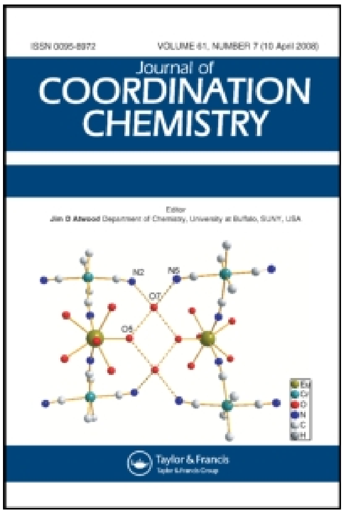

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B. I. Kharisov[ab]; U. Ortiz Méndez[a]; L. A. Garza-Rodríguez[a]; H. M. Leija Gutiérrez[a]; A. Medina Medina[a]; S. S. Berdonosov[c]
[a] Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N.L., México [b] Institute of Physical Chemistry and Electrochemistry, Moscow State University, Moscow, Russia [c] Department of Chemistry, Moscow State University, Moscow, Russia

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Use of various activated forms of elemental nickel and copper for the synthesis of phthalocyanine at low temperature

B. I. KHARISOV*†‡, U. ORTIZ MÉNDEZ†, L. A. GARZA-RODRÍGUEZ†,
H. M. LEIJA GUTIÉRREZ†, A. MEDINA MEDINA† and S. S. BERDONOSOV§

†Universidad Autónoma de Nuevo León, A.P. 18-F, C.P. 66450,
Ciudad Universitaria UANL, San Nicolás de los Garza, N.L., México
‡Institute of Physical Chemistry and Electrochemistry
Moscow State University, Moscow, Russia
§Department of Chemistry, Moscow State University, Moscow, Russia

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The synthesis of non-substituted metal phthalocyaninates, starting from phthalonitrile in various non-aqueous solvents, by using chemically activated nickel in two forms (commercial pyrophoric metal and synthesized Rieke nickel) and copper (Rieke copper) at low temperatures (0–50°C), is described. The presence of activated metal causes the rapid formation of phthalocyanine metal complexes (PcM) in low-weight alcohols. A reaction mechanism is proposed which includes the participation of small metallic aggregates as matrices for phthalonitrile cyclization.

Keywords: Nickel phthalocyaninate; Rieke metals; Synthesis at low temperature

1. Introduction

Various routes can yield metal-free phthalocyanine (PcH_2) or its metal complexes (PcM) at low temperature (0–50°C) from phthalonitrile. In particular the direct electrochemical procedure [1–8] with the use of sacrificial metal anodes or metal salts, or by using solid strong bases [9], UV-irradiation of the reaction system [10], or even by means of elemental metals [11] have been used. At low temperature, the presence of a strong base such as CH_3ONa [9], or defects located on the surface of elemental metals [11], could start the process of phthalonitrile tetramerization. So, at 0–50°C any source of additional local energy could be useful for heterogeneous synthesis of phthalocyanine or its metal complexes, although the formation rate is much slower when compared to the more classical processes at $T > 100°C$.

Metals in activated form [12], in particular those obtained from anhydrous metal salts and alkali metals (so-called Rieke metals, in particular Rieke nickel [13–23]), could be extremely useful to carry out PcM synthesis at low temperature. In particular,

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*Corresponding author. Email: bkhariss@ccr.dsi.uanl.mx

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highly reactive magnesium [24] was successfully used for obtaining phthalocyanine in 38% yield. The peculiarity of such pyrophoric forms of metals is their high number of high-energy defects and imperfections in the metal surface; as a result, Rieke metals are much more active in comparison to the same metals in their "standard" form (sheet, wire or non-active powder). Non-activated metals [11, 25] were also used to produce phthalocyanines at different temperatures, as well as metal alloys [26].

Ultrasonic treatment was reported to increase the rates of solid-state reactions for the synthesis of copper phthalocyanine through the reaction of phthalonitrile and CuCl [27]. Ultrasonic treatment of a heterogeneous reaction system containing phthalocyanine precursors (in particular phthalonitrile) and activated elemental metal [28] could optimize the cyclization process.

