

Heterogenized Platinum Group Metal Porphyrinates: Catalytic Activity in Liquid-Phase Hydrogenation Reactions

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Dedicated to Professor Andrej Fedorovich Mironov on the Occasion of his 80th Birthday

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This paper describes the first systematic study of the catalytic activity of palladium, ruthenium and osmium 2,3,7,8,12,13,17,18-octaethylporphyrinates heterogenized on silica gel in the reactions of liquid-phase hydrogenation of organic compounds. Parameters of the catalytic activity of the studied porphyrin/silica gel systems in the reduction of substances containing nitro group and double bond were obtained. The possibility to adjust the activity and selectivity of the hydrogenation reactions catalysts based on porphyrin complexes by varying the nature of central metal cation and mass ratio of the impregnated complex was shown. The dependence of reduction selectivity on the presence of substituents in the organic substrate was established for nitrobenzenes.

Keywords: Porphyrin, complex, palladium, ruthenium, osmium, hydrogenation, nitrobenzene, supported catalyst.

Каталитические свойства гетерогенизированных порфиринов металлов платиновой группы в реакциях жидкофазной гидрогенизации

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Впервые проведено систематическое исследование каталитической активности гетерогенизированных на силикагеле 2,3,7,8,12,13,17,18-октаэтилпорфиринов палладия, рутения и осмия в реакциях жидкофазного гидрирования органических соединений. Получены параметры каталитической активности изученных систем порфирин/силикагель при восстановлении веществ, содержащих нитрогруппу и двойную связь. Показана возможность регулирования активности и селективности катализаторов реакций гидрогенизации на основе комплексов порфиринов варьированием природы центрального катиона металла и массовой доли нанесённого комплекса. Установлена избирательность восстановления нитробензолов в зависимости от наличия заместителя в органическом субстрате.

Ключевые слова: Порфирин, комплекс, палладий, рутений, осмий, гидрирование, нитробензол, нанесенный катализатор.

Introduction

The processes of liquid-phase hydrogenation of organic compounds is widely employed in many areas of chemistry and chemical technology: in fine organic synthesis, in the production of pharmaceuticals, perfumery materials, additives to polymers, rubber and motor fuel *etc.* One of the fundamental problems of fine organic synthesis is the design of novel catalysts with the desired activity parameters, while selectivity and environmental safety are currently having an ever increased priority. Thus, highly selective catalysts that model natural enzymes, are of a specific interest.

Transition metal phthalocyanines and porphyrinates are known to be a promising group of redox reactions catalysts.^[1] The ability of metal porphyrinates to catalyze oxidation of organic and inorganic compounds is directly linked to the possibility of axial coordination of various substrates and on their activation. It should be noted that metal porphyrinate catalysts have found an important application in the catalytic oxidation of hydrogen sulfide, mercaptans and other RSH compounds with atmospheric oxygen.^[2] These processes are by now used in desulfurization of oil refining products and natural gas, wastewater, in the production of rubber accelerators and some pharmaceuticals. Complexes of transition metals with porphyrin and phthalocyanine ligands have proved to be efficient reduction catalysts for some nitrogen-containing compounds such as nitrate and nitrite,^[3,4] unsaturated compounds,^[5] ketones^[6] and solvated protons.^[7] It stands to mention that the majority of studies covering the catalytic properties of porphyrins has been conducted on homogenous systems.^[1,2,8,9] Therefore, extending the scope of the search for novel porphyrin catalysts unambiguously presents a significant scientific and practical interest.

An important matter, clearing of which would allow the synthesis of novel compounds with the desired set of properties, is finding correlations of adsorption and catalytic properties of porphyrins, in particular heterogenized on various carriers, with the structure of the macrocyclic ligand, the nature of the central metal atom^[1,2,8,9] and the reaction medium.^[10] Thus, particularly interesting are the porphyrins with pronounced electron-withdrawing properties that can act as electron scavengers and stabilize the central metal cation in lower oxidation states or unusual spin states. Presumably, such compounds would exhibit specific catalytic properties in reduction reactions.

The poor solubility in organic solvents and the low specific surface area are known to limit the application of crystalline metal porphyrinates in heterogeneous catalysis as most of the active sites are unavailable to the reactants. One of the ways to improve the efficiency of porphyrin catalysts is their "heterogenization", *i.e.* impregnation of carriers with extended surface.

Though some data on heterogenization of porphyrins has been published,^[11,12] many aspects remain debated, such as the localization of the active sites, the symmetry of the impregnated complex and its orientation in relation to the carrier surface, as well as the nature of interaction between the catalyst and the carrier. As these factors play a major role in defining the catalytic properties, it is fair to say that the choice of the carrier is crucial in the creation of catalysts

based on metal porphyrinates. Different grades of silica gel are optimal carriers according to the literature data.

The goal of the present study is to investigate the catalytic activity of metal porphyrinates, heterogenized on silica gel, in hydrogenation reactions of unsaturated organic compounds bearing a nitro or a carboxyl group as well as the search of activity-nature of the central atom correlations.

Experimental

Palladium(II) 2,3,7,8,12,13,17,18-octaethylporphyrinate and ruthenium(II) and osmium(II) aqua carbonyl 2,3,7,8,12,13,17,18-octaethylporphyrinates were used in the work.

