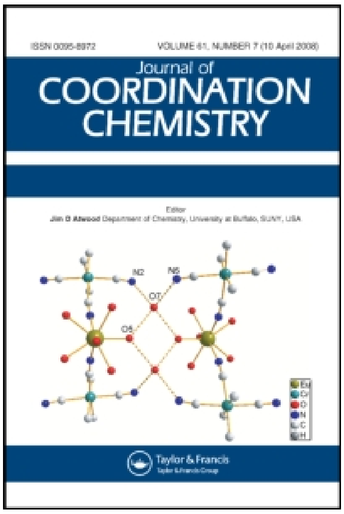

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Use of elemental copper and nickel, supported in alumina, for preparation of non-substituted metal phthalocyaninates at low temperature

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Synthesis of non-substituted metal phthalocyaninates starting from phthalonitrile in various non-aqueous solvents in the presence of elemental copper and nickel, supported in alumina, is described. Special attention is paid to phthalocyanine formation at relatively low temperatures (20–50°C). It is shown that the presence of supported elemental metals increases the rate of PcM formation.

Keywords: Phthalocyanines; Supported metals; Synthesis at low temperature

1. Introduction

Various routes can yield PcH_2 or PcM at low temperature (20–50°C) from phthalonitrile, in particular the direct electrochemical procedure with use of sacrificial metal anodes or metal salts [1, 2], use of solid strong bases [3], by UV-irradiation of the reaction system [4, 5] or with use of elemental metals [6–8]. At low temperatures an additional "impulse" is needed for the cyclization process; surface energy of strong base (solid CH_3ONa) [3] or extra energy of defects in the surface of elemental metals [7] or zeolites [9] could serve as such an impulse to reach the energy barrier. So, any source of additional energy could be useful for successful synthesis at low temperatures.

Phthalonitrile is a relatively expensive precursor for phthalocyanine industry in comparison with urea and phthalic anhydride and, so, this precursor is used only for academic purposes. However, obtaining phthalocyanines from the cheapest precursors requires relatively drastic conditions (>180°C, catalysts and promoters); use of phthalonitrile allows quantitative-yield reactions at milder conditions (100–130°C). With a further decrease of temperature to 0°C, energy saving in phthalocyanine production from this precursor would compete with its relatively high cost.

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So, understanding of cyclization mechanisms of this and other phthalocyanine precursors at low temperatures could help to elaborate an optimal route for facile production of pigments in mild conditions.

Elemental metals in the supported form in an inert matrix such as graphite, TiO_2 or Al_2O_3 [10] can be applied in various organic and organometallic reactions as a source of a free metal. The structural peculiarity of such systems is the presence of metal aggregates in very disperse form on the TiO_2 or Al_2O_3 structure; as a consequence, such "supported" systems are much more active in comparison with the same metals in their "standard" form (sheet, wire or non-active powder).

On the basis of the reported results on the use of various elemental metals of different natural activity (non-activated chemically) [6] and highly active pyrophoric [7] and Rieke metals [8] for phthalocyanine preparation, we assumed that elemental metals in the supported form should also have activity in phthalonitrile cyclization at lower temperatures in comparison with the traditional techniques. In this work, supported copper and nickel on an alumina matrix were prepared and used for phthalocyanine formation at 20–50°C in a weak ultrasonic field.

2. Experimental part

2.1. *Materials and equipment*

Phthalonitrile, neutral alumina, 30% solution of CH_3ONa in CH_3OH, and PcH_2 (Aldrich) as a standard were used as supplied. Selected solvents (methanol, ethanol, *N*,*N*-dimethylethanolamine, and ethoxyethanol, from Aldrich and Fisher) were dried and distilled by standard methods before use. An organic microanalyser (Perkin-Elmer) was used for C, H and N content determination. Infrared and UV/visible (in pyridine) spectra were recorded on Bruker (Tensor 27) and Perkin-Elmer instruments, respectively. Ultrasonic treatment of reaction systems was carried out in the ultrasonic cleaners of different capacity (3 and 11 L), as well as, in some cases, using a stronger ultrasonic source (sonic dismembrator, Fisher, model 500; it was not used in all cases). The crystal phases of all samples were characterized by X-ray diffraction using a Siemens D-5000 instrument with Cu-Kα radiation at a scan rate of 0.05° at $2\theta\,\mathrm{min}^{-1}$ and 40 kV/30 mA. The surface areas of the powders were measured using a Quantachrom, Autosorb-1 surface area analyser. Nitrogen adsorption isotherms were obtained at 77 K, after the samples were degassed below 10^{-3} Torr and 200°C for 8 h. The BET adsorption model was applied for the interpretation of the N_2 isotherms to evaluate the surface area. Scanning electronic microscope (SEM) photomicrographs were obtained to study the $M\text{-}Al_2O_3$ (M = supported Cu or Ni) used as a surface reaction in the phthalocyanine synthesis. A Carls Zeiss DSM950 model was used, at 30 kV/50 mA and 9-mm working distance.

