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Catalytic properties of metal-phthalocyanines in reactions involving hydrogen

E M Sul'man, B V Romanovskii

Contents

I. Introduction	609
II. The structure of phthalocyanines	609
III. The catalytic activity of phthalocyanines and the mechanism of their activation	610
IV. Reactions with participation of hydrogen	610
V. Phthalocyanines on carriers	611

Abstract. The catalytic properties and the mechanism of activation of phthalocyanines in reactions with participation of hydrogen are examined. The mechanism of the catalytic action of phthalocyanines is discussed. Two types of active centres ('metallic' and 'organic') are distinguished in the phthalocyanine molecule. Problems associated with the fixation of phthalocyanine catalysts on carriers are considered. The bibliography includes 120 references.

I. Introduction

Phthalocyanines (Pc), which are structural analogues of chlorophyll and haem, were discovered in the 1920s.[1] The complexes of phthalocyanines with alkali and alkaline earth metals contain the metal in an ionic form and may be decomposed by acids and even water, whereas transition metals in complexes with phthalocyanines, which form a covalent bond, are, on the other hand, surprisingly stable.[2] Phthalocyanines possess a number of unusual properties and have found various applications.[3-5]

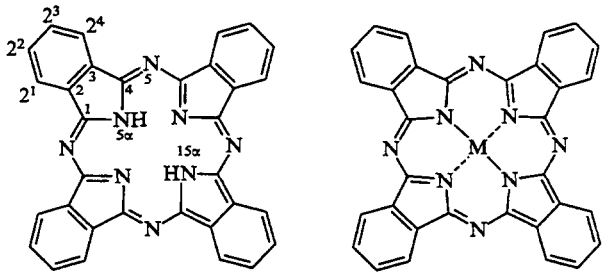
The first information about the catalytic activity of phthalocyanines[6] appeared in 1938. In the course of the succeeding 55 years, metal-phthalocyanines (PcM) have been used as catalysts of the oxidation of aromatic hydrocarbons[7-20] propene,[21-24] aldehydes,[25] acids,[25,26] alkenes[6,27] alcohols[8,28] ketones[29] sulfur-containing compounds,[30-34] and nitrogen[35] and carbon[36] oxides, of the dehydrogenation of alcohols[37-42] and hydrocarbons,[43-47] of photodehydrogenation,[48] of the decarboxylation of carboxylic acids,[49] of the decomposition of peroxide compounds,[50-62] hydrazine,[14,63,64] and formic acid,[65] of isomerisation,[7] of polymerisation,[50] of the ortho–para conversion of hydrogen and deuterium exchange,[66] of the reduction of nitrogen oxide with hydrogen[67-69] and with carbon monoxide,[67,70] of electrochemical processes,[71] and of the reduction of organic compounds.[37,72-79]

E M Sul'man Department of Biotechnology and Chemistry, Tver' State Technical University, nab. A.Nikitina 22, 170026 Tver', Russian Federation. Fax (7-082) 231 62 92
B V Romanovskii Laboratory for Kinetics and Catalysis, Department of Physical Chemistry, Chemistry Department, Lomonosov Moscow State University, Vorob'evy Gory, 119899 Moscow, Russian Federation. Fax (7-095) 939 31 85

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II. The structure of phthalocyanines

The structure of phthalocyanines was first considered by Dent et al.[80] It was shown by X-ray diffraction[81,82] that metal-phthalocyanines have planar molecules.



Both crystalline α- and β-modifications of phthalocyanines exist.[83,84] The mutual phase transitions of the α- and β-forms occur on boiling in acid and organic solvents and also as a result of mechanical and thermal influences. The hypsochromic shift of the IR absorption band of phthalocyanine molecules at 720–730 cm^{-1} is regarded as a sign of the $\alpha \rightarrow \beta$ transition.[84] In a mixture of the α- and β-forms, this band is split. The distance between the molecules in the crystals of both modifications are the same (Fig. 1), but the orientations of the molecules relative to the

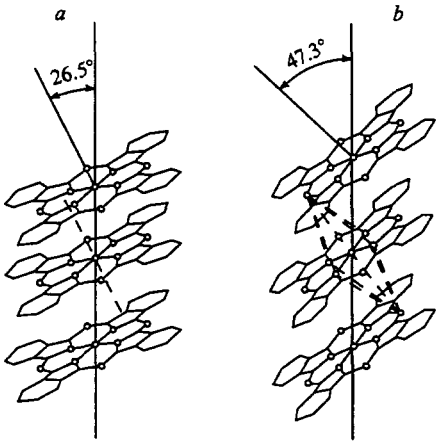


Figure 1. Arrangement of the molecules in the crystals of α-PcM (*a*) and β-PcM (*b*).

crystallographic axes different.[85] In the β-form, the metal atom of the chelate unit coordinates the nitrogen atoms of the neighbouring molecules, which serve as extra-ligands relative to the complex forming metal (Fig. 1). The higher stability of the β-form is attributed to the interaction between the metal atom and the nitrogen atoms of the neighbouring PcM molecules.[86] The different crystalline modifications of PcM can therefore exhibit different catalytic activities.

III. The catalytic activity of phthalocyanines and the mechanism of their activation

By virtue of their high chemical stability,[66] phthalocyanines can be used as model substances under conditions including catalytic investigations.

The wide variety of the reactions catalysed by metal-phthalocyanines[87] apparently reflect the characteristic features of their structure. As a consequence of their planar structure and the presence of an extensive electron conjugation system, the phthalocyanine molecules are fairly mobile and are capable of being coordinated to substrate molecules.

In the phthalocyanine molecule, it is possible to distinguish two types of active centres: the 'metallic' centre incorporating the complex forming metal and the 'organic' centre.[88] The latter includes the nitrogen atoms of the azo-bridges, which have an enhanced electron density. The application of quantum-chemical calculations[89,90] made it possible to determine the electron populations and the effective charges of the individual atoms in the phthalocyanine molecule and to discover the presence of donor and acceptor centres. The electron populations of the different atoms in the PcCo molecule are characterised by the following values:[89]

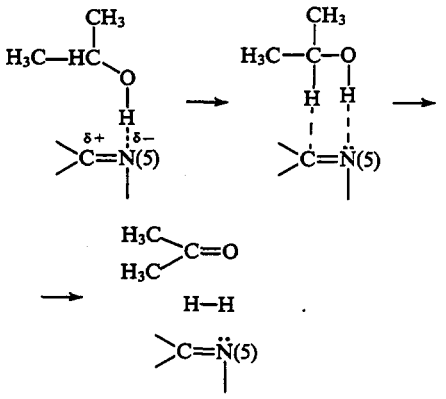
N(5α)	C(1)	C(2)	C(2¹)	C(2²)	N(5)
5.148	3.927	3.995	4.031	4.041	5.179

It follows from these data that the nitrogen atoms behave as electron-donating centres. The effective charge on the cobalt atom (+0.359) indicates the interaction of the orbitals of the organic ligand with the atomic orbitals of the metal and electron transfer between the metal and the π-electron system of the ligand. Either the metal or the organic ligand or both centres simultaneously exhibit a catalytic activity in various reactions.[8] The catalysis by metal-phthalocyanines is influenced by the number of electrons in the $3d^n4s^2$ atomic orbitals of the metal and in the molecular orbitals of the ligand.[91]

