Use of zeolites for phthalocyanine synthesis at low temperature

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Non-substituted phthalocyanines have been synthesised starting from phthalonitrile in various non-aqueous solvents in the presence of two different zeolites of the clinoptilolite type is studied. The zeolites are shown to be effective matrices for phthalonitrile cyclisation at relatively low temperatures (0–40°C).

Keywords: phthalocyanine, zeolites, synthesis at low temperature

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Various routes can yield classic metal-free phthalocyanine (PcH_2) or metal phthalocyaninates (PcM) at low temperature (0–40°C) from phthalonitrile as a precursor. For example, use of elemental metals in different grade of activation,[1,2] direct electrochemical procedure with use of sacrificial metal anodes or metal salts,[3,4] use of solid strong bases,[5] and by UV-irradiation of the reaction system.[6] A recent article[2] should be especially emphasised, in which softest conditions for Pc obtaining were offered using a series of primary alcohols and elemental metals at room temperature.

At low temperatures, an additional "impulse" is needed for the cyclisation process; thus the surface energy of a strong base (solid CH_3ONa)[5] or extra energy of defects in the surface of elemental metals[2] could serve as such an impulse to reach the energetic barrier. So, any source of additional energy could be useful for successful synthesis at low temperatures. In this respect, cavities of zeolites and other microporous materials could serve as a source of such extra energy. Recently, some reviews on the synthesis, characterisation, and applications of free phthalocyanines and their metal complexes in cavities of inorganic host materials (clays, zeolites, aluminumphosphates, and mesoporous molecular sieves)[7-9] and reports of experimental results[10-17] have been published.

Use of ultrasonic treatment to increase of the rates of solid-state reactions in the synthesis of copper phthalocyanine by the reaction of phthalonitrile with CuCl was reported.[18] We supposed that use of a heterogeneous reaction system, containing phthalocyanine precursors (in particular, phthalonitrile), in appropriate conditions should optimise the cyclisation process.

Following the considerations above to optimise the low-temperature preparation of phthalocyanines, five routes are being developed in our laboratory: (1) UV-irradiation of the reaction system (without metals); (2) use of elemental metals in the form of finely divided metal powders and *Rieke* metals[19] as "matrices" for phthalonitrile cyclisation and Pc core formation; (3) use of zeolites and other microporous materials, (4) direct electrochemical synthesis using sacrificial anodes and even cathodes, and (5) use of so-called "supported metals".[19] We now present the experimental results corresponding to the third technique.

The zeolite, used in this work (clinoptilolite) is a common zeolite occurring in arid soils. It is a member of the tectosilicate family. The silica in this compound is fully-polymerised forming structures with large cavities filled with water and cations. The general formula for natural zeolite is $(Li, Na, K)_a(Mg, Ca, Sr, Ba)_d[Al_{a+2d}Si_{n-(a+2d)}O_{2n}]\cdot mH_2O$.[20] The unit cell is monoclinic and characterised on the basis of 72 O atoms ($n = 36$) and $m = 24$ water molecules, with Na^+, K^+, Ca^{2+} and Mg^{2+} as the most common charge-balancing cations. The dimensions of the open channel in clinoptilolite are 0.89×0.35 nm^2 for the 10-member ring and 0.44×0.030 nm^2 for the 8-member ring, large enough for a small exchangeable cations but small for organic head groups.

According to,[21] the XRD powder pattern of clinoptilolite has the following refined composition: $|Na_{1.84}K_{1.76}Mg_{0.2}Ca_{1.24}(H_2O)_{21.36}|[Si_{29.84}Al_{6.16}O_{72}]$; space group: C12/m1; with cell parameters: $a = 17.662$Å, $b = 17.911$Å, $c = 7.407$Å, $\alpha = 90°$, $\beta = 116.40°$, $\gamma = 90°$. Clinoptilolite zeolite has been used as surface of reaction in different processes. The sorption kinetics of hexadecyltrimethylammonium on natural clinoptilolite showed that it is limited by the external cation-exchange sites.[22] The sorption of non-polar aromatic contaminants on modified clinoptilolite has been reported.[23]

The cation-exchange properties of clinoptilolite are well-known. The cation-exchange equilibrium on the natural clinoptilolite for pairs of anions Na^+–Cs^+, Na^+–NH_4^+, and NH_4^+–Cs^+ was examined[24] and a thermodynamic model was proposed for the description of cation-exchange equilibrium on clinoptilolite.[25] The adsorption characteristics of high-exchange clinoptilolites were studied, proving the separation of CH_4/N_2 and other gas mixtures.[26] The Y-type zeolites have been also used for phthalocyanine preparation: and *in situ* synthesis of transition-metal (Ni, Co, Fe, Mn, Ru and Os) phthalocyanines entrapped within the zeolite cavities was described.[27] The formed zeolite-included phthalocyanines were found to be active for low-temperature oxidation of carbon monoxide and reduction of nitric oxide.