2.2. *Preparation, characterization and use of supported elemental metals in synthetic procedures*

The supported copper or nickel on alumina were prepared as follows. The alumina powder (50 g) was put into 200 mL of aqueous 20% solution of the corresponding metal

Table 1. Specific area for surfaces of alumina and supported metal-alumina phases.

System	BET area $m^2\,g^{-1}$
Al_2O_3	126.9
Al_2O_3-Cu	43.00
Al_2O_3-Ni	39.99

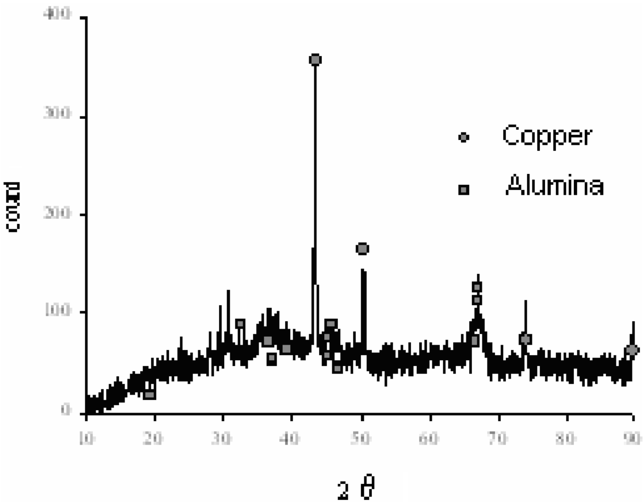

Figure 1. X-ray patterns of Al_2O_3-Cu.

salt ($CuSO_4 \cdot 5H_2O$ or $NiCl_2$) and stirred for 10 min. 5–8 mL of NH_3 (10% aqueous solution) was added to pass these salts to the corresponding insoluble hydroxides and the formed mixture was stirred for 10 min. Then the powder was filtered, heated in an oven at 300–350°C for 5 h and collocated into the tube, through which the flow of dry hydrogen was passed for 4 h at 350°C. The obtained powder was kept for further use to carry out phthalonitrile cyclization processes. Table 1 shows specific area for the surfaces of alumina and copper (nickel), supported on it. For the copper-aluminium oxide system, the copper metal phase was identified as a main phase and aluminium oxide phase was also identified, as is shown in figure 1; for the nickel-aluminium oxide system, the bohemite {AlO(OH)} was identified as a main phase and the crystalline phases of nickel, bunsenite (NiO) and aluminium oxide (Al_2O_3) were also found, as shown in figure 2. The phthalocyaninate products obtained using copper and nickel supported on alumina are in fibre form. The phthalocyaninate fibres formed over Cu-alumina are bigger than fibres formed over Ni-alumina. The copper metal species contribute to better formation of these fibres than the metallic nickel and impurity of nickel oxide over alumina.

Generally, a metal-alumina powder (3–5 g) was added to the solution (20 mL of a solvent), containing 3–5 g of phthalonitrile and 5 drops of 30% solution of CH_3ONa in methanol. The flask was put into an ultrasonic cleaner and maintained under treatment at 20–50°C for 24–72 h. Then the formed blue product was separated from unreacted

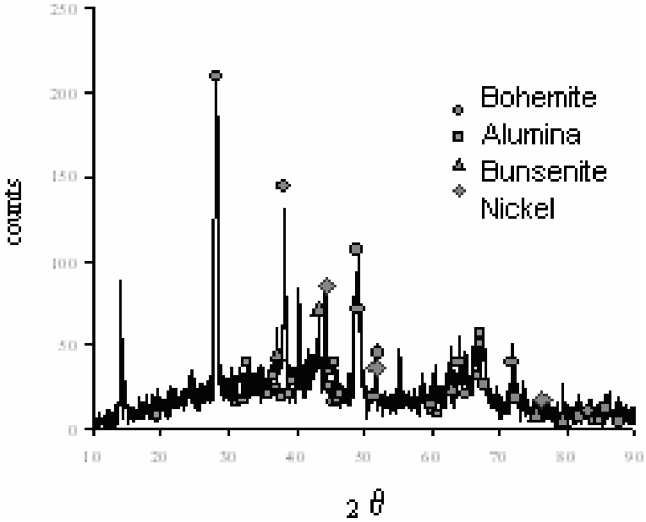

Figure 2. X-ray patterns of Al_2O_3-Ni.