Gudkov[47] put forward the hypothesis that O_2 may be coordinated to PcCo via the central metal atom and the organic ligand. The shielding of the central atom by ligands, for example by pyridine,[92-94] in the axial position hinders the binding of O_2 to the metal of the chelate unit[95] and hence alters the catalytic activity of PcM in oxidation reactions. The decisive role of the central metal atom in catalysis has been confirmed experimentally.[6,14] The bond in the PcM···O_2 complex is formed as a result of electron transfer both from the π orbital of oxygen to the d_{z^2} orbital of the metal and by the electron transfer in the opposite direction — from the $d\pi$ orbital of the metal to the antibonding π^* orbitals of oxygen; the first process predominates.[37]

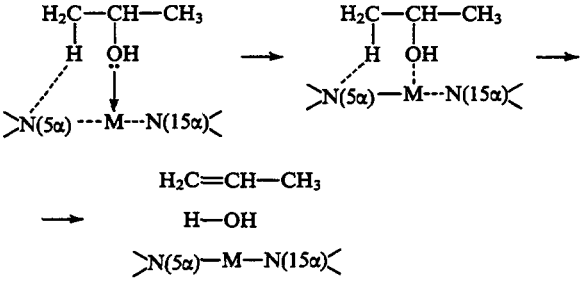
EPR and electronic spectroscopic data have led to the conclusion that O_2 is coordinated to the organic part of the metal complex of phthalocyanine.[96-98] Judging from the nature of the spectrum in the visible region,[97] one may postulate the coordination of O_2 to a ring nitrogen atom. The change in the nature of the EPR spectrum of phthalocyanine in the presence of O_2[99] made it possible also to put forward the hypothesis that oxygen interacts with the central metal atom. However, oxidation of the organic ligand by the metal ion can yield the same results. Thus both the 'organic' and the 'metallic' active centres may be catalytically active.

The studies of the mechanisms of the PcM-catalysed reactions, for example the mechanism of the dehydrogenation of isopropyl alcohol in the presence of complexes of phthalocyanines with transition and nontransition metals, where the metal atom may be shielded, are of undoubted interest.[40-42,100] It has been suggested that the isopropyl alcohol molecule is activated on the 'organic' active centre. The coordination centre in the organic ligand is the bridging N(5) nitrogen atom, which has a lone pair and forms a bond with the hydrogen atom of the hydroxy group:



The role of the metal of the chelate unit is to ensure electron transfers via the central atom of the PcM molecule.

The dehydration of isopropyl alcohol requires two-centre coordination, where the oxygen atom of the hydroxy group transfers its electron to the metal atom, while the hydrogen atom of the methyl group forms a bond with the nitrogen atom of the chelate unit.



Thus the metal atom may be either an electron acceptor or donor and this determines the specificity of the activity of the PcM.

In the decomposition of formic acid to H_2 and CO_2 on the β-forms of Cu-, Fe-, Co-, Ni-, and Zn-phthalocyanines at 200–300 °C, zero order with respect to the substrate was observed in all cases, while the apparent activation energy was 80–100 kJ mol^{-1}.[101] Thus the nature of the central metal atom did not affect the process. Moser and Thomas[7] believe that the chelate unit, the CH groups of the benzene rings, the nitrogen *meso*-atoms, and the carbon atoms of the pyrrole rings may be reactive. Depending on the type of reaction catalysed, the catalytic activity may be exhibited under certain conditions by either one or several of these centres at once.

IV. Reactions with participation of hydrogen

The available information about the reactions with participation of molecular hydrogen catalysed by metal-phthalocyanines is extremely limited.[66,102,103] It has been suggested[66] that in the ortho–para conversion of hydrogen and in deuterium exchange on PcCu and PcH_2, the H–H bond may be dissociated both heterolytically, i.e.

$$H_2 \longrightarrow H^+ + H^-,$$

or homolytically, i.e.

$$H_2 \longrightarrow 2H^{\cdot}.$$

The second pathway appears more probable.

Reaction	E/kJ mol^{-1}	
	PcH_2	PcCu
$p\text{-}H_2 \xrightarrow{150-360\ ^\circ C} o\text{-}H_2$	24	21
$H_2 + D_2 \xrightarrow{<100\ ^\circ C} 2\,HD$	–	42

The apparent activation energies for the ortho–para conversion of H_2 on monomeric and polymeric PcCu are not the same. The polymeric form is capable of desorbing hydrogen in the ratio Cu : H = 1 : 1, which permits ready diffusion of hydrogen through the polymer.[66] An increase in the conjugation length on passing from the monomeric to the polymeric phthalocyanine may lead to the equalisation of electron density over the entire PcM molecule, which is accompanied by a decrease in the effective charges on the central metal atom and the organic ligand.

In the related cobalt-tetraphenylporphyrin–TiO_2 ($CoTPP/TiO_2$) catalytic system,[67] the porphyrin ring serves as the adsorption centre for hydrogen.

The study of the adsorption of hydrogen on the pre-evacuated $CoTPP/TiO_2$ and H_2TPP/TiO_2 showed that H_2TPP/TiO_2 and $CoTPP/TiO_2$ adsorb 13.5 and 19.6 mmol of H_2 per gramme of the catalyst under comparable conditions. This led to the indisputable conclusion that hydrogen is activated by the 'organic' active centre. The study of the kinetics of the reduction of NO on $CoTPP/TiO_2$ confirmed the dissociative nature of the adsorption of hydrogen.[67] Fig. 2 shows that nitric oxide is activated by the central metal atom.

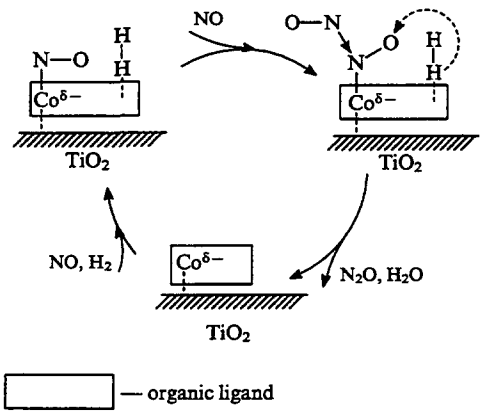
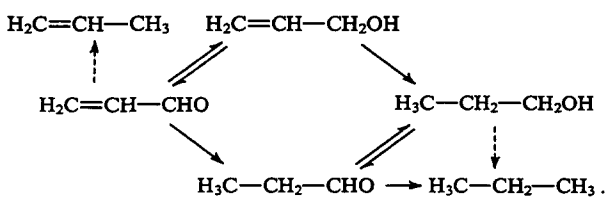


Figure 2. Schematic illustration of the reduction of NO on $CoTPP/TiO_2$.

The study of the hydrogenation of ethyne by a metal tetrahydroborate in the presence of sulfonated CoTPP led to the conclusion that ethyne is activated on the central metal atom.[72]

The following scheme has been proposed for the hydrogenation of allyl alcohol on PcNi at 100–300 °C:[104]



Other pathways leading to the conversion of allyl alcohol, for example directly into propene, are not taken into account in the above scheme.

