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Reactions of Ferrocene with Phthalonitrile on the Surface of Oxide Powders

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Abstract—The reaction of ferrocene with phthalonitrile at 200°C in a vacuum in the absence of solvents forms crystals of the monoclinic phthalocyanine β phase and ferrocene polymerization products. The use of oxide powders (SiO_2, V_2O_5) as a surface for the reaction of ferrocene with phthalonitrile makes it possible to obtain iron phthalocyanines. The samples of pure compounds and deposited phthalocyanine complexes were analyzed by electronic absorption and IR spectroscopy, and X-ray diffraction.

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Catalysts based on phthalocyanine metal complexes (PcM) fixed on oxide supports are presently widely used in as catalysts in chemical and petrochemical processes [1, 2]. Phthalocyanine coatings on the surface of oxide powders can be obtained by various procedures, both using ready phthalocyanines and by directly synthesizing phthalocyanine complexes from aromatic nitriles and inorganic and organic metal compounds [3].

To obtain phthalocyanine systems immediately on the surface of inorganic oxide supports, we used reactions of organometallic compounds with aromatic nitriles. Previously we obtained low-molecular and polymeric metal phthalocyanines from metal carbonyls and aromatic nitriles by reactions on the surface of SiO_2 and TiO_2 powders and studied the catalytic and photocatalytic activity of these systems in sulfide oxidation reactions [4].

The interest in reactions of organometallic compounds occurring either in the solid phase or on the surface of solid supports is defined by the unique properties of these systems, which allows their use both for preparative synthesis of new organic metal complexes and for preparing organometallic compound–inorganic support composite materials [5].

The mobility of the (C_nH_n) rings in solid $(C_nH_n)_x \cdot ML_y$ π complexes is known to be almost the same as their mobility in solutions [5, 6], and the high adsorption capacity of these compounds on the surface of oxide supports should result in certain activation of metal–ligand bonds. However, there have been scarce data on the use of solid-phase reactions of metallocenes for synthesizing phthalocyanine metal complexes. Zakharov et al. [7] have studied the reaction of ferrocene adsorbed in the cavities of Y zeolite with phthalonitrile vapors in a vacuum at 100–150°C, yielding iron(II) phthalocyanine.

Ferrocene derivatives can be used as orientants in the processes of directed heterogeneous growth of PcM films [8]. We showed previously [9] that reactions of oxidized forms of ferrocene and its derivatives with aromatic nitriles, carried out in solutions, provide $[(\eta^5\text{-CpFe-}\eta^1\text{-Cp})(PN)_2]^+An^-$ molecular complexes. Phthalonitrile (PN) and tetracyanobenzene readily form polyindoline systems under the action of ferrocenyllithium in tetrahydrofuran at room temperature [9].

In this work we present the results of studying reactions of ferrocene with phthalonitrile without supports and in the adsorption layers on the surface of SiO_2 powders of various dispersity and on V_2O_5 microcrystals.

The reaction between solid ferrocene and phthalonitrile, mixed in a 1:4 ratio, occurs in evacuated ampules at 210°C in the melt of the components. The main reaction product formed quantitatively is phthalocyanine (PcH_2). According to the X-ray phase analysis, it was a pure monoclinic β phase. The electronic absorption spectrum of the resulting macrocycle (Fig. 1) corresponds to published data [8]. Therefore, in this

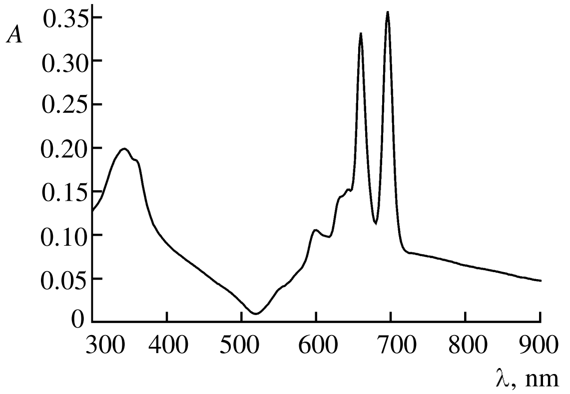

Fig. 1. Electronic absorption spectrum of PcH_2 in *o*-dichlorobenzene.