alumina by shaking and decanting with the solvent, washed with ethanol in Soxhlet equipment and dried in air. Some experiments were carried out without ultrasonic treatment. Difficulties in separation of alumina and metal phthalocyaninate phases were observed because of their presence in solid forms, so phthalocyaninate samples, used for chemical analysis, were taken from those parts of flasks which were far from the alumina phase.

2.3. *Purification and identification of the products*

Phthalocyanines formed were purified by washing with hot ethanol in a Soxhlet extractor and dried in air. The products were characterized by metal content by atomic absorption spectroscopy. According to elemental analysis data, compositions of the best samples of the obtained products correspond to typical metal phthalocyanines PcM:

Copper phthalocyaninate: Found/Calcd, wt.%: Cu (10.25/11.04), C (65.07/66.72), N (18.55/19.46), H (2.05/2.78).

Nickel phthalocyaninate: Found/Calcd, wt.%: Ni (9.55/10.29), C (67.01/67.28), N (18.90/19.63), H (2.41/2.80).

Some variations of composition (0.05–0.30%) were observed in different experiments. The IR spectra (KBr pellet) of copper phthalocyaninate contain the following main bands (cm^{-1}): 3500–3380(vs, w), 2929(m), 2851(m) {ν(C–H)}; 2300–2280(s), 1730(vs), 1622(s), 1514(m) {ν(C–C) of benzene rings}; 1472(m) {ν(C–C) of pyrrol rings}; 1365(s) (pyrrol nuclei-*meso*atoms of N); 1320(m), 1150(s) {γ(C–H)}. Spectra of nickel phthalocyaninate are similar. Some absorption bands (2865 and 2705 cm^{-1}) are absent in the standard PcH_2 spectra, which has additional bands at 622, 675, 690, 720, 1309 and 1500 cm^{-1}. IR spectra of the same PcM, obtained in different solvents, are almost

Table 2. Yield range for metal phthalocyaninates in four selected solvents.

Temperature (°C)	System	Yield, * (wt.%)
Supported copper		
50	Methanol	30–42
	Ethanol	25–40
	Dimethylethanolamine	38–45
	Ethoxyethanol	40–45
35	Methanol	25–35
	Ethanol	27–35
	Dimethylethanolamine	35–45
	Ethoxyethanol	37–45
23	Methanol	20–35
	Ethanol	22–35
	Dimethylethanolamine	25–30
	Ethoxyethanol	20–30
Supported nickel		
50	Methanol	35–45
	Ethanol	22–35
	Dimethylethanolamine	32–45
	Ethoxyethanol	30–41
35	Methanol	22–34
	Ethanol	28–40
	Dimethylethanolamine	30–40
	Ethoxyethanol	34–43
23	Methanol	15–25
	Ethanol	18–30
	Dimethylethanolamine	20–34
	Ethoxyethanol	18–27

*With use of ultrasound. Yields were 5–8% lower in case of its non-application.

identical (the difference is in the peak intensity). Data (nm) of PcCu in pyridine are the following: 692–693, 659–660 (*Q*-band), 602–604.

3. Results and discussion

According to the chemical analysis of the formed products, copper and nickel phthalocyaninates of 90–95% purity (for phthalocyanine chemistry, such grade of purity of formed products is normal) are formed as final products, in which traces of alumina were detected due to the impossibility of a complete separation of metal phthalocyaninate and supporting material, although their densities are distinct (the separation is possible due to this fact). The range of yields for metal phthalocyaninates (four parallel experiments) are presented in table 2. In comparison with non-activated commercial copper and nickel powders and pyrophoric metals [7], yields with the supported form of metals are between non-activated and Rieke metals. Thus, at 50°C, yields of nickel phthalocyaninate in methanol under ultrasound treatment are as follows: nickel powder (25–30%), supported nickel (35–45%), Rieke nickel (40–47%).