In addition, the hypothesis has been put forward that hydrogen is activated on the nitrogen atoms of the PcM molecule.[104] It was later confirmed by other investigators with the aid of adsorption methods.[67] The independence of the activation of PcM in the isopropyl alcohol dehydrogenation reaction of the nature of the central atom[105] led to the conclusion that the nitrogen atoms of the azo-bridges participate in the activation of isopropyl alcohol.

Thus molecular hydrogen may be activated on both the 'metallic' and 'organic' active centres of metal-phthalocyanines and metal-porphyrins. The results of the study of the hydrogenation of acetylenic alcohols on modified palladium catalysts and carriers led to the hypothesis that the C≡C bond is activated on the 'organic' centre, while hydrogen is activated on the metal.[106]

V. Phthalocyanines on carriers

Covalent binding, coordination in the axial position, adsorption methods, and direct synthesis on the carrier surface were used for the fixation of metal-porphyrins, including phthalocyanines, on oxide carriers.[95] The last two methods are most widely used.

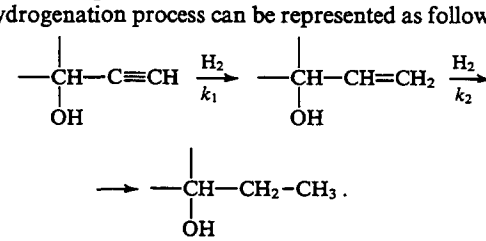
In order to increase the catalytic activity of metal-phthalocyanines and to facilitate the control of the selectivity of the reactions, the fixation of PcM on various carriers is resorted to.[95, 103, 105–108] This prevents the aggregation of the complexes and makes it possible to achieve molecular dispersion.

A fivefold increase in the catalytic activity of cobalt-phthalocyanine in the oxidation of 2-mercaptoethanol after the fixation of the catalyst on the polymeric carrier was noted.[109] The immobilisation of H_2TPP in a polymer matrix is used for the same purposes.

The catalytic activities of monomeric and polymeric phthalocyanines, deposited on carbon carriers, in the decomposition of H_2O_2 depend on the nature of the complex forming metal and on the characteristic features of the carrier.[103] The activity of the monomeric phthalocyanines decreases in the sequence Os ≫ Fe > Ru > Pt > Pd, Ir, whilst that of polymeric ones diminishes in the sequences Fe > Co ≫ Ni > Cu and Fe > Os, Pt, Ru > Ir, Rh, Pd.

Oxide carriers with a high chemical and thermal stability are widely used for porphyrins.[95, 107]

The selective hydrogenation of C_5, C_{15}, and C_{20} acetylenic alcohols in the presence of PcM (M = Pd, Ni, Cu, Co), deposited on oxides (Al_2O_3, SiO_2), has been investigated[76] varying the nature of the solvent, the PcM deposition method, and the amount of the active component in the carrier. The overall scheme for the hydrogenation process can be represented as follows:



The alcohol dehydrogenation and dehydration reactions take place together with the reactions shown above.

In order to elucidate the influence of the nature of the solvent, a study has been made of the hydrogenation of a C_{15} acetylenic alcohol in solutions in isopropyl alcohol, methanol, and hexane (0.4 M) in the presence of $PcNi/SiO_2$ (5% Ni).[77] The catalyst was prepared by the preliminary impregnation of SiO_2 (specific surface 200 m^2 g^{-1}) with an aqueous $NiCl_2$ solution and subsequent treatment with phthalonitrile vapour (250–320 °C), drying, and thermoevacuation. The selectivity and activity of the

catalyst obtained in this way as regards the formation of the C_{15} ethylenic carbinol were found to be a maximum in hexane and a minimum in methanol.

The influence of the nature of the solvent on the heterogeneous catalytic system is determined by a whole series of factors. The solvent is adsorbed on the catalyst, altering the free energy of the surface and its charge,[110] which may affect the mode of the reaction and its selectivity. The solvation constants, the adsorption coefficients, and the rate of conversion of the intermediate surface compound into the reaction products depend on the nature of the solvent.[111] The adsorption from solutions is competitive in character and the adsorption of substrates can therefore be greatly influenced by the ability of the solvent to form coordinate bonds with the catalyst.[76]

Not only the activity of the catalyst in the reactions involving the hydrogenation of the C≡C bond of acetylenic alcohols but also the mechanism of the catalytic activity depend on the method used to deposit PcM on the oxide (from concentrated H_2SO_4 or benzene). Catalysts obtained by depositing Co-, Cu-, and Ni-phthalocyanines from solutions in H_2SO_4 accelerate the reduction of acetylenic alcohols to the same extent. The catalysts prepared by fixation on a carrier of a PcM from a solution in benzene and those obtained from phthalonitrile can be arranged in the following sequence in terms of their activity in the synthesis of ethylenic alcohols: PcPd > PcNi > PcCo.[76]

The rate of oxidation of propan-2-ol in the presence of PcCo is higher than in the presence of PcNi.[66] It has been suggested that the catalytically active centre in this reaction is the central metal atom, as in the hydrogenation reaction.[76]

Thus, depending on the method of preparation of the catalyst, different atoms or groups of atoms of the PcM molecule enter into the reaction complex.

When the PcM/oxide heterogeneous systems are used, it is necessary, as in the case of metallic catalysts on carriers, to take into account the interaction between the active component and the carrier, which not only influences the activity of the catalytic system but is also capable of altering the mode of the process.

The higher catalytic activity of $PcNi/Al_2O_3$ compared with $PcNi/SiO_2$ can be explained by the influence of the carrier on the active component of the catalyst.[76] The Ni $2p_{3/2}$ binding energy (E_b) in the $PcNi/Al_2O_3$ system proved to be lower by 1 eV than in the initial PcNi (according to a patent,[69] E_b = 865.0 eV in this case).

The catalytic properties of PcCo deposited on silica gel by direct synthesis on the surface and of $PcFe/SiO_2$ obtained by the joint grinding of PcFe and SiO_2 [105] have been investigated. When the deposited catalyst is used, the reaction of isopropyl alcohol involves predominantly dehydration and not dehydrogenation. This is evidently associated with an increase, as a result of dispersion, in the number of centres responsible for dehydration or with the influence of the carrier on the catalytic activity of PcM. The catalytic activity of PcCo on silochrome, referred to unit mass of the active phase, is higher by 1–2 orders of magnitude than the activity of crystalline PcCo in the reactions of isopropyl alcohol.[112]

The highest activity of CoTPP in the reduction of CO is attained when TiO_2 is used as the carrier, whereas in the decomposition of H_2O_2 the best carrier is NiO.[59,113] When CoTPP is attached to TiO_2, electron density is transferred from the carrier to the CoTPP molecule, which is accompanied by the formation of a radical-anion and a change in the effective charge on the atoms of the chelate unit. This has been confirmed by XPES data for the binding energies (expressed in eV) in the CoTPP and $CoTPP/TiO_2$ systems:

	Co $2p_{3/2}$	Co $2p_{1/2}$	N 1*s*
CoTPP	781.0	796.4	397.3
$CoTPP/TiO_2$	780.2	795.6	398.6

The EPR spectra of benzene solutions of CoTPP and $CoTPP/TiO_2$ differ appreciably (Fig. 3).[113] Comparison of the electronic absorption spectra of CoTPP in a benzene solution with the spectra of CoTPP deposited on SiO_2 and TiO_2 showed [109] that the use of SiO_2 as the carrier alters the intensity of the absorption bands (AB), whereas new absorption bands appear when the TiO_2 carrier is employed (Fig. 4).