Experimental

Phthalonitrile, 30% solution of CH_3ONa in CH_3OH, and standard PcH_2 (*Aldrich*) were used as supplied. Solvents (methanol, ethanol, benzene, 1-propanol, 1-pentanol, 2-butanol, THF, ethoxyethanol, and dimethylethanolamine, (all from Aldrich and Fisher) were distilled by standard methods before use. An organic microanalyser (Perkin-Elmer) was used for C, H and N microanalysis. IR and UV/visible spectra (in pyridine) were recorded on Perkin-Elmer and Lamboda 12 instruments, respectively. Selective ultrasonic treatment of reaction systems was carried out in low-power ultrasonic cleaners of different capacity (3 and 11 l).

Characterisation of the zeolites: Two samples of natural national zeolites were obtained from Nutek, S.A. de C.V., (part of the IDISA group). Samples were identified by colour (green and blue). The crystal phases of both samples were characterised by X-ray diffraction using a Siemens D-5000 instrument, with Cu–K_α radiation at a scan rate of 0.05° 2θ/min and 40 kV/30 mA. Elemental analysis was carried out using Flame Atomic Adsorption Spectrometry. The surface areas of the powders were measured using a Quantrom, 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 granite zeolite (blue) used as surface reaction in the phthalocyanine synthesis. A Carls Zeiss DSM950 model was used, at 30 kV/50 mA and 9-mm working distance.

Use of zeolites in synthetic procedures. Zeolite powder (1.00 g) was added to a non-aqueous solvent (10 ml), containing phthalonitrile (1.00 g) and 5 drops of 30% solution of CH_3ONa in methanol. The flask was put into an ultrasonic cleaner and maintained under treatment a $T = 0$–40°C for 24–72 h. Some experiments were carried out without ultrasonic treatment. Then the formed blue product was separated from zeolite using difference in densities by shaking and decanting with the solvent 2–4 times.

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Purification and identification of the products: The phthalocyanine formed was purified by washing with hot ethanol in Soxhlet equipment and dried in air. According to elemental analysis data, compositions of the obtained products correspond to phthalocyanine (PcH_2). Some variations of composition (0.05–0.30%) were observed in different experiments, which is absolutely normal for phthalocyanine chemistry. The products were also analysed for presence of metal ions that could appear from the zeolites; which demonstrated that external metal ions are practically absent in PcH_2 (0–0.3%). The IR spectra (KBr pellet) of the phthalocyanine contain the following main bands (cm^{-1}), among others: 3500–3380(v.s.,w), 2815m, 2504m {ν(C-H)}; 2300–2280(s), 1730(v.s.), 1607(s), 1524(m) {ν(C–C) of benzene rings}; 1448(m) {ν(C–C) of pyrrol rings}; 1385(v.s.), 1365(s) (pyrrol nuclei-*meso*atoms of N); 1320(m), 1309 (m), 1150(s) {γ(C–H)}, 720, 690, 675 and 622. UV/vis. data (nm) of PcH_2 are the following: 692–693, 659–660 (*Q*-band), 640, 602-604. These spectra are similar to those of the standard PcH_2 (Aldrich).

Results and discussion

The XRD patterns of both zeolites are shown in Fig. 1. The clinoptilolite phase was identified as main phase for both samples. Crystalline phases of quartz (SiO_2) and calcite ($CaCO_3$) were also found in the green zeolite. In Table 1 the raw material analysis on the dry base is shown. The CaO percentage in the green form is higher than in the blue; this supports the XRD results. The BET analysis results are presented in Table 2. The green zeolite presents a higher surface area than blue, however, its activity is lower in the studied surface reactions due, in our opinion, to the presence of $CaCO_3$, which is "inert" in relation to the phthalonitrile cyclisation.

In Fig. 2 scanning electron photomicrographs of the blue zeolite are presented. In micrograph A) a classic crystalline morphology of clinoptilolite is observed; crystals appear from a cavity and the organic material covers part of some crystals. The detail of organic material deposited on a crystal is shown in micrograph B), here the organic single particle size estimated from the SEM image is about 500 nm.

Among all solvents used, methanol, ethanol, THF, and benzene are shown to be the most effective for phthalocyanine formation at low temperature (0–40°C) (Table 3). The formation of the product takes place slowly for 12–72 h; the reaction is more rapid using additional ultrasonic treatment: in case of its application, the reaction is completed 2–3 times more rapidly. The green zeolite yields are at least two fold smaller in the same conditions. Other solvents used (ethoxyethanol and dimethylethanolamine) do not show considerable yields of PcH_2: only traces were observed. In control experiments in absence of zeolites, only traces of products are formed over 5–7 days in the mentioned solvents in the same conditions.

Comparing the obtained data with our previous results with use of elemental metals in different grade of activation,[1] it becomes clear that use of Raney nickel or more active pyrophoric nickel is more effective for phthalonitrile cyclisation and the yields are considerably higher. However, the zeolites also have a certain activity in these conditions and are undoubtedly useful at low temperature for phthalonitrile cyclisation forming a metal-free product.

Conclusions

The clinoptilolite-type zeolites are shown to be effective matrices in the synthesis of metal-free phthalocyanine starting from phthalonitrile at relatively low temperatures (0–40°C).