A scanning electron photomicrograph of the nickel-aluminum oxide system is shown in figure 3. Formed organic material and nickel aggregates covering part of some crystals are shown in figure 4. A scanning electron photomicrograph of the

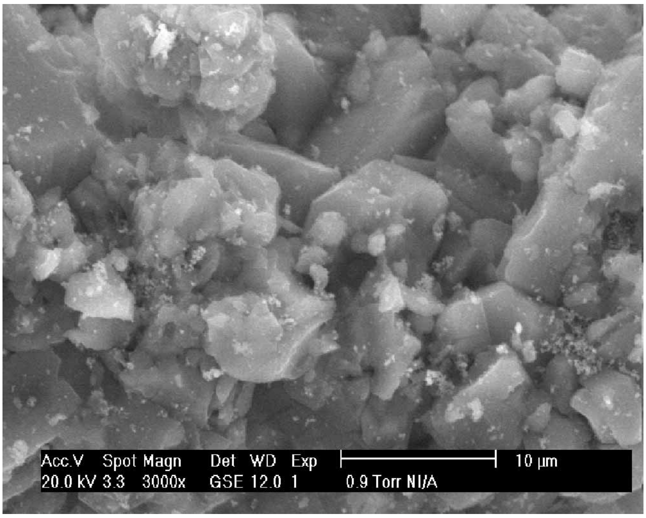

Figure 3. The nickel particles deposited on a crystaline surface of aluminium oxide.

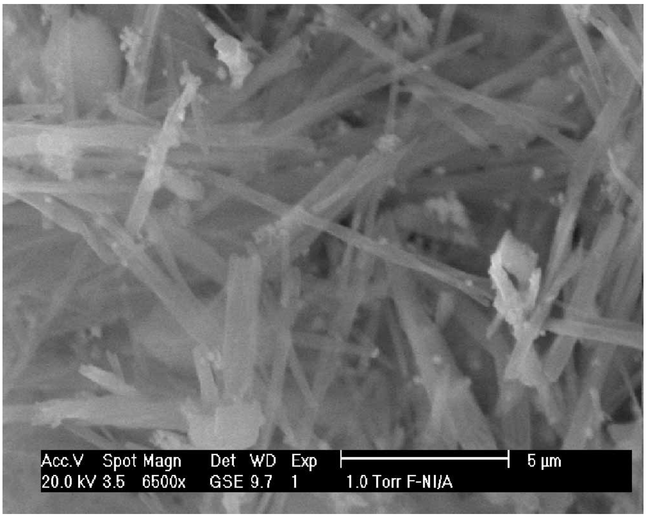

Figure 4. The nickel phthalocyaninate and nickel particles are presented deposited on a crystalline surface of aluminium oxide.

copper-aluminium oxide system is presented in figure 5. Copper phthalocyaninate in the form of fibres on aluminium oxide and small particles of copper are shown in figure 6.

Higher surface energies of supported forms of the metals in comparison with standard of metal powders may contribute to easier cyclization of phthalonitrile and, as a consequence, lower initial temperature of this process. Evidently, high numbers of defects and imperfections in small metal aggregates make them very active, not only in respect of phthalonitrile cyclization, but also in other reported organic reactions [10]. The proposed mechanism with participation of small supported copper and nickel

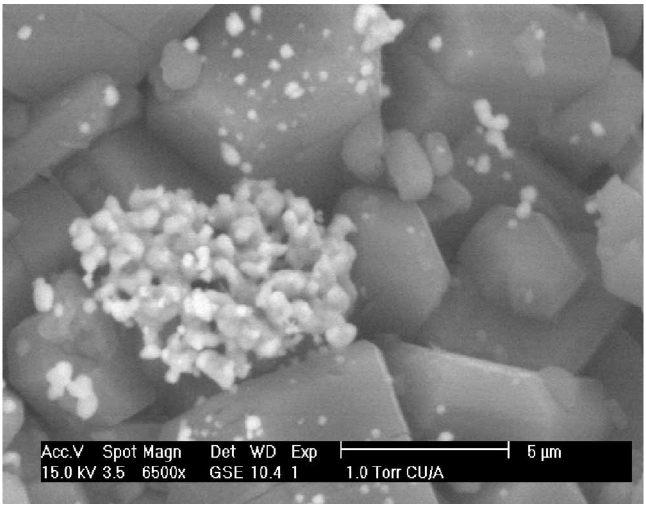

Figure 5. The copper particles deposited on a crystalline surface of aluminium oxide.