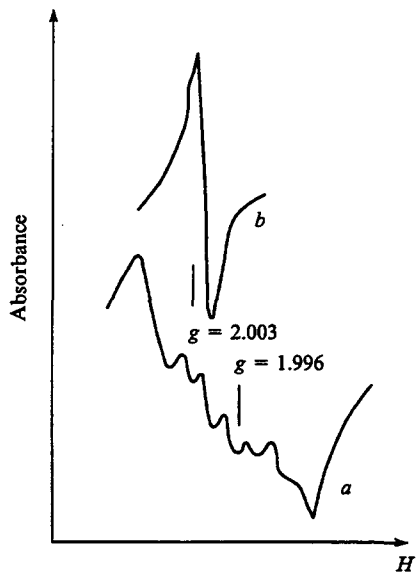


Figure 3. EPR spectra of a benzene solution of CoTPP (*a*) and of CoTPP deposited on TiO_2 (*b*). The spectra were obtained at −196 °C after evacuation at 20 °C.

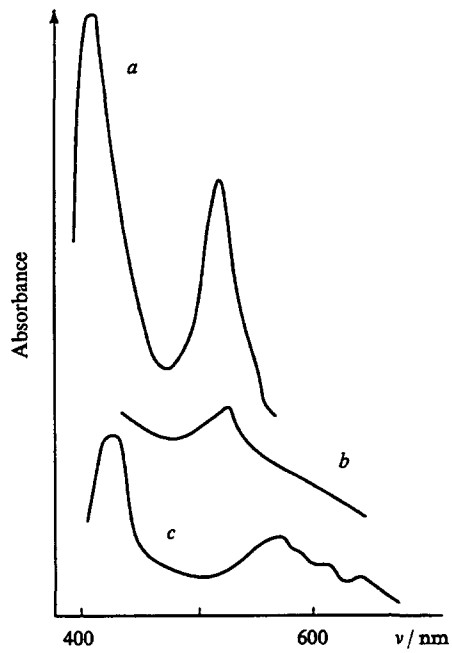


Figure 4. Electronic absorption spectra of CoTPP in benzene solution (*a*) and of CoTPP deposited on SiO_2 (*b*) and TiO_2 (*c*).

An XPES study of cobalt-phthalocyanine deposited on a zeolite led to the conclusion that the carrier influences mainly the nitrogen meso-atoms.[69] Instead of the narrow N 1*s* singlet, characteristic of PcCo, a poorly resolved doublet was noted. The Co $2p_{2/3}$ binding energy hardly changed after the fixation of PcCo on the zeolite. Hence it was concluded that the nitrogen *meso*-atoms are nonequivalent owing to the protonation of the

immobilised complexes.[95,114] The acid centres of the carrier are protonated:

$$PcCo + 2H^+ = (PcCoH_2)^{2+}.$$

In the fixation on oxides chemisorbed water molecules may play the role of the proton-donating species.

Detailed study of the state of the oxygen in the molecular adduct with PcCo immobilised on aluminium oxide[115] showed that Al_2O_3 activates specifically the PcCo molecule. The bond between the complex and the surface is then formed via electron transfer from the atomic orbital of the metal in the chelate unit to an unoccupied atomic orbital of a surface aluminium atom.

On passing from the multilayer to the monolayer coverage of the oxide carrier by the phthalocyanine, the catalytic activity of the immobilised PcM increases.[76] A further tenfold decrease in the PcM concentration on the carrier results in a low catalytic activity. It is noted that the molecules of different gases (CO, O_2, H_2) are capable of dissolving in the PcM crystal lattice.[66]

One of the authors of the present review investigated the kinetics of the hydrogenation of C_5 and C_{20} acetylenic alcohols on $PcCo/SiO_2$ (0.2% of PcCo deposited from solution in sulfuric acid) and $PcNi/Al_2O_3$ (0.2% of Ni deposited from solution in benzene).[75] On $PcCo/SiO_2$, the dependence of the half-reaction time ($\tau_{0.5}$) for ethynyldimethylmethanol (a C_5 acetylenic alcohol) on $q = C_0/C_c$, where C_0 is the initial alcohol concentration and C_c the catalyst concentration, passes through a minimum. The power exponent n is -0.7 and 0.2 respectively for the left- and right-hand branches of the $\tau_{0.5} \sim q^n$ relation. The half-reaction time is directly proportional to the initial concentration of ethynyldimethylmethanol.

In order to specify more precisely the site where H_2 is located in the PcM molecule, sorption studies were performed.[76] The measurements were carried out in solution in hexane at 100 °C. After the introduction of the adsorbent into the reaction volume with vigorous stirring sorption of H_2 was observed. The amount of nickel-phthalocyanine corresponding to 1 g of $PcNi/Al_2O_3$ is capable of absorbing 0.4×10^{-4} of a mole of H_2 (Table 1). On dividing this figure by the number of moles of nickel in the same gramme of $PcNi/Al_2O_3$ (this is equal to 0.35×10^{-4} of a mole), we obtain ~1.18. Thus it is possible to postulate that the H_2 molecule binds preferentially to the central metal atom.

Table 1. The adsorption of hydrogen on Al_2O_3 and $PcNi/Al_2O_3$ at 100 °C.

Adsorbent	P_{H_2} /MPa	Amount of absorbed hydrogen, $10^4 V$/mol g^{-1}
Al_2O_3	0.1	1.07
$PcNi/Al_2O_3$ (0.2% Ni)	0.1	1.47
	10.1	2.09
$PcNi/Al_2O_3$ (0.2% Ni) in the presence of pyridine[a]	0.1	0.82

[a] The amount of pyridine introduced was 8×10^{-5} mol.

In order to test this hypothesis, the Ni atom in PcNi was shielded with pyridine. The pyridine-treated $PcNi/Al_2O_3$ sorbed hydrogen less effectively than the carrier. It is known that the pyridine introduced into the system forms an axial coordinate bond with the metal atom in the chelate unit and behaves as an electron donor in relation to the latter.[92,93] The latter factor suggests that, like the oxygen molecule,[41] the hydrogen molecule can behave as a ligand in relation to the central metal atom.

The interaction of the components of the reaction system with the nitrogen atoms of the pyrrole rings may abolish the influence of the nature of the central metal atom. For example, as a result of the strong effect of the carrier on the metal, the latter may lose the capacity to participate in the activation of hydrogen. Since $PcNi/Al_2O_3$ sorbs more hydrogen at an elevated pressure than at atmospheric pressure (Table 1), one may postulate the coordination of H_2 also to the organic ligand. The retardation of the hydrogenation of the C_5 and C_{20} acetylenic alcohols at $P_{H_2} > 8.1$ MPa was accounted for by this factor.