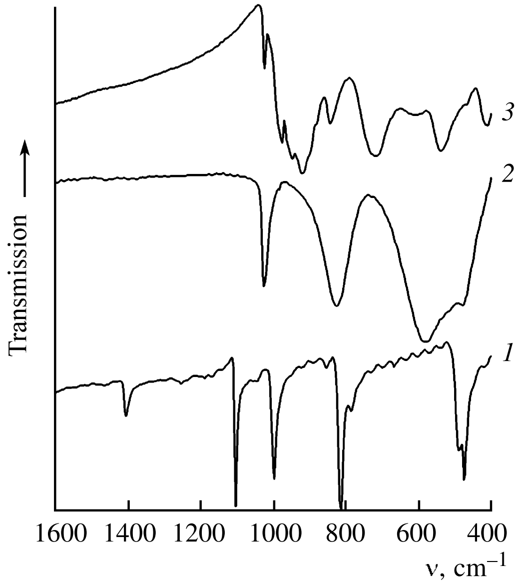

Fig. 2. IR spectra of (*1*) ferrocene, (*2*) vanadium(V) oxide, and (*3*) $V_2O_5(FcH)_{0.15}$ intercalation complex.

reaction, ferrocene plays the role of both a template agent and a hydrogen donor, forming a polyferrocenylene film on the walls of the reactor, and needle-shape crystals of phthalocyanine grow on this very film.

By studying the reaction of ferrocene with phthalonitrile, adsorbed on the surface of silicon oxide of various dispersity (380 and 160 m^2 g^{-1}), we found that the degree of support dispersity, reaction temperature, and the way the reagents have been deposited on the surface of silicon oxide do not essentially affect the direction of the reaction resulting in formation of iron phthalocyanine and free phthalocyanine. The ratio of the reaction products is mostly affected by the ratio of the concentrations of the starting reagents to the surface area of the support.

Adsorption of ferrocene on SiO_2 is known to give the cationic forms Fe$^+$ and (FeH)$^+$ [10]. The cationic forms of ferrocene do not tend to form stable complexes with electron-donor ligands of any kind. Reactions with such ligands result in destruction of ferrocene and cleavage of Cp ligands. Coordination of nitrile molecules on metal yields an iron-containing phthalocyanine ring. If the concentrations of the reagents are low (estimated so that to cover the oxide surface with a monomolecular layer of phthalocyanine), iron phthalocyanine is mainly formed. At increased reagent concentrations on the surface of SiO_2 of the same dispersity, a mixture of iron phthalocyanine and metal-free phthalocyanine.

Of special interest for obtaining catalytic systems is V_2O_5, which is due to its intrinsically high catalytic activity in oxidation organic compounds, high redox potential, and high electronic and ionic conductivities. In our work we used microcrystalline vanadium(V) oxide of orthorhombic modification with the lattice parameters *a* 11.50(2), *b* 3.56(3), and *c* 4.36(8) Å, particle size 200–700 nm, and specific surface area 3.7 m^2 g^{-1}.

The layered structure of V_2O_5 favors its facile intercalation with organic molecules, thus determining high reactivity of vanadium oxide in the reactions with organic complex-forming compounds [11]. The reaction of vanadium(V)oxide with phthalonitrile at 300°C gives vanadyl phthalocyanine (PcVO) in high yield.

By DTA we determined the temperature ranges for the reactions of ferrocene with V_2O_5, of phthalonitrile with V_2O_5, and of ferrocene with phthalonitrile deposited on vanadium(V) oxide. In the FcH/V_2O_5 system at 240°C, ferrocene is intercalated into the layered structure of vanadium(V) oxide to give a $V_2O_5(FcH)_{0.15}$ complex. The IR spectra of the starting compounds and resulting intercalation complex are given in Fig. 2. The Mössbauer spectrum of $V_2O_5 \cdot (FcH)_{0.15}$ (Fig. 3) shows that ferrocene is oxidized upon intercalation to give the ferricenium ion. This is evidenced by a substantial decrease of the quadrupole splitting (from 2.35 to 0.66 mm s^{-1}); therewith, the isotope shift changes only slightly, which results from charge transfer from ferrocene to vanadium oxide lattice and formation of the ferricenium cation. Along with this, the spectral data also point to appearance of a noticeable amount of bivalent iron. It seems to be iron oxide FeO resulting from ferrocene oxidation.

In the Debye powder pattern of the intercalation complex lattice, additional bands appear, and a slight change in interplanar spacings is observed, which suggests that the symmetry of V_2O_5 crystals is lowered to the monoclinic syngony. Furthermore, bands of FeO were identified. The ferricenium cation and iron oxide impart magnetic properties to the resulting material. Recently Okino and Matsubayashi [12] reported the preparation of intercalation complexes of metallocenes in the lattice of hydrated vanadium(V) oxide.