Phthalonitrile is a relatively expensive precursor for the phthalocyanine industry in comparison to urea and phthalic anhydride and is used only for academic purposes. However, obtaining phthalocyanines from the cheapest precursors requires relatively drastic conditions (>180°C, catalysts and promoters). In this respect, the use of phthalonitrile allows easy-to-carry-out quantitative-yield reactions at milder conditions (100–130°C). With a further decrease in temperature, energy saving in phthalocyanine production from this precursor would compete with its relative high cost. Understanding of cyclization mechanisms of this and other phthalocyanine precursors, at low temperatures, could help elaborate an optimal route for facile production of pigments at mild conditions.

At present, in order to optimize the low-temperature preparation of phthalocyanines, five routes are being developed in our laboratory: (1) UV-irradiation of the reaction system (without the use of metals) [10, 29]; (2) use of elemental metals in the form of finely divided metal powders [30] and Rieke metals as "matrices" for phthalonitrile cyclization and Pc core formation; (3) use of so-called "supported metals" on an inorganic matrix (these metals have been described in detail before [12]), (4) using zeolites and other microporous materials (without metals) [31], and (5) direct electrochemical synthesis [32–35] using sacrificial anodes and even cathodes. In this work, we present the experimental results of the second technique.

2. Experimental part

2.1. *Materials and equipment*

Phthalonitrile, DBU, 30% solution of CH_3ONa in CH_3OH, and PcH_2 (Aldrich) as a standard, were used as supplied. Solvents (propanol, *i*-propanol, *n*-butanol, *i*-butanol, *t*-butanol, 1-pentanol, 1-hexanol, ethyleneglycol, DMEA, and ethoxyethanol, from Aldrich and Fisher) were distilled before use. Methanol was stirred with anhydrous CaO and distilled over CaO. To purify absolute ethanol, magnesium (5 g) and $CHCl_3$ (3 drops) were added to 60 mL ethanol; when almost all magnesium was converted to MgO, 900 mL ethanol was added and then twice distilled over CaO. THF was stored over iron powder to prevent the formation of peroxides. Before use, THF was filtered, boiled with a few drops of 0.5% CuCl, to eliminate peroxides, and distilled over metallic sodium. Commercial pyrophoric nickel (under a water layer) was used directly as supplied.

Determination of C, H and N content was carried out on a Perkin-Elmer CHNS/O Analyzer (Series II 2400). Infrared and UV/visible spectra (in pyridine) were recorded on Bruker (Tensor 27) and Perkin-Elmer spectrometers, respectively. Ultrasonic treatment of every reaction system was carried out in ultrasonic baths of different capacity (3 and 11 L), as well as by means of a stronger ultrasonic source (Sonic dismembrator, Fisher, Model 500; which was used in some cases).

2.2. *Synthesis procedures using activated elemental nickel and copper*

The Rieke nickel was prepared following several procedures [12, 36, 37]. All manipulations with compound precursors and activated nickel, were carried out in a glove box filled with nitrogen and dried with P_4O_{10} or in the apparatus shown in figure 1. Commercial anhydrous nickel chloride, oven dried at 130°C before use (~17 g, 0.13 mol), metallic potassium (~9.8 g, 0.25 mol) in the form of small pieces, and THF (350 mL), freshly distilled over metallic sodium, were introduced in a 500 mL flask with refrigerant. The system was kept in the glove box and vigorous stirring was applied with simultaneous gradual heating up to the THF boiling point (66°C). Heating and stirring were stopped after 12 h, leaving the flask at rest for 3 to 5 h in order to precipitate the metal formed. Then the remaining THF was decanted, a new portion of fresh THF (250–300 mL) was added, the mixture was stirred again for 5 min and then kept at rest for 1 h. The last operation was repeated once again.

The powder obtained (a mixture of Rieke nickel and KCl, formed as a result of the reduction of $NiCl_2$) was kept for further use in phthalonitrile cyclization processes. The Rieke copper was prepared similarly from anhydrous copper iodide (22.80 g, 0.1197 mol), metallic potassium (4.62 g, 0.1182 mmol) in the form of small pieces, naphthalene (1.7455 g, 0.0136 mol) and freshly distilled THF (400 mL). Since the activity of freshly obtained Rieke metals generally decreases [12] in some hours or days, due mainly to further agglomeration of small metal particles, the Rieke nickel and copper obtained were promptly used for phthalocyanine preparation, usually within 48 h of its preparation.