The IR spectra of the initial $PcNi/Al_2O_3$ (0.2% Ni) catalyst contain absorption bands characteristic of the surface OH groups of aluminium oxide.[76] After treatment with hexane at 100 °C and $P_{H_2} = 0.1$ MPa, these bands disappeared as a result of the adsorption of hexane on the carrier.[116] In the IR spectrum of the hydrogen-treated specimen, absorption bands appeared at 1680 cm^{-1} and those at 1090 and 1165 cm^{-1} intensified (Fig. 5). Using the principle of group frequencies as a guide, the former absorption band was assigned to the vibrations of the C=N bond and the last two bands were assigned to C–N vibrations, although much caution must be exercised when this is done in relation to a chelate ring. The facts presented indicate that contact between the catalyst and the solvent under hydrogen weakens the interaction of the phthalocyanine ligand with the central metal atom. This may be associated with the transfer of electron density from hydrogen to the metal atom.

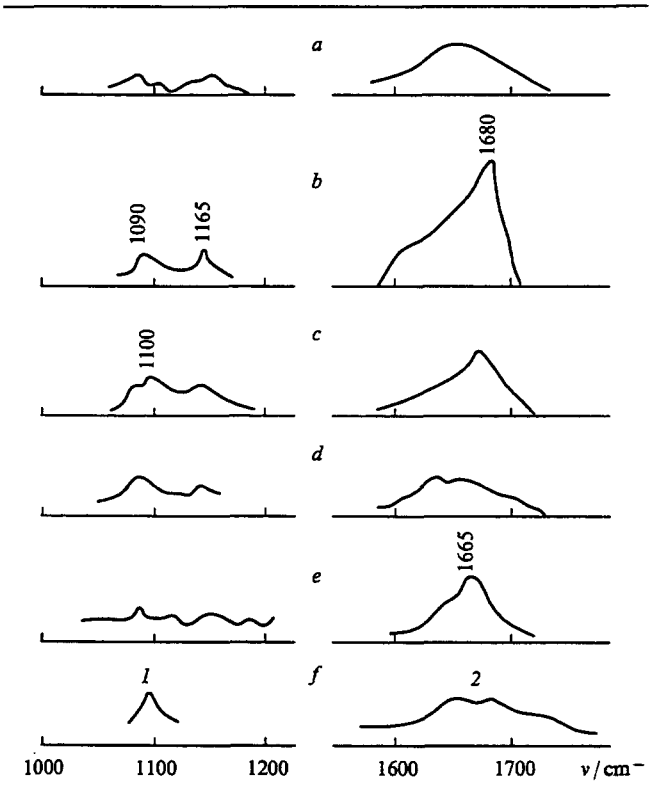


Figure 5. IR spectra of $PcNi/Al_2O_3$: (*a*) initial specimen; (*b*) specimen obtained after contact with H_2 in hexane; (*c*) after successive treatment with hydrogen on the C_{20} acetylenic alcohol; (*d*) after successive treatment with hydrogen and the C_5 acetylenic alcohol; (*e*) after treatment with pyridine; (*f*) after treatment with the C_{20} ethylenic alcohol (*1*) or after successive treatment with pyridine and the C_{20} acetylenic alcohol (*2*). Only those parts of the spectra are illustrated where a difference was observed between the specimens. The specimens for analysis were prepared as mulls in liquid paraffin.

In order to test this hypothesis, $PcNi/Al_2O_3$ was treated with pyridine which is an electron-donating extra-ligand in relation to the metal atom, after which an absorption band appears in the IR spectrum at 1665 cm^{-1}. This band was also assigned to the C=N bond vibrations, the intensity of which increases as a result of the coordination. After successive treatment of $PcNi/Al_2O_3$ with hydrogen and with a C_{20} acetylenic alcohol, a decrease in the intensity of the 1680 cm^{-1} absorption band was observed, whereas the replacement of the C_{20} by the C_5 alcohol resulted in

the complete disappearance of the absorption. This suggests that acetylenic alcohols with a shorter chain are adsorbed more effectively on phthalocyanine catalysts, i.e. the series based on the adsorption capacity of alcohols, which they exhibit in relation to modified palladium catalysts, is, as it were, reversed.[117] In addition, the acetylenic and ethylenic C_{20} alcohols coordinated to the catalyst absorb at 1100 cm^{-1}. The 1100 cm^{-1} absorption band is characteristic of the vibrations of the C–O bond in tertiary alcohols.[118] Such coordination of alcohols promotes the occurrence of the dehydration reaction together with hydrogenation.

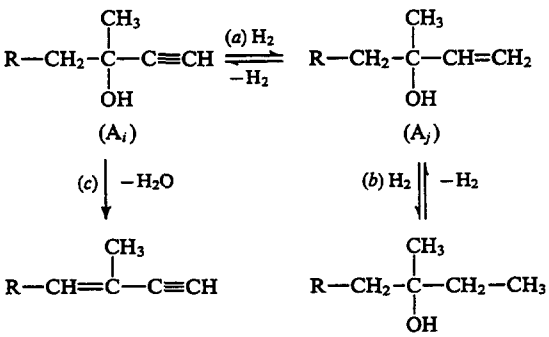
In order to elucidate the centre for the interaction of the acetylenic alcohol with PcNi, the heterogenised catalyst was treated in succession with pyridine and the C_{20} acetylenic alcohol. This resulted in the disappearance of the absorption at 1665 cm^{-1}. The nickel in the specimen treated in this way was shielded by pyridine and the substrate could be coordinated only to the organic ligand in the PcM, namely to the nitrogen *meso*-atoms. After treatment with pyridine, the catalyst did not exhibit an activity in the hydrogenation of the C_{20} acetylenic alcohol at 100 °C and $P_{H_2}=0.1$ MPa. This can be explained by the impossibility of activating hydrogen on such a catalyst.

No changes are observed after the adsorption of substrates in the IR spectra of the $PcCo/SiO_2$ catalyst prepared by the adsorption on SiO_2 of cobalt-phthalocyanine from solution in concentrated sulfuric acid. This is caused mainly by the low PcCo concentration (0.2%) on the carrier surface. At this PcCo concentration on the silica gel surface (specific surface 26 $m^2\ g^{-1}$), the coverage should amount to ~15% of the monolayer coverage and should consist of isolated patches. We may note that even for the 1.5-layer coverage, the molecular PcCo is deposited nonuniformly on silica gel.[105]

The apparent activation energy for the hydrogenation of the C_{20} acetylenic alcohol on $PcCo/SiO_2$ was approximately 2.3 times smaller than for the hydrogenation of the C_5 acetylenic alcohol, which has been attributed to the different adsorption capacities of these alcohols.