According to DTA, the reaction of phthalonitrile with vanadium(V) oxide occurs in the range 270–300°C to give vanadyl phthalocyanine. The reaction of ferrocene with phthalonitrile deposited on vanadium(V) oxide at a temperature lower than the ferrocene intercalation temperature (210°C) yields iron phthalocyanine (PcFe) and PcVO. We could perform qualitative analysis of the mixture of phthalocyanines by means of electronic spectroscopy, using different solvents and relying on their different dissolving ability toward the two phthalocyanines (Fig. 4). Tetrahydrofuran dissolves PcVO but does not dissolve iron phthalocyanine. When PcVO is removed from the surface of vanadium(V) oxide with THF, the electronic spectrum of the treated sample, recorded in DMF, contains a single PcFe band. The reaction at 270°C results in exclusive formation of PcVO, i.e. intercalated ferrocene does not react with phthalonitrile. In this case, we have a composite material containing the ferricenium cation and vanadyl phthalocyanine in the oxide matrix.

EXPERIMENTAL

The electronic absorption spectra in DMF, THF, and *o*-dichlorobenzene were measured on a Perkin–Elmer Lambda-2 spectrometer. The IR spectra in KBr were recorded on a Perkin–Elmer SP-1000 instrument.

The Mössbauer spectra were measured on an MS-22-01 spectrometer in the constant accelerations mode with a ^{57}Co source in a Cr matrix. The calibration was carried out against sodium nitroprusside (quadrupole splitting 1.7034 mm s^{-1}). The X-ray phase analysis was carried out on a DRON-3M diffractometer (CuK_α radiation, graphite monochromator).

The specific surface areas of oxides were measured on a Beta Scasaam-4200 (29.9% N_2) instrument. Ferrocene, phthalonitrile (Fluka) and V_2O_5 (orthorhombic, specific surface area 3.7 $m^2 g^{-1}$) (Riendel-de-Haen) were used as received. Silicon dioxide (quartz, specific surface area 160 and 380 $m^2 g^{-1}$), purchased from Aldrich, was first heated for 4 h under vacuum at 350°C.

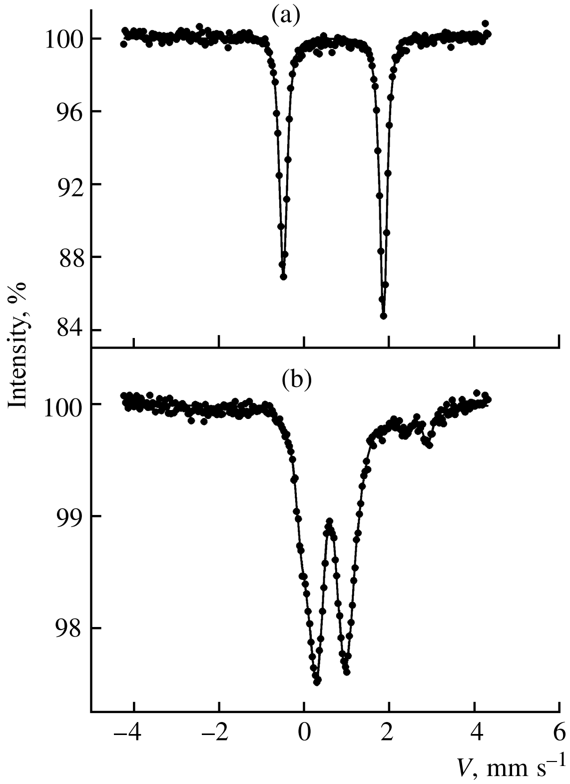

Fig. 3. Mössbauer spectrum of (a) ferrocene and (b) $V_2O_5(FcH)_{0.15}$ intercalation complex.

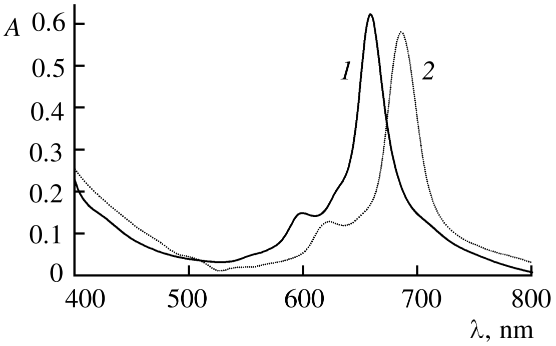

Fig. 4. Electronic absorption spectra of (*1*) PcFe and (*2*) PcVO in DMF.