Generally, a Rieke (or commercial pyrophoric nickel) metal (~0.2 g, as calculated for a pure metal) was added to the solution (20 mL of a solvent), containing 3.5 g of phthalonitrile and 0.5 mL of a 25% solution of CH_3ONa in methanol, or without CH_3ONa; in this last case to elucidate a possibility of phthalonitrile cyclization on active sites of pyrophoric metal without nucleophilic attack on the nitrogen atom of the phthalonitrile CN group, performed by such standard activators as sodium methylate (first step of a classic process for phthalonitrile cyclization). In comparison to the reaction conditions in our previous work [30], a lower nickel (copper) : phthalonitrile ratio was used (1 : 8 against 1 : 4 for an equimolar reaction ratio). The flask was placed inside an ultrasonic cleaner and maintained under treatment at $T = 0$ to 50°C for 12 to 72 h. The blue product formed was separated from the unreacted metal by shaking the mixture and transferring the contents into a filtration funnel (to ensure the quantitative collection of the product, the flask was filled with hot ethanol and shaken to remove the phthalocyanine sticking to the walls), decanting the lighter nickel (copper) phthalocyaninate phase with the solvent, then washing with ethanol in Soxhlet equipment and finally dried in air. Parallel experiments were carried out without either

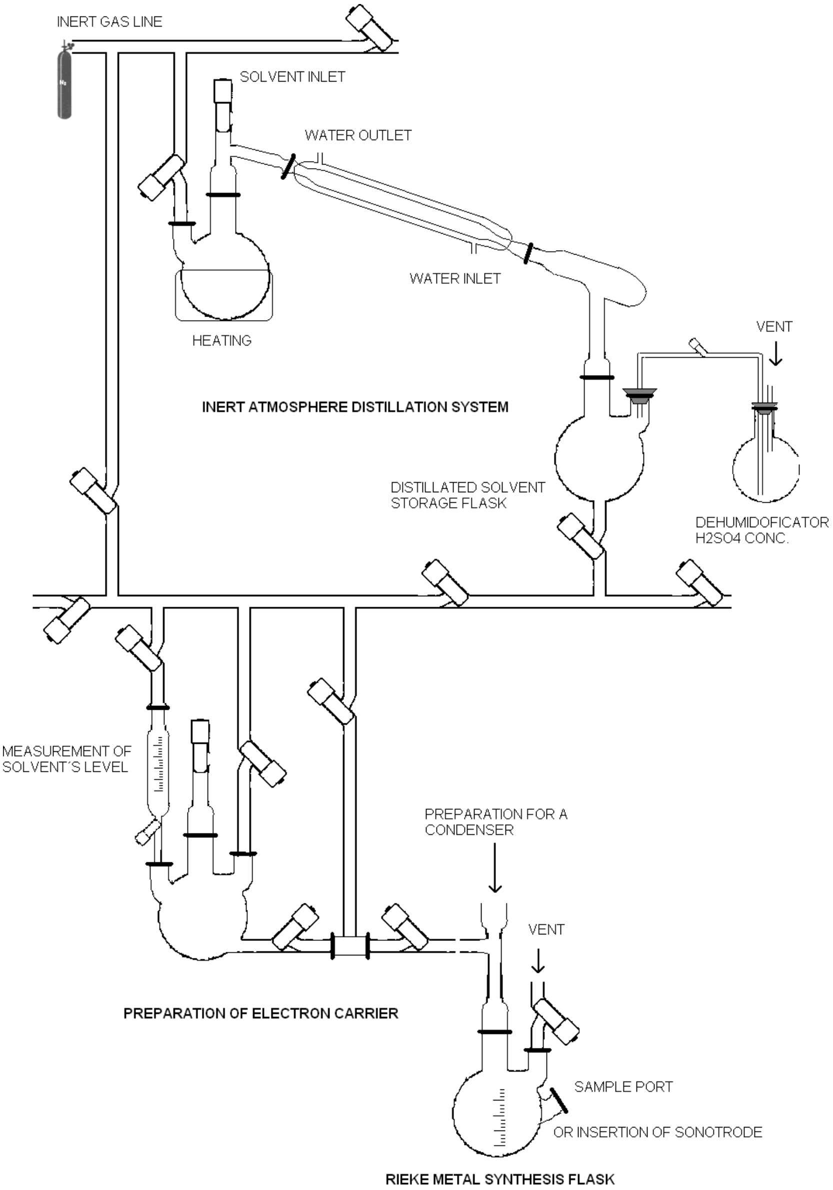

Figure 1. Equipment for synthesis of Rieke metals.