* * *

Thus it has been established by kinetic, adsorption, and IR spectroscopic methods that hydrogen and the acetylenic alcohol are coordinated at different active centres of the immobilised metal-phthalocyanine. The conversion of acetylenic alcohols on phthalocyanine complexes of metals, attached to oxide carriers, can be represented by the following scheme:



If it is supposed that hydrogen and the substrate are activated on different active centres (Z and Z'), then reaction (*a*) should include the following stages:

$$A_i + Z' \overset{K_i}{\rightleftharpoons} A_iZ', \quad (1)$$

$$H_2 + Z' \overset{K_m}{\rightleftharpoons} H_2Z, \quad (2)$$

$$H_2Z \overset{K_n}{\rightleftharpoons} 2H + Z, \quad (3)$$

where A_i is the substrate and K_i, K_m, and K_n are the equilibrium constants of stages (1), (2), and (3) respectively. The surface reaction must be reversible:

$$A_iZ' + 2H \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A_jZ', \quad (4)$$

$$A_jZ' \overset{K_j}{\rightleftharpoons} A_j + Z', \quad (5)$$

where k_4 and k_{-4} are the forward and reverse rate constants for stage (4) respectively, whilst K_j is the equilibrium constant of stage (5). It is assumed that stages (1), (2), (3), and (5) are fast.

In addition account must be taken of the adsorption of the solvent (hexane) on the carrier and on the PcM.

It is postulated that the substrate and the solvent are adsorbed on the same active centres Z':

$$Solv + Z' \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} Solv\ Z', \quad (6)$$

where Solv is the solvent and k_6 and k_{-6} are the forward and reverse rate constants for stage (6).

If account is taken only of the adsorption of the solvent and the occurrence of stage (5) in the reverse direction is neglected, then the rate of the reaction under static conditions can be described by the following kinetic equation:

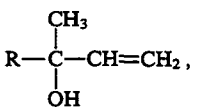
$$W = \frac{k_4k_{-6}K_iK_mK_nN_{Z_0'}C_aC_H^2}{k_kC_{Solv}},$$

where C_a, C_H, and C_{Solv} are the concentrations of the acetylenic alcohol, hydrogen, and the solvent respectively and Z_0' is the total number of active centres for the adsorption of the substrate or the solvent.

If the catalyst concentration C_c is constant and the hydrogenation takes place in concentrated solutions, account must be taken only of the adsorption of the acetylenic alcohol. The rate of reaction can then be represented in the form

$$W = k_4K_mK_nC_kC_H^2.$$

The above investigation led to the development of a procedure for the preparation of ethylenic alcohols having the general formula



R = $CH(CH_3)_2(CH_2)_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3-$,
$CH(CH_3)_2(CH_2)_3CH(CH_3)(CH_2)_3-$, or
$C(CH_3)_2=CH-(CH_2)_2-$,

by the hydrogenation of the corresponding acetylenic alcohols in the presence of PcM on Al_2O_3 or SiO_2 in an organic solvent.[76] The yield of the ethylenic alcohols reaches 99.2%–99.8%.

The following general features are characteristic of the selective hydrogenation of acetylenic alcohols on PcM immobilised on inorganic carriers: (a) the process takes place via an intermediate heteroligand complex (solvent–substrate–hydrogen–catalyst–carrier)[119] which has a 'multistory' structure; (b) the nature and amount of the components of the complex influence the catalytic activity of the PcM and the process selectivity; (c) the reactants are activated on different active centres ('metallic' and 'organic'). The catalytic system under discussion should be regarded as homogeneous-heterogeneous, which is confirmed by the nonlinear relations between the rates of the reactions and the ratio of the concentrations of the components of these reactions.

By virtue of their unusual properties, metal-phthalocyanines are promising catalysts of many processes.[103] The immobilisation of the PcM on carriers makes it possible to achieve the maximum catalytic activity per unit mass of the active phase and to regulate the mode of reaction of the substrate. The catalytic activity exhibited by both the central metal atom and the atoms of the organic ligand in the PcM confirms the hypothesis[120] that 'organometallic' active centres are formed on deposited palladium catalysts and that the substrate and hydrogen are activated separately on centres of different nature.