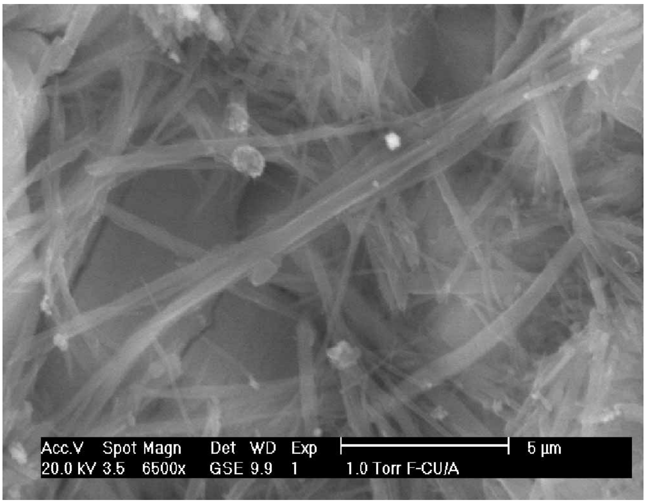

Figure 6. Copper phthalocyaninate and copper particles deposited on a crystalline surface of aluminium oxide.

aggregates M_n/Al_2O_3 (precursors of copper and nickel ions) is presented in figure 7. In a difference with the reported classic mechanism with participation of copper ions in phthalonitrile cyclization (studied with use of metal salts or non-activated elemental metals) [13, 14], we proposed participation of small aggregates M_n of metallic copper and nickel existing in the alumina matrix. M_n/Al_2O_3 is a metallic aggregate inside the alumina structure, possessing a high number of defects, which, under applied ultrasonic treatment, forms preferential sites of reaction and further allows elimination of metal atom(s) reacting with organic substrate. Alternatively, in case of application of a stronger ultrasonic treatment, these aggregates can be eliminated completely from the