CH_3ONa (table 1), or ultrasonic treatment. Real phthalocyanine yields in absence of ultrasonic treatment were always lower (1.5–2 times).

2.3. *Product purification and identification*

Formed phthalocyanines were purified by washing with hot ethanol in Soxhlet equipment and dried in air. The products were characterized by metal content by means

Table 1. Yields of metal phthalocyaninates, obtained from pyrophoric nickel and Rieke nickel and copper. Yields were calculated on phthalonitrile basis.

Temperature (°C)	Solvent	PcNi* yield starting from pyrophoric nickel, with/without CH_3ONa	PcNi yield* starting from Rieke nickel, with/without CH_3ONa	PcCu yield starting from Rieke copper, with/without CH_3ONa
50	Methanol	50/15	45/20	52/11
	Ethanol	25/19	31/17	28/13
	1-Propanol	32/11	26/16	20/5
	1-Butanol	35/11	27/14	38/7
35	Methanol	27/13	18/2	25/7
	Ethanol	25/11	11/8	15/8
	1-Propanol	20/5	14/10	9/2
	1-Butanol	22/9	16/7	23/11
25	Methanol	41/11	39/15	32/9
	Ethanol	31/18	25/4	36/12
	1-Propanol	25/17		
	i-Propanol	10/traces		
	1-Butanol	40/25		
	i-Butanol	13/traces		
	t-Butanol	Traces/0		
	1-Pentanol	15/traces		
	1-Hexanol	Traces/0		
	THF	23/traces		
20	Methanol		17/4	21/7
	Ethanol		11/7	9/2
	1-Propanol		4/2	>5/traces
	1-Butanol		6/6	>5/traces
10	Methanol	14/5	16/traces	13/traces
	Ethanol	25/10	22/8	15/traces
	1-Butanol	23/12	15/traces	6/traces
0	Methanol	7/traces	11/traces	>7/traces
	Ethanol	25/traces	15/traces	11/traces
	1-Propanol	11/traces	8/traces	>4/traces

*Traces of products were observed in other solvents used (ethyleneglycol, DMEA, and ethoxyethanol).

of atomic absorption spectroscopy and elemental determination (C, N, H). The elemental analysis data for the samples show the best correspondence of calculated/found data; composition of the products obtained correspond to typical metal phthalocyaninates PcM and the data for the found/calculated ratio was, in wt.%, as follows: nickel phthalocyaninate Ni (10.12/10.29), C (67.34/67.28), N (18.93/19.63), and H (2.88/2.80); copper phthalocyaninate: Found/Calcd wt.%: Cu (10.21/11.04), C (65.09/66.72), N (18.40/19.46), H (2.03/2.78). Some variations of composition (0.05–0.30%) were observed in different parallel experiments. Not all samples of metal phthalocyaninates formed showed such coincidence of calculated and experimental data; however, analyzing a wide number of publications on phthalocyanine chemistry and our own work, to obtain products with a 85–95% purity is absolutely normal for these compounds. Using various forms of activated nickel (commercial pyrophoric and obtained Rieke forms), results in a better grade of MPc purity in comparison with similar experiments using magnesium and zinc, in activated forms (these results, where the purity of final products is about 90–95%, will be reported soon).

The IR spectra (KBr pellet) of both nickel and copper phthalocyaninates contain the following strong and medium bands (cm^{-1}), among other weaker bands: 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) {$\nu(N_{pyrr}–C\alpha)$}; 1320(m), 1150(s) {γ(C–H)}. 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, 1010, 1309 and 1500 cm^{-1}. IR spectra of the same PcM, obtained in different solvents, are almost identical (the difference is in the peak intensity) and correspond to those reported earlier [38].