References

1. P Karrer *Lehrbuch der Organischem Chemie* (Translated into Russian; Leningrad: Goskhimizdat, 1960)
2. D Nenitescu *Chimie Organica de Costin* Vol. 2 (Translated into Russian; Moscow: Izd. Inostr. Lit., 1963)
3. Jpn. Appl. 1 292 066; *Ref. Zh. Khim.* 4 N 252P (1992)
4. Fr. Appl. 2 634 464; *Ref. Zh. Khim.* 4 N 253P (1992)
5. V A Perfil'ev, E A Venediktov, in *5-ya Vsesoyuz. Konferentsiya po Koordinatsionnoi i Fizicheskoi Khimii Porfirinov (Tez. Dokl.)* [The Fifth All-Union Conference on Coordination and Physical Chemistry of the Porphyrins (Abstracts of Reports)] (Ivanovo: Chemical Engineering Institute, 1988) p. 151
6. A H Cook *J. Chem. Soc.* 1761 (1938)
7. P Moser, A L Thomas *J. Chem. Educ.* **41** 245 (1964)
8. L M Il'ina, Candidate Thesis in Chemical Sciences, Moscow State University, Moscow, 1974
9. H Kropf *Ann. Chim. (Paris)* **637** 73 (1960)
10. H Kropf *Ann. Chim. (Paris)* **637** 111 (1960)
11. J M Van Tilborg, A D Vreugdenhi *Tetrahedron* **31** 2825 (1975)
12. T I Andrianova, A I Sherle, A A Berlin *Izv. Akad. Nauk SSSR, Ser. Khim.* 531 (1973)
13. S Z Roginskii *Elektronnye Yavleniya v Geterogennom Katalize* (Electronic Phenomena in Heterogeneous Catalysis) (Moscow: Nauka, 1975)
14. S D Levina, T I Andrianova, M M Sakharov *Zh. Fiz. Khim.* **40** 1229 (1966)
15. T Hara, V Ohkatsu, T Osa *Chem. Lett.* 103 (1973)
16. T Hara, V Ohkatsu, T Osa *Bull. Chem. Soc. Jpn.* **48** 85 (1975)
17. F Shtainbakh *Kinet. Katal.* **16** 1094 (1975)
18. V E Errero-Palensuela, S A Borisenkova, V A Seleznev, A V Artemov *Vestn. Mosk. Univ., Ser. 2, Khim.* **19** 714 (1978)
19. S A Borisenkova, A V Artemov, V V Kurylev, in *Materialy 4-go Sovetsko-Frantsuzskogo Seminara po Katalizu* (Proceedings of the Fourth Soviet-French Seminar on Catalysis) (Tbilisi: Institute of Physical Chemistry of the Academy of Sciences of the Georgian SSR, 1978) p. 96
20. V E Errero-Palensuela, A V Artemov, S A Borisenkova *Vestn. Mosk. Univ., Ser. 2, Khim.* **20** 471 (1979)
21. V Ragaini, P Carniti, C Rainalci, F Morazzoni *Chim. Ind.* **58** 473 (1976)
22. I I Ioffe, G A Zapevalov *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 430 (1977)
23. S Z Roginskii *Probl. Kinet. Katal.* **15** 12 (1973)
24. I I Ioffe, G A Zapevalov, in *Katalizatory, Soderzhashchie Nanesennye Kompleksy (Materialy Vsesoyuz. Soveshchaniya)* [Catalysts Containing Deposited Complexes (Proceedings of All-Union Conference)] (Novosibirsk: Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, 1978) p. 203
25. V Ohkatsu, T Hara, T Osa *Bull. Chem. Soc. Jpn.* **50** 696 (1977)
26. S Paquot, F Goursak *Bull. Soc. Chim. Fr.* **17** 172 (1950)
27. C Paquot *C. R. Hebd. Seances Acad. Sci.* **209** 171 (1939)
28. N I Ionescu, D Popescu *Rev. Roum. Chim.* **27** 481 (1982)
29. C Paquot *Bull. Soc. Chim. Fr.* **12** 450 (1945)
30. A D Simonov, N N Kundo, E Kh Mamaeva, L A Akimova *Zh. Prikl. Khim.* **50** 307 (1977)
31. A D Simonov, I P Keier, N N Kundo *Kinet. Katal.* **14** 988 (1973)
32. N N Kundo, I P Keier *Zh. Fiz. Khim.* **42** 1352 (1968)
33. S A Borisenkova, E P Denisova, T A Danilova, O I Kozunenko *Issledovanie Okisleniya Nekotorykh Serosoderzhashchikh Soedinenii v Prisutstvii Ftalotsianinovykh Kompleksov* Moscow, 1969 (Investigation of the Oxidation of Some Sulfur-Containing Compounds in the Presence of Phthalocyanine Complexes, Moscow, 1969) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) No. 1802-74 (1974)
34. V S Pozii, S A Borisenkova, in *6-aya Vsesoyuz. Nauch. Konferentsiya po Okisleniyu Organicheskikh Soedinenii v Zhidkoi Faze "Okislenie-86" T. 2 (Tez. Dokl)* [The Sixth All-Union Scientific Conference on the Oxidation of Organic Compounds in the Liquid Phase 'Oxidation-86' Vol. 2 (Abstracts of Reports)] (L'vov: L'vov University, 1986) p. 89
35. I Mochida, K Takeyashi, H Fujitsu, K Takashita *Chem. Lett.* 327 (1976)
36. B V Romanovskii, R E Mardaleishvili, V Yu Zakharov *Kinet. Katal.* **18** 255 (1977)
37. S Naito, K Tamaru *Z. Phys. Chem.* **94** 150 (1975)
38. V Yu Zakharov, O M Zakharova, B V Romanovskii, R E Mardaleishvili *React. Kinet. Catal. Lett.* **6** 133 (1977)
39. V Yu Zakharov, O M Zakharova, B V Romanovskii, R E Mardaleishvili *Vestn. Mosk. Univ., Ser. 2, Khim.* **19** 137 (1978)
40. S A Borisenkova, L M Il'ina, A P Rudenko *Zh. Fiz. Khim.* **50** 1712 (1976)
41. V E Errero-Palensuela, S A Borisenkova, P I Nekrasov *Issledovanie Prevrashchenii Izopropilovogo Spirta v Prisutstvii Katalizatorov Tetraizoporfinovogo Ryada* Moscow, 1979 (Investigation of the Conversions of Isopropyl Alcohol in the Presence of Catalysts of the Tetraisoporphyrin Series, Moscow, 1979) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) No. 1105-79 (1979)
42. F Steinbach, K Hiltner *Z. Phys. Chem.* **83** 126 (1973)
43. V Yu Zakharov, Author's Abstract of Candidate Thesis in Chemical Sciences, Moscow State University, Moscow, 1977
44. A Wolberg, J Manassen *J. Am. Chem. Soc.* **92** 2982 (1970)
45. J Manassen, A Bar-Ilan *J. Catal.* **17** 86 (1970)
46. A Bar-Ilan, J Manassen *J. Catal.* **33** 68 (1974)
47. C B Gudkov, Author's Abstract of Candidate Thesis in Chemical Sciences, Moscow State University, Moscow, 1981
48. O L Kaliya, N A Kuznetsova, in *Naukoemkie Khimicheskie Tekhnologii (Materialy II Mezhdunar. Konferentsii) Moscow, 1994* [Chemical Technologies with a High Scientific Content (Proceedings of the Second International Conference) Moscow, 1994] p. 28
49. S A Borisenkova, N E Davidenko, A P Rudenko, in *Katalizatory, Soderzhashchie Nanesennye Kompleksy (Materialy Vsesoyuz. Soveshchaniya)* [Catalysts Containing Deposited Complexes (Proceedings of All-Union Conference)] (Novosibirsk: Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, 1980) p. 129
50. A A Balandin, V I Spitsyn, A P Rudenko, A P Dobrosel'skaya *Kinet. Katal.* **8** 808 (1967)
51. J H Kropf *Chem. Eng. Technol.* **36** 759 (1964)
52. V A Grin, S N Pobedinskii, in *Voprosy Kinetiki i Kataliza (Mezhvuz. Sb. Nauch. Trudov)* [Problems of Kinetics and Catalysis (Intercollege Collection of Scientific Reports)] (Ivanovo: Ivanovo Chemical Engineering Institute, 1979) p. 66
53. H Kropf, S K Ivanov, R Direcks *Ann. Chim. (Paris)* 2046 (1974)
54. H Kropf, S K Ivanov, I Zink *Ann. Chim. (Paris)* 2055 (1974)
55. H Kropf, J Spangenberg, A Hofer, H Wenk *Ann. Chim.* 1242 (1974)
56. P K Tarasenko, S A Borisenkova, V A Novikov *Vestn. Mosk. Univ., Ser. 2, Khim.* **20** 380 (1979)
57. H Kropf, J Spangenberg, A Gunst, J Hinrichsen *Ann. Chim. (Paris)* 1242 (1980)
58. S V Vul'fson, O L Kaliya, O L Lebedev, E A Luk'yanets *Zh. Fiz. Khim.* **10** 1757 (1974)
59. I Mochida, A Yasutake, H Fujitsu, K Takeshita *J. Phys. Chem.* **86** 3468 (1982)
60. S N Pobedinskii, A A Trofimenko, L R Bychkova *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **26** 316 (1983)
61. I Okura, N Kim-Thuan, T Keii *J. Mol. Catal.* **5** 293 (1979)