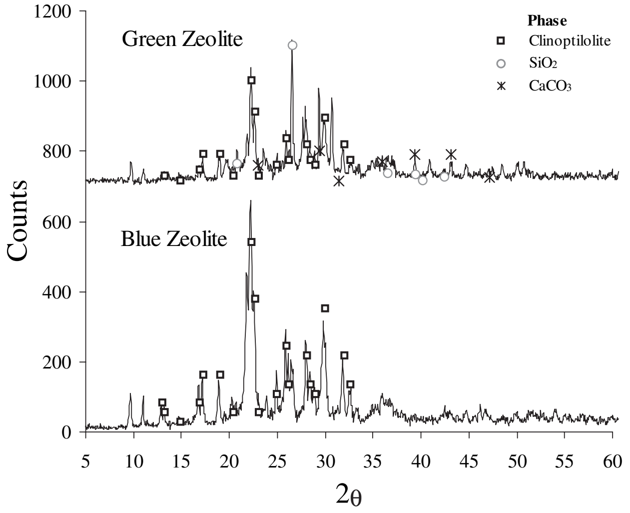


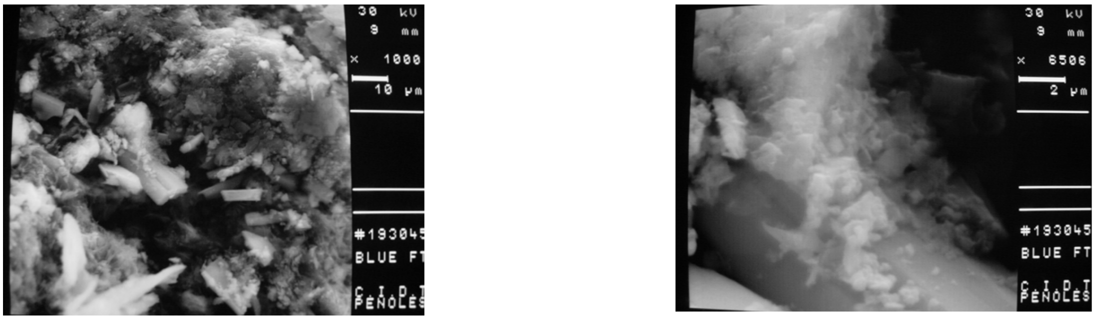
Fig. 1 X-Ray patterns of the zeolites.

Table 1 Composition of natural zeolites

Material	Green zeolite	Blue zeolite
SiO_2	76.20	85.68
Al_2O_3	8.39	8.15
Na_2O	0.33	1.95
CaO	6.94	1.00
K_2O	2.25	1.31
MgO	0.10	0.02
Fe_2O_3	1.75	0.30
MnO_2	0.10	0.02
TiO_2	0.56	0.57
P_2O_5	<0.05	<0.05

Table 2 BET Specific area measurements

Zeolite	BET area m^2/g
Green	38.4
Blue	29.6



(A)

(B)

Fig. 2 SEM photomicrographs of blue zeolite covered for the phthalocyanine product. Classical crystalline of clinoptilolite morphology is showing in (A) and the organic product particles are presented deposited on a crystalline shape of clinoptilolite in (B).

Table 3 PcH_2 yields in different conditions

Zeolite	Temperature[a]/°C	Phthalocyanine yield (wt.%) in the solvents[b]						
		Benzene	Methanol	Ethanol	1-Propanol	1-Pentanol	2-Butanol	THF
Blue	0	10–15	12–17	10–12	5–8	5–10	7–11	11–15
	5	20–24	17–22	16–20	13–17	10–15	11–17	18–24
	10	23–26	25–30	23–30	18–20	16–20	15–20	21–25
	15	20–27	32–35	30–36	25–30	20–25	20–27	22–28
	20	35–42	40–45	37–40	32–35	25–32	32–35	33–43
	25	55–60	60–68	60–65	50–54	48–55	45–55	52–60
	30	54–65	65–73	66–70	50–57	55–59	52–55	55–65
	35	60–64	65–72	60–72	52–59	55–60	50–58	57–63
	40	65–70	70–76	65–75	55–60	57–65	58–65	60–64
Green	0, 5, 10, 15	Traces						
	20	7–11	10–17	11–16	5–12	7–10	8–12	5–11
	25	20–26	25–28	23–26	15–20	10–18	14–18	20–25
	30	20–25	25–30	25–30	20–28	18–27	20–25	18–26
	35	20–27	25–29	23–28	20–25	20–25	20–27	20–24
	40	22–28	26–32	26–30	22–26	21–25	20–25	22–25

[a] All reaction systems were kept at the given temperature for 72 hr.

[b] CH_3ONa as an activator was added. The data of five independent experiments were used for calculation of yield. The yield was calculated on the phthalonitrile basis. No ultrasonic treatment was applied.

The reactions, carried out in different non-aqueous solvents, show different yields of the final product depending on temperature and solvent nature. Methanol, ethanol, benzene, and THF show the best yields of the metal-free phthalocyanine.

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