3. Results and discussion

According to the chemical analysis of the products, metal phthalocyaninates of 96–98% purity are formed in both cases (from commercial pyrophoric and Rieke metals). This is in agreement with the classic investigations carried out by Linstead and others [39–44] showing that nickel and copper, as well as iron, form strong bonds with phthalocyanine macrocycle N-atoms, starting from metal salts or elemental metals, and they cannot be "extracted" from the macrocycle without total decomposition. In our previous short report [30], it was elucidated that, despite the presence of a small amount of water (which affects phthalocyanine preparation, as do other polar solvents with a high donor number), formation of nickel phthalocyaninate takes place relatively rapidly in various non-aqueous solvents at room temperature and very fast under conditions of ultrasonic treatment. In control experiments without activated metallic nickel, in particular with nearly the same amount of water, or in a water-free system, no phthalocyanine formation was observed. The observed metal phthalocyaninate yields were distinct in various solvents used (methanol, ethanol, propanol, *i*-propanol, *n*-butanol, *i*-butanol, *t*-butanol, 1-pentanol, 1-hexanol, THF) and almost always higher yields were obtained in the presence of CH_3ONa used to start the reaction (table 1). Traces of products were observed when other solvents were used (ethyleneglycol, DMEA, and ethoxyethanol). Low-weight alcohols contribute to macrocycle formation; in using pyrophoric nickel, the presence of an activator (CH_3ONa) is preferable, although not compulsory, for carrying out the reaction in some solvents.

When using activated Rieke metals, prepared from anhydrous salts and metallic potassium, the yields (table 1) in various solvents are similar and, again, always higher in methanol and ethanol, as for commercial pyrophoric nickel. It is worth noting that a decrease of the molar ratio metal : phthalonitrile from the stoichiometric 1 : 4 [30] to 1 : 8, leads to a considerable decrease in the yields of nickel phthalocyaninate from almost quantitative [30] to 45% and lower. On the contrary, the use of excess activated metal leads to higher yields due to a considerable increase of a number of reaction matrices (defects in the metal surface). It is also noted that in some cases not all the activated metal takes part in reactions even after 72 h of ultrasonic treatment. As shown in table 1, the presence of activated metal eliminates the need of an activator (CH_3ONa), although in this case yields are lower.

As mentioned before [30], commercial "dry" Raney nickel from Aldrich did not have high activity in comparison to the phthalonitrile cyclization using pyrophoric "aqueous" nickel ("underwater") and Rieke nickel (having specific surface area of 32.7 $m^2 g^{-1}$ [12, 18]), as used in the present work. This can be explained as due to surface oxidation processes (in the case of "dry" metal) which are absent in the case of the last two forms of nickel. Additionally, particle sizes of activated nickel (particles of powder ~100 nm in diameter may agglomerate to ~1–2 micron) are much smaller in comparison to the particles of "dry" Raney nickel (20–40 micron), so a higher number of defects of the first two forms contributes to easier cyclization of phthalonitrile and, as a consequence, a lower initial temperature for this process. Evidently, the higher number of defects and imperfections in the activated metal (Cu, Ni, Mg, Zn, etc.) surface, and the smaller size of the metal aggregates increases activity not only in the phthalonitrile cyclization, but also in other organic reactions reported [12–23]. The proposed mechanism for activated Ni, which involves the participation of small metal aggregates Ni_n (precursors of metal ions) in the presence of CH_3ONa, is presented in figure 2 (we suppose that the mechanism with activated copper is similar). Different to the classical mechanism with participation of metal ions in the phthalonitrile cyclization (studied before using metal salts), this mechanism uses the participation of small aggregates of metallic nickel or copper existing on the Rieke metal surface. Since M_n is an aggregate existing on the main metal surface, or even independently, it possess a higher number of defects, which, under ultrasonic treatment form preferential sites for reaction and further allows the elimination of metal atoms reacting with an organic substrate. When ultrasonic treatment is applied, these aggregates can be eliminated completely from the main metal surface and serve as a center for phthalonitrile cyclization. On the basis of the experimental data (table 1), cyclization on the metal surface also occurs if CH_3ONa is absent, with neutral alcohols attacking the phthalonitrile, less actively than to sodium methoxide.

Review of the available literature shows the mechanism of phthalocyanine formation by using nickel salts was reported only in the case of urea and phthalic anhydride as precursors 30 years ago [45]. For copper phthalocyanine formation from non-activated copper, CuCl and $CuCl_2$, there is more information, in particular a recent report [46]. The reported mechanism involves participation of a metal surface and an organic substrate under an ultrasonic field [12, p. 138], includes the creation of defects and of preferential sites of reaction on the metal surface, and the effect of further "extraction" of a metal atom "associated" to an organic partner. The first main step of the process is similar to that described [12], resulting in formation of free metal atoms, then the reaction takes place similarly to well-known phthalonitrile cyclization on a metal matrix [46].