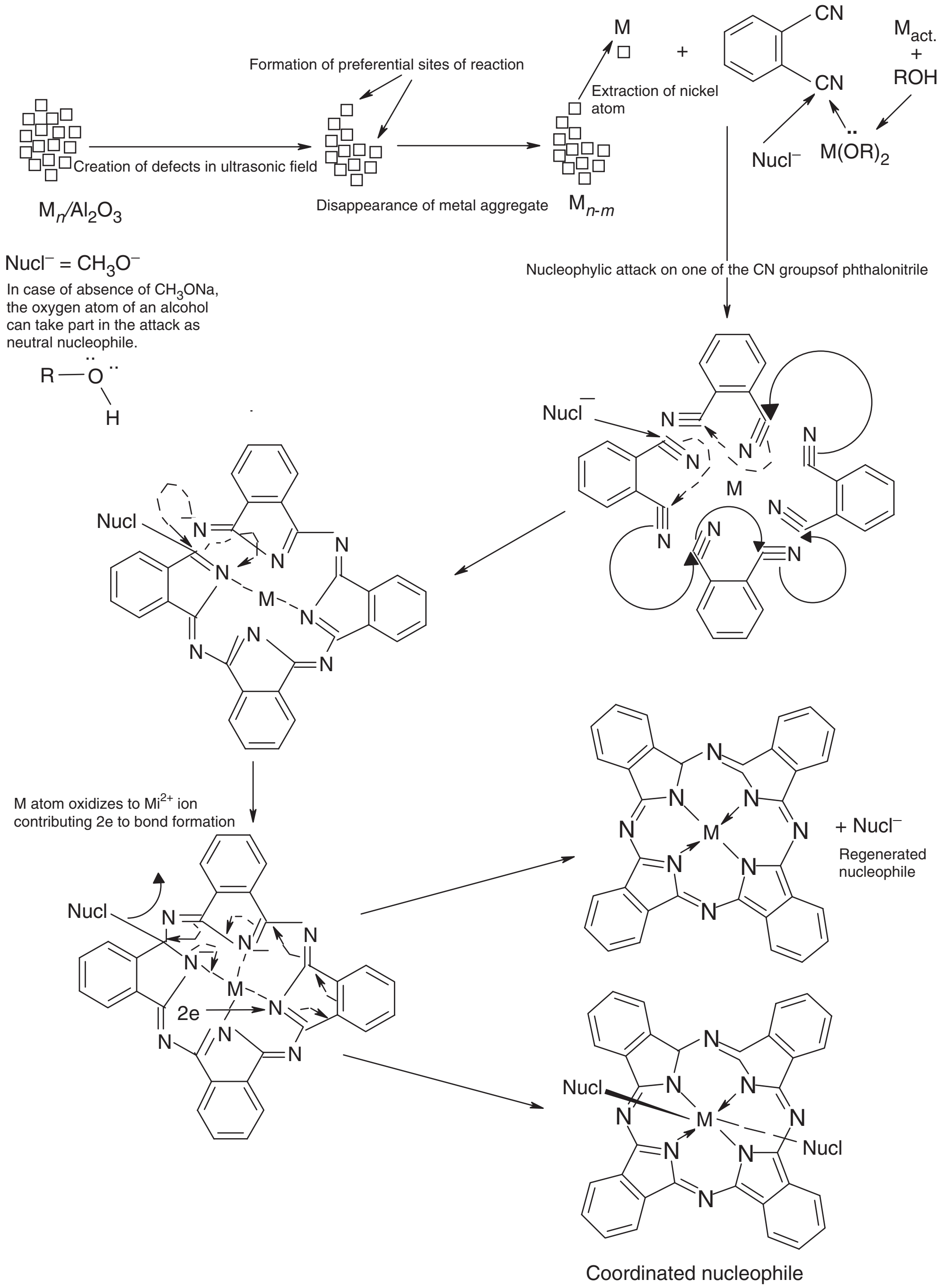

Figure 7. Mechanism of phthalonitrile cyclization on the supported metal-alumina.

internal alumina surface and further, being destroyed by US field and forming metal atoms, serve as centers for phthalonitrile cyclization. An additional interaction between small metal aggregates and alcohol forming an alcoholate could take place. This compound, although having low-solubility in ROH, should have sufficient activity to carry out a nucleophilic attack on the phthalonitrile CN-group. That's why phthalonitrile cyclization takes place even without sodium methylate, although with much lower yields. In total, phthalonitrile cyclization on metal aggregates takes place due to (1) many defects in their surface and (2) partial dissolution of metallic aggregates in alcohols increasing nucleophile concentration.

Review of available literature shows no extensive discussion of reaction mechanisms of phthalocyanine formation on a metal ion matrix (except copper [14], whose phthalocyaninate is widely used in the pigment industry and, so, its formation processes from various precursors and metal sources (Cu, CuCl, $CuCl_2$) have been carefully studied). Additionally to the previously mentioned mechanism of cyclization starting from phthalonitrile [13], the mechanism of phthalocyanine formation with use of a nickel salt was reported in case of use of urea and phthalic anhydride as precursors as far back as more than 30 years ago [15]. In general, the reported mechanism with participation of an elemental metal surface and an organic substrate in an ultrasonic field [10, p. 138] includes creation of defects and preferential sites of reaction on the metal surface and further "extraction" of a metal atom, associated to an organic partner. In case of supported metals, organic matter should first penetrate inside the alumina internal structure and then contact the metal aggregates. So, the supported metals, used in the present work, have shown slightly lesser activity in respect with reaction of phthalonitrile cyclization in comparison with "free" pyrophoric and Rieke metals without an inert matrix [7, 16].

Comparing various routes for decrease of temperature for phthalocyanine preparation use of activated and supported metals is much more effective in comparison to other routes (UV-irradiation [4, 5], electrosynthesis [1, 2, 12, 17] (this way at low temperatures leads to traces of products, but it serves perfectly at temperatures over 80°C) and use of zeolites [9]). Temperature of synthesis depends on the activity of metal particles and theoretically may be decreased below 0°C. Also, nature of the non-aqueous solvent has a primordial role in order to carry out such an interaction at low temperatures. As a recommendation for further investigations in this area, supported metals could be successfully used for synthesis of soluble (in water or organic solvents) phthalocyanines. In this case, there is no problem of a full separation of alumina and formed product.

4. Conclusions

Non-substituted copper and nickel phthalocyaninates were obtained from phthalonitrile as a precursor and supported copper and nickel on an alumina matrix at low temperatures (20–50°C). In comparison with non-activated commercial copper and nickel powders, the supported form is more efficient in cyclization of phthalonitrile in a series of non-aqueous solvents, although their activity is less than pyrophoric and Rieke metals. The mechanism, including small metal aggregates is proposed. It is suggested that high quantity of defects and imperfections on the surface of metal aggregates contributes to cyclization of phthalonitrile at low temperatures. The described approach could be used in development of a direct synthesis of metal (iron, cobalt, manganese) phthalocyaninates on alumina to be applied in heterogeneous catalysis.

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