The reactions were performed in evacuated ampules at the FcH-to-PN ratio of 1 : 4. Reagents were deposited on powders successively from the vapor phase and by simply mixing the ingredients. The ampules were heated for 35 h. The initial reaction temperature was determined by DTA. The reagent ratios required for obtaining a monomolecular phthalocyanine layer on the oxide surface were estimated from the specific surface area of the oxide. Taking into account that the effective surface area of a phthalocyanine molecule is 1.7 nm^2, we found that to form a monomolecular phthalocyanine layer on the surface of the support requires 0.1 mol of phthalocyanine per 100 m^2 of the surface. Provided the yield is quantitative, this corresponds to 0.1 mmol of iron in ferrocene and 0.4 mmol of phthalonitrile.

Reaction of ferrocene with phthalonitrile. *a. Without support.* Solid ferrocene, 0.56 g, and 1.54 g of phthalonitrile were thoroughly mixed, and the mixture was placed into an ampule. The ampule was evacuated (10^{-2} mm Hg), sealed, and heated for 35 h at 210°C. The resulting material was washed in a Soxhlet apparatus first with acetone and then with THF. A violet substance, 1.53 g (90%), was obtained. Electronic absorption spectrum (*o*-chlorobenzene), λ_{max}, nm: 330, 660, 688. IR spectrum, ν, cm^{-1}: 717, 730, 751 (CH); 1006 (NH); 1306, 1318, 1338, 1386 (C=C); 3290 (NH).

b. On SiO_2 (160 $m^2 g^{-1}$). Ferrocene, 0.14 g, phthalonitrile, 0.41 g, and 5 g of SiO_2 were mixed. Two sample preparation procedures were used. The first involved mechanical mixing of the starting materials under argon. The second involved deposition of ferrocene and phthalonitrile on the support from the vapor phase. The samples were loaded into ampules, and the ampules were evacuated, sealed, and heated for 35 h at 210°C. The resulting material was washed in a Soxhlet apparatus first with acetone and then with THF. Electronic absorption spectrum of the extracted compound (DMF): λ_{max} 660 nm. When the concentrations of ferrocene and phthalonitrile were increased by a factor of 10, the electronic absorption spectrum in *o*-chlorobenzene showed the following bands, λ_{max}, nm: 330, 660, 688.

c. On SiO_2 (380 $m^2 g^{-1}$). Ferrocene, 0.037 g, phthalonitrile, 0.102 g, and 0.5 g of SiO_2 were mixed. Two sample preparation procedures were used (see procedure *b*). Electronic spectrum of the extracted compound (DMF): λ_{max} 660 nm. When the concentrations of ferrocene and phthalonitrile were increased by a factor of 10, the electronic absorption spectrum in *o*-chlorobenzene showed the following bands, λ_{max}, nm: 330, 660, 688.

d. On V_2O_5. Ferrocene, 0.333 g, phthalonitrile, 0.917 g, and 5 g of V_2O_5 were thoroughly mixed. The mixture was placed into an ampule. The ampule was evacuated, sealed, and heated for 35 h at 210°C. The reaction product was washed in a Soxhlet apparatus with acetone. Electronic spectrum of the extracted compound, λ_{max}, nm: 660, 686 (DMF); 345, 685 (THF). The product was then washed with THF in a Soxhlet apparatus. Electronic spectrum of the extracted compound (DMF): λ_{max} 660 nm.

In another experiment, the same mixture was heated at 270°C. The reaction product was washed in a Soxhlet apparatus with acetone. Electronic spectrum of the extracted compound, λ_{max}, nm: 346, 686 (DMF); 343, 685 (THF).

Reaction of phthalonitrile with V_2O_5. Phthalonitrile, 0.917 g, and 5 g of V_2O_5 were thoroughly mixed. The mixture was placed into an ampule. The ampule was evacuated, sealed, and heated for 35 h at 300°C. The reaction product was washed in a Soxhlet apparatus first with acetone and then with THF. Electronic spectrum of the extracted compound, λ_{max}, nm: 346, 686 (DMF); 343, 685 (THF).

Reaction of ferrocene with V_2O_5. Ferrocene, 0.333 g, and 5 g of V_2O_5 were thoroughly mixed. The mixture was placed into an ampule. The ampule was evacuated, sealed, and heated for 35 h at 240°C. The reaction product was washed with hexane. IR spectrum, ν, cm^{-1}: 1026 (VO); 1001 (CH; 978, 844, 719 (VO); 540, 412 (FeCp). Found, %: C 8.50; H 0.67. $V_2O_5(FcH)_{0.15}$. Calculated, %: C 8.57; H 0.71.

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