Comparing various routes for decreasing the temperature to produce phthalocyanine developed in our laboratory, it is clear that the use of activated metals is much more effective than ultraviolet treatment [29], zeolites [31], and direct electrochemical synthesis starting from sacrificial metal anodes [34, 35]. Activity of metal particles clearly depends on the temperature which, theoretically, may be decreased down to 0°C. Also, a non-aqueous solvent has the primordial role to carry out such an interaction at low temperatures. The best solvents found were methanol and ethanol, although other alcohols also function for this type of low-temperature reactions.

4. Conclusions

Non-substituted nickel and copper phthalocyaninates were obtained from phthalonitrile and metals in different forms: pyrophoric nickel and Rieke copper and nickel

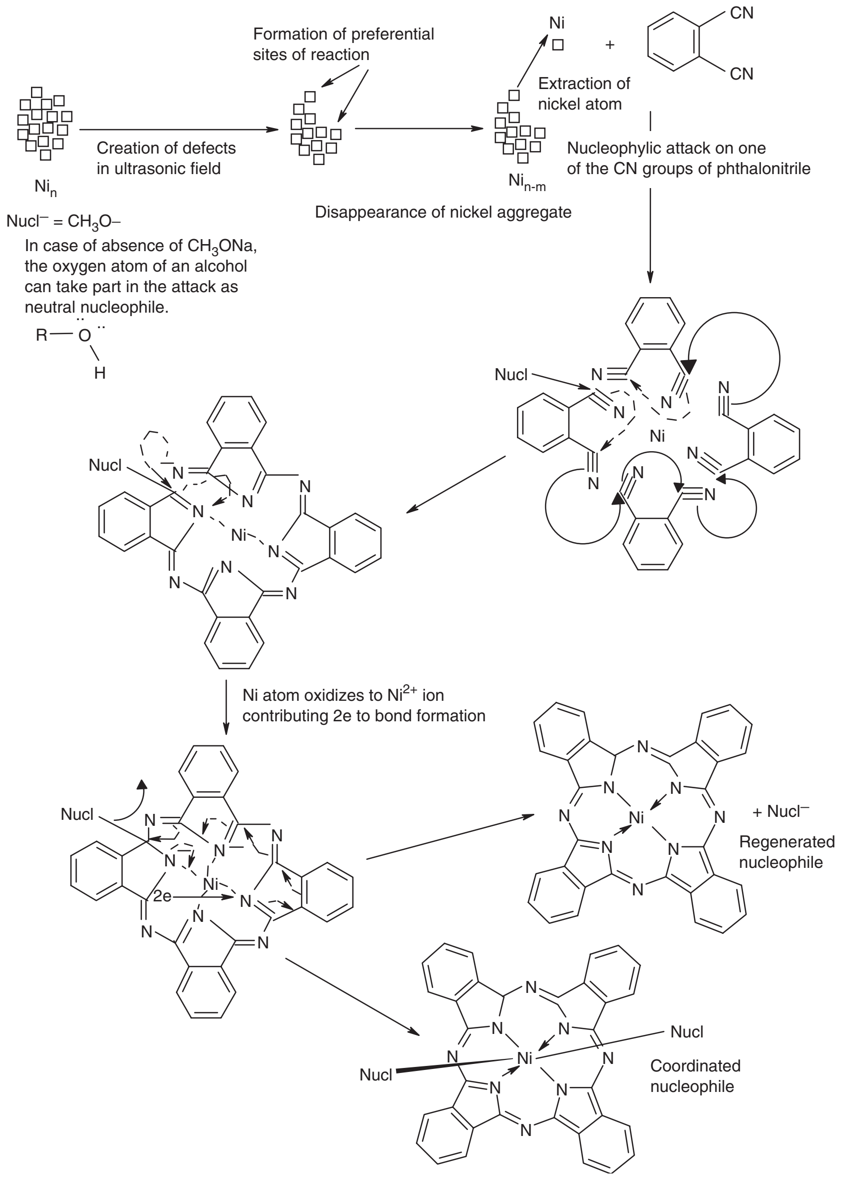

Figure 2. Proposed mechanism of phthalonitrile cyclization on the activated nickel surface.

at temperatures of 0–50°C. Both forms of nickel perform in a very promising way for the cyclization of phthalonitrile in a series of non-aqueous solvents. The reaction mechanism includes small metal aggregates on the surface of the activated metal. It is suggested that more defects and imperfections on the surface of the activated forms of both metals contributes to cyclization of phthalonitrile at low temperature.

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