62. US P. 4 992 602; *Ref. Zh. Khim.* 4 N 18P (1992)
63. F Steinbach, M Zobel *Z. Phys. Chem.* **111** 113 (1978)
64. D M Wagnerova, E Schwertnerova, I Verek-Siska *Collect. Czech. Chem. Commun.* **38** 756 (1973)
65. S Tanaka, T Onishi, K Tamaru *Bull. Chem. Soc. Jpn.* **41** 2557 (1968)
66. N I Ionescu, P Popescu *Rev. Chim. (Bucharest)* **34** 18 (1983)
67. I Mochida, K Setsugu, H Fujitsu, K Takeshita *J. Phys. Chem.* **87** 1524 (1983)
68. O M Zakharova, Author's Abstract of Candidate Thesis in Chemical Sciences, Moscow State University, Moscow, 1982
69. Russ. P. 1 703 650; *Byull. Izobret.* (1) 114 (1992)
70. E S Spiro, G V Antoshin, O P Tkachenko, Kh M Minachev, in *Structure and Reactivity of Modified Zeolites* (Amsterdam, 1984) p. 31
71. M R Tarasevich, K A Radyushkina *Kataliz i Elektrokataliz Metalloporfirinami* (Catalysis and Electrocatalysis by Metalloporphyrins) (Moscow: Nauka, 1982)
72. E B Fleischer, M Krishnamurty *J. Am. Chem. Soc.* **94** 1382 (1972)
73. S Naito, M Ichikawa, K Tamaru *J. Chem. Soc., Faraday Trans.* **68** 1451 (1972)
74. E M Sul'man, Doctoral Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, 1989
75. E M Sul'man *Usp. Khim.* **63** 981 (1994) [*Russ. Chem. Rev.* **63** 923 (1994)
76. E M Sul'man, Author's Abstract of Doctoral Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, 1989
77. E M Sul'man, B V Romanovskii, T V Ankudinova, I Yu Tyamina, S P Dorozhko, O S Popov, in *5-ya Vsesoyuz. Konferentsiya po Koordinatsionnoi i Fizicheskoi Khimii Porfirinov (Tez. Dokl.)* [The Fifth All-Union Conference on Coordination and Physical Chemistry of the Porphyrins (Abstracts of Reports)] (Ivanovo: Chemical Engineering Institute, 1988) p. 207
78. USSR P. 1 401 672; *Byull. Izobret.* (21) 270 (1988)
79. S Sakaki, S Mitarai, K Onkubo *Chem. Lett.* 195 (1991)
80. C E Dent, R P Linstead, A R Cove *J. Chem. Soc.* 1039 (1934)
81. J M Robertson, J Woodward *J. Chem. Soc.* 219 (1937)
82. J M Robertson, J Woodward *J. Chem. Soc.* 36 (1940)
83. J H Shap, M Lardon *J. Phys. Chem.* **72** 3230 (1968)
84. A I Sidorov, I P Kotlyar *Opt. Spektrosk.* **11** 175 (1961)
85. B D Berezin *Koordinatsionnye Soedineniya Porfirinov i Ftalotsionina* (Coordination Compounds of the Porphyrins and Phthalocyanine) (Moscow: Nauka, 1978)
86. T V Silina, B G Aristov *Zh. Vses. Khim. O-va im D I Mendeleeva* **19** 77 (1974)
87. A Miyazawa, J Tsutsui, S Yoshitomi, T Sato, Y Yoshimura, H Shimada, N Matsubayashi, A Nishijima *J. Jpn. Petrol. Inst.* **36** 291 (1993)
88. S Z Roginskii, M M Sakharov *Zh. Fiz. Khim.* **42** 1331 (1968)
89. A M Schaffer, M Gouterman, E R Davidson *Theor. Chim. Acta* **30** 9 (1973)
90. V G Maslov *Teor. Eksp. Khim.* **16** 93 (1980)
91. K Sakamoto, J Sonobe, F Shibamiya *J. Jpn. Soc. Colour Mater.* **63** 385 (1990)
92. F Cariati, D Galizzioli, F Marazzoni, C Busetto *J. Chem. Soc., Dalton Trans.* 556 (1975)
93. F A Walker *J. Am. Chem. Soc.* **95** 1154 (1973)
94. N Kawashima, T Suzuki, K Meguro *Bull. Chem. Soc. Jpn.* **49** 2029 (1976)
95. B V Romanovskii, in *5-i Mezhdunar. Simpozium po Svyazi Mezhdu Gomogennym i Geterogennym Katalizom (Tez. Dokl.)* [The Fifth International Symposium on the Relation between Homogeneous and Heterogeneous Catalysis (Abstracts of Reports)] (Novosibirsk: Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, 1986) Vol. 2, Part 1, p. 40
96. Y Ogata, K Marumo, T Kwan *Chem. Pharm. Bull.* **17** 1194 (1969)
97. A E Cahill, H Taube *J. Am. Chem. Soc.* **73** 2847 (1951)
98. J M Assour, S E Harrison *J. Phys. Chem.* **68** 872 (1964)
99. K Yamamoto, T Kwan *J. Catal.* **18** 354 (1970)
100. V A Novikov, Candidate Thesis in Chemical Sciences, Moscow State University, Moscow, 1978
101. T G Borisova, Candidate Thesis in Chemical Sciences, Moscow State University, Moscow, 1982
102. M Hronec, J Ilavsky *Petrochemia* **23** 89 (1982)
103. O A Golubchikov, B D Berezin *Usp. Khim.* **55** 1361 (1986) [*Russ. Chem. Rev.* **55** 768 (1986)]
104. H Kropf, D J Witt *Z. Phys. Chem.* **76** 331 (1971)
105. S A Borisenkova, A S Erokhin, V A Novikov *Zh. Fiz. Khim.* **56** 2304 (1985)
106. US P. 4 913 802; *Ref. Zh. Khim.* 2 P 186P (1991)
107. T Hara *Chem. Ind. Jpn.* **37** 390 (1986)
108. US P. 4 897 180; *Ref. Zh. Khim.* 2 P 187P (1991)
109. T A Maas, M Kuijer, J Zwart *J. Chem. Soc., Chem. Commun.* 86 (1976)
110. A N Frumkin, V E Kazarinov, G Ya Tysyachnaya *Dokl. Akad. Nauk SSSR* **198** 145 (1971)
111. D V Sokol'skii *Gidrirovanie v Rastvorakh* (Hydrogenation in Solutions) (Alma-Ata: Izd. Akad. Nauk Kaz. SSR, 1962)
112. D Gassan, S A Borisenkova, A N Pryakhin *Adsorbtsionnye Ftalotsianinovye Katalizatory: Metody Polucheniya, Struktura i Kataliticheskaya Aktivnost'. Sistema PcCo–SiO_2* Moscow, 1983 (Adsorption Phthalocyanine Catalysts: Methods of Preparation, Structure, and Catalytic Activity. The PcCo–SiO_2 System, Moscow, 1983) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) No. 5343-83 (1983)
113. I Mjchida, K Isuji, K Setsugu *J. Phys. Chem.* **84** 3159 (1980)
114. U Ahrens, H Kuhl *Z. Phys. Chem.* **37** 1 (1963)
115. M Barzaghi, T Beringhelli, F Morazzoni *J. Mol. Catal.* **14**, 357 (1982)
116. A G Kiselev, V I Lygin *Infrakrasnye Spektry Poverkhnostnykh Soedinenii* (Infrared Spectra of Surface Compounds) (Moscow: Nauka, 1972)
117. E M Sulman, O S Popov, A Yermakova, A A Belyaev *React. Kinet. Catal. Lett.* **36** 59 (1988)
118. K Nakanishi *Infrared Absorption Spectroscopy* (Translated into Russian; Moscow: Mir, 1965)
119. E I Klabunovskii, A A Vedenyapin *Asimmetricheskii Kataliz. Gidrogenizatsiya na Metallakh* (Asymmetric Catalysis. Hydrogenation on Metals) (Moscow: Nauka, 1980)
120. A I Sidorov, E M Sul'man, L M Bronshtein, T V Ankudinova, Yu E Avtushenko *Kinet. Katal.* **34** 87 (1993)