



Synthesis and catalytic properties of hybrid materials based on organically modified silica matrix with cobalt phthalocyanine



Ilya A. Tarasyuk, Ilya A. Kuzmin, Yuriy S. Marfin*, Artur S. Vashurin, Alena A. Voronina, Evgeniy V. Rumyantsev

Department of Inorganic Chemistry, Ivanovo State University of Chemistry and Technology, 7, Sheremetevsky Str., Ivanovo, Russia

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ABSTRACT

Hybrid materials with Co(II) phthalocyanine immobilized on organically modified silica matrices were obtained. Morphological characteristics of obtained materials were tested by scanning electron and atomic force microscopy techniques and laser diffraction analysis. Covalent immobilization of catalyst was proved by IR spectroscopy data concerning position and intensity of characteristic vibrations for matrix and phthalocyanine. Synthesized materials were evaluated as catalysts for the oxidation of RSH compounds under the temperature and pH variation. Reaction rate constants and activation parameters were estimated. The value of pH about 10 was found to be optimal for the diethyldithiocarbamate oxidation in the presence of studied catalysts. The changing of the limiting step from kinetic to diffusion was observed at 303.15 K for hybrids with mercaptoalkyl and aminoalkyl substituted matrices.

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1. Introduction

Silica matrix is an effective carrier of different molecules such as metal complexes [1]. Obtained hybrids have a good chemical and thermal stability [2]. There are different methods for production of such hybrid structures [3]. The sol-gel synthesis is used more often than the others because of its easiest realization and possibility to vary the structure and morphology of products [4]. Metal complexes of phthalocyanines (MePc) could be used as the organic fragment of such systems [5] for the following practical applications: nonlinear optics [6], photodynamic therapy [7] and as effective catalysts [8]. Silicon alkoxides, e.g. tetraethoxysilane (TEOS) [9], and their organically modified analogs [10] could be used as the precursors for silica matrixes.

Sol-gel method were used in present work for the synthesis of organically modified silica matrixes with cobalt (II) tetrasulfophthalocyanine (CoPc). Three different precursors: mercaptopropyltrimethoxysilane (MPTMOS), aminopropyltrimethoxysilane (APTAMOS), chloropropyltrimethoxysilane (CPTMOS) were used

for matrix synthesis. The precursor variation allowed us to investigate the influence of matrix nature on the degree of complex immobilization and catalytic activity of anchored CoPc. CoPc immobilized on non-modified silica was used for comparison.

2. Experimental

2.1. Reagents

Cobalt phthalocyanine tetrasulfonic acid (CoPc, Fig. 1) was synthesized by a known Weber-Busch method [11]. Obtained blue – green precipitate was separated by filtrating, washed with ethanol-methanol mixture (3:1) and dried. The regioisomeric mixture of sulfonated phthalocyanines was the final reaction product. Structure of complex was confirmed by methods of electronic absorption spectroscopy, IR-spectroscopy, ¹H NMR and elemental analysis.

IR spectra (KBr ν , cm^{-1}) 1720, 1632, 1502, 1452, 1489, 1409, 1379, 1134, 1049, 935, 770, 618. Elemental analysis for $\text{C}_{32}\text{H}_{16}\text{N}_8\text{O}_{12}\text{S}_4\text{Co}$, %: C 39.51, H 1.87, N 11.53. Found: C 37.82, H 1.79, N 11.18. ¹H NMR (500 MHz): δ_{H} 7.91 (Ar-H), 8.29 (Ar-H), 8.53 (Ar-H).

Tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$, 99.99% “Ecos-1”, Russia), triethylamine ($\text{N}(\text{C}_2\text{H}_5)_3$, 99.5%, “Panreac”, E.U.), sodium diethyldithiocarbamate ($\text{C}_5\text{H}_{10}\text{NS}_2\text{Na}$, 99%, “Chimmed”, Russia) were used without additional purification. Copper sulfate (CuSO_4 , 98%, “Chimmed”, Russia) was dried in vacuum oven at 353 K. Mercaptopropyltrimethoxysilane ($\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ “Aldrich”,

Abbreviations: CoPc, cobalt (II) tetrasulfophthalocyanine; TEOS, tetraethoxysilane; MPTMOS, mercaptopropyltrimethoxysilane; APTAMOS, aminopropyltrimethoxysilane; CPTMOS, chloropropyltrimethoxysilane; DTC, sodium *N,N*-diethylcarbamodithioate.

* Corresponding author.

E-mail addresses: y.marfin@gmail.com (Y.S. Marfin), asvashurin@mail.ru (A.S. Vashurin).

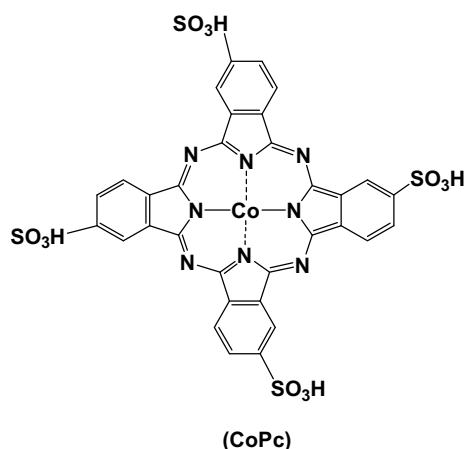


Fig. 1. Structural formula of investigated CoPc.

