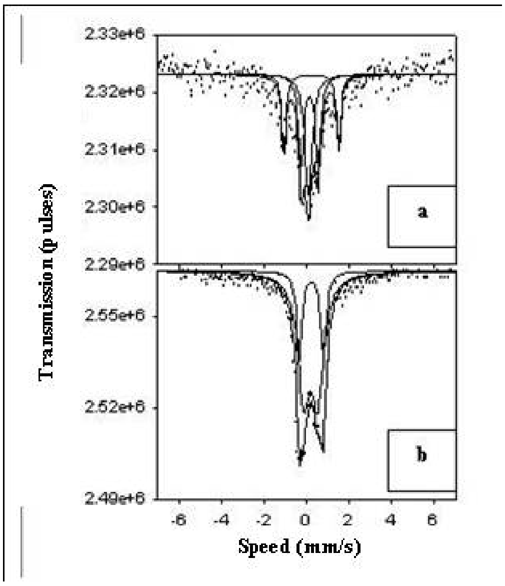


Fig. 3. Mössbauer spectra of ferrite Ni/Zn$Fe_2O_4$ (a) and (b) P3 sample

### F. Oxidation tests

The catalytic activity of the phthalocyanines considerably depends on the central metal ion. The order of the catalytic activity decreases as follows: Fe > Co > Ni > Cu > H, the last one, the metal free phthalocyanine, having the lowest activity.

The action mode of this heterogeneous catalyst is similar to the usually used catalysts, but has the advantage that the active sites within the phthalocyanines are mostly homogeneous; the metal atoms of the phthalocyanines are always situated in the same atomic shell of the macromolecule under the crystal surface. Depending on the structure of the metal atoms energetic levels adducts can be formed with the reagents, the catalytic activity being closely connected to the substrate - catalyst interactions. The activity is growing up proportionally with the solid phthalocyanines electrical conductivity and is influenced by the carrier material.

The phthalocyanines, simple or deposed on different inorganic support, were used as catalysts in oxidation processes of several classes of compounds (alcohols, ketones and acids).

A reactor of Pyrex glass on a “fluidized bed” was used, as oxidation vessel the reacting substance represents the medium, the air is the carrier; the mobile phase is assured by the submicron catalyst (the iron phthalocyanine, simple or deposed on substrate).

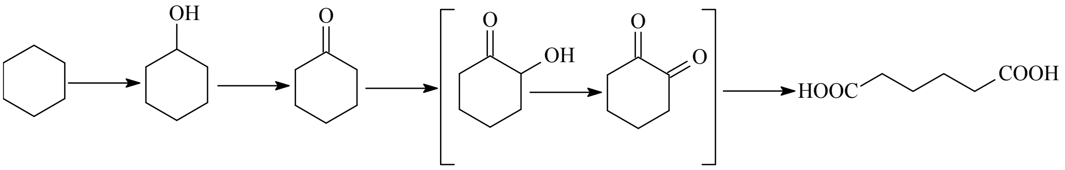
The experimental data regarding the air oxidation of the cyclohexane in the presence of new synthesized catalysts based on phthalocyanines (PhFe) and phthalocyanines deposed on ferrites is given in Table 3.

*Table 3*

**Experimental data regarding the air oxidation of the cyclohexane in the presence of the catalyst based on phthalocyanines (PhFe) and phthalocyanines deposed on ferrites (P2 and P3)**

| Test no. | Catalyst | Cyclohexane conversion (%) | Transformed cyclohexane (g) / catalyst (g) / hour | Reaction products (%) | | |
|---|---|---|---|---|---|---|
| | | | | Ciclohexanol | Ciclohexanone | Adipic acid |
| 1 | PhFe | 15.77 | 0.66 | 41 | 59 | - |
| 2 | P2 | 27.5 | 1.15 | 28 | 48.5 | 23.5 |
| 3 | P3 | 22.5 | 0.94 | 78 | 18 | 4 |

The analysis of the results shows that the immobilization of the phthalocyanines on the ferrites leads to an increase of the conversion with about 12% for the catalyst P2 and about 7 % for the catalyst P3, compared to iron phthalocyanine. Moreover, new distribution of the reaction products was observed when using the catalysts based on phthalocyanines deposed on ferrites. If cyclohexanol and cyclohexanone were obtained as main reaction products in the case of no immobilized phthalocyanines, in the case of the catalysts deposed on ferrites, adipic acid (23.5% in the case of catalyst P2 and only 4% for catalyst P3) appears also as an oxidation product. If the oxidation sequence of cyclohexane is:



the higher catalytic effect of the mixture P2 (containing iron, nickel, cobalt) has to be underlined, leading to an advanced oxidation of the cyclohexane which results in the final product (adipic acid). In the case of compound P3, which contains zinc, the reaction can be stopped to intermediary products, the major product being cyclohexanol.

## 4. Conclusions

The paper presents the preparation of some new ferrites-phthalocyanine composites with potential use as heterogeneous catalysts.

The new synthesis used for the preparation of metal free phthalocyanine consists in the synthesis of sodium phthalocyanine, followed by demetallation and offers an easy and reproductible preparation route, leading to highly pure compounds.

The original catalysts were obtained by the template reaction of lithium- or metal free phthalocyanines and ferrites.

The values of the hyperfine field and the isomer shifting of the magnetic sites (tetrahedral and octahedral) of magnetite were identified in the Mössbauer spectra of $Ni/CoFe_2O_4$ treated with metal free phthalocyanine or lithium phthalocyanine. The width of the lines corresponding to octahedral sites is generated by the presence of $Co^{2+}$ and $Ni^{2+}$ ions in the spinelic structure.

These composites were used as catalysts in the air oxidation process of cyclohexane.

It was observed an increase of the cyclohexane conversion when using as catalyst the new composites based on phthalocyanines deposed on ferrites, compared to iron phthalocyanine, and a new distribution of the reaction products was also obtained. Only cyclohexanol and cyclohexanone were obtained when using iron phthalocyanine, whereas when using catalysts deposed on ferrites, adipic acid appears as an important oxidation product.

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