USA), chloropropyltrimethoxysilane ($\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, “Aldrich”, USA), aminopropyltrimethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, “Aldrich”, USA) (Fig. 2).

Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99%, “Chimmed” Russia), was dried with metallic Sodium before using; chloroform (CHCl_3 , 99.9%, “Chimmed” Russia) was dried using the method described in [12] before the experiment. Chloroform fraction with boiling point temperature of 343.3 K was used. Bidistilled water was used in all experiments.

2.2. Equipment

Characteristics of light absorption of hybrid materials aqueous suspensions or solutions for catalytic experiments (in that case the studying system was filtered to remove the catalyst particles prior to the spectral experiment) were recorded on in 190–1100 nm wavelength range by the spectrophotometer UV1800 (“Shimadzu”, Japan). Investigations were carried out in quartz cuvettes with a thickness of the absorbing layer of 10 mm placed in a Peltier thermostatic cell at 298 K. The IR spectra of hybrid materials samples in KBr tablets were recorded with a FT-IR spectrophotometer Avatar 360 FT-IR spectra (“Thermo Nicolet”, USA) in the frequency range of 400–4000 cm^{-1} at room temperature.

Particle size of synthesized materials was measured by laser diffraction method with Analysette 22Compaq («FRITCH», Germany). Water suspension under the constant stirring was used

for the experiment. Aggregates were crushed by ultrasonic treatment before the experiment.

Hybrid materials were analyzed with SEMLEO 1550 scanning microscope in the Center of Micro-Nanotechnology (CMI), EPFL. Ethanolic suspensions of hybrid materials were prepared for the analysis (5 ml ethanol and 20 mg of sample). Obtained suspensions were deposited by monolayer on spherical copper substrate with 1 cm radius and dried at room temperature on air and then with vacuum. This samples were loaded in electron microscope cell and exposed to vacuum of 10^{-7} mbar. Working distance between the electron gun and surface of the sample was 3–4 mm. Electron supply voltage was a 3–5 kV. Surface study of the samples was done with two types of signal: 1) InLens (high definition detector); 2) SE2 (topography detector). Scanning speed was varied from 1 to 3 pixel averaging.

Atomic-force microscopy in contact mode was done by atomic-force microscope SolverP47-PRO («NT-MDT», Russia) with «Nova» PC program package. Scanning step was 0.6 nm.

pH values of the solutions were controlled with pH meter S220 Seven Compact (Metler Toledo, Switzerland). Relative error of pH determining was ± 0.002 .

Oxygen concentration were maintained in reactor via micro compressor. Solvated oxygen concentration control was made with Portable DO Meter FG4 (Metler Toledo, Switzerland).

2.3. Hybrid materials synthesis

Hybrid materials were synthesized and purified in accordance to previously described technique [13]. Appropriate alkoxide was used as a precursor in the synthesis. The following molar ratio of the reactants was used:

Alkoxide: H_2O : $\text{C}_2\text{H}_5\text{OH}$ – 1:4.5:10

Triethylamine as a polycondensation catalyst was added dropwise to the reaction mixture each 10 min after the homogenization of reaction mixture (Total volume of added catalyst was 0.35 ml). The resulting hybrid materials were dried under vacuum at gradually raising temperature up to 353 K. Drying was stopped after reaching a constant mass of the sample. After drying the hybrid materials were washed 3 times with water: the amount of solvent in each of the washes was 10 ml; the suspensions were stirred for 5 min, centrifuged and the solutions were separated from the sediments. All portions of the washed liquid were poured and the total amount of non-entrenched complex was determined for each hybrid. CoPc free matrixes were synthesized in all cases

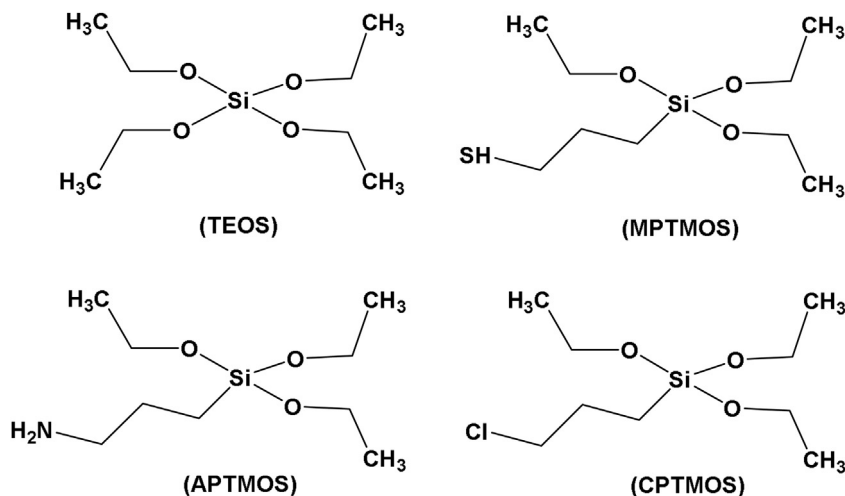


Fig. 2. Structure of used matrix precursors.

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