Palladium(II) 2,3,7,8,12,13,17,18-octaethylporphyrinate (PdOEP) was synthesized according to known procedure^[13] by heating for 2 h a solution of the ligand porphyrin and 3-fold palladium chloride in refluxing dimethyl formamide. The solvent was then distilled off and the residue was dissolved in chloroform and subjected to chromatography on silica gel. UV-Vis (benzene) λ_{\max} nm (lg ϵ): 547.0 (4.81), 513.0 (4.42), 394.0 (5.30). ¹H NMR (CDCl₃, 500 MHz) δ ppm: 10.12 s (4H, *meso*-H), 4.10 q (16H, CH₂-ethyl), 1.90 t (24H, CH₃-ethyl); HMDS was used as the internal standard.

Ruthenium(II) aqua carbonyl 2,3,7,8,12,13,17,18-octaethylporphyrinate (RuOEP) was synthesized according to the known procedure^[14] by refluxing for 3 min a phenolic solution of 2,3,7,8,12,13,17,18-octaethylporphyrin and Ru₃(CO)₁₂. The cooled reaction mixture was dissolved in chloroform, consequently washed with water, weak alkali and again water, then subjected to chromatography on silica gel eluting with a benzene:methanol 100:1 mixture. UV-Vis (benzene) λ_{\max} nm (lg ϵ): 550.0 (4.34), 519.0 (4.11), 397.0 (5.24). ¹H NMR (CDCl₃, 500 MHz) δ ppm: 9.95 s (4H, *meso*-H), 4.05 q (16H, CH₂-ethyl), 1.95 t (24H, CH₂-ethyl), 0.08 s (2H, H₂O); HMDS was used as the internal standard.

Osmium(II) aqua carbonyl 2,3,7,8,12,13,17,18-octaethylporphyrinate (OsOEP) was obtained in a similar manner to the ruthenium porphyrinate. The reaction time was 10 min. UV-Vis (benzene) λ_{\max} nm (lg ϵ): 537.0 (4.34), 509.0 (4.11), 394.0 (5.24). ¹H NMR (CDCl₃, 500 MHz) δ ppm: 9.93 s (4H, *meso*-H), 3.99 q (16H, CH₂-ethyl), 1.83 t (24H, CH₂-ethyl), 0.06 s (2H, H₂O); HMDS was used as the internal standard.

The catalysts were prepared by precipitating the porphyrin complexes onto the surface of silica gel (supplied by Scientific Adsorbents, 63-200 mesh, specific surface 480 m²/g, pore volume 0.75 cm³/g (60 Å)) from saturated solutions in benzene being evaporated with constant vigorous stirring of the suspensions. The mass ratio of the impregnated tetrapyrrolic complexes was 0.5 %, thereby the active component content in the catalysts was: PdOEP – 7.8 μ mol/g, RuOEP – 7.8 μ mol/g, OsOEP – 6.5 μ mol/g

The catalytic properties of thus produced samples of heterogenized porphyrinates (PdOEP/SiO₂, RuOEP/SiO₂, OsOEP/SiO₂) were studied for nitro group and double bond (carbon-carbon and carbon-oxygen) reduction in the following molecules: nitrobenzene, 4-nitrophenol, sodium maleate and acetone. These model compounds were chosen as their reduction mechanisms are well studied.^[15-21] Water was used as the reaction medium.

Hydrogenation was conducted by a static method in a closed vessel with varied stirring rate of the liquid phase (5 to 60 rps) which allowed the exclusion of the external mass transport influence on the experimental data. The design of the reactor enabled the measurement of the reaction rate by the volume of consumed hydrogen. The used procedure for the kinetic experiment is described elsewhere.^[15,19]

Correlations of the absorbed hydrogen and the reactant concentrations with the reaction time were observed in the course of the experiment. The data set obtained in a series of parallel experiments was used to construct kinetic curves for the reactions

Table 1. Conditions of the liquid-phase hydrogenation reactions.

Substrate	Catalyst	T, K	V _{solvent} , ml	m _{cat} , g	m _{sub} , g	Stirring rate, rps
4-nitrophenol	PdOEP/SiO ₂	303, 323	70	0.5	0.025, 0.140	5–60
	RuOEP/SiO ₂			0.8		
	OsOEP/SiO ₂			1.0		
nitrobenzene	PdOEP/SiO ₂	303, 323	70	0.5	0.025, 0.140	5–60
	OsOEP/SiO ₂			1.0		
sodium maleate	PdOEP/SiO ₂	303, 323	70	0.5	0.8	5–60
	RuOEP/SiO ₂			1.0	1.6	
acetone	PdOEP/SiO ₂	303, 323	70	0.5	0.025	5–60
	OsOEP/SiO ₂			1.0	0.140	

and to calculate the hydrogenation reaction rates on the basis of hydrogen, intermediate and final products, including the cases of high and low concentrations of the substances being hydrogenated. The utilized procedures of kinetic measurements allowed the determination of reaction rates and constants with a 3.5–7 % experimental error.

The reaction conditions for liquid-phase hydrogenation of the model compounds on the studied catalyst samples are presented in Table 1.

The composition of the reaction mixtures in the course of the reactions was performed by liquid chromatography on a Shimadzu LC-6A instrument equipped with an UV-VIS detector (tungsten and deuterium lamps). The immobile phase was Lichrosorb RP-18 (5 μm particles), while the mobile phase was aqueous acetonitrile. The optimal column temperature and the exact eluent composition were matched individually for each system. Calibration using pure starting compounds and final products as well as their mixtures was conducted before the analysis. The relative error of the concentration determinations did not exceed 1.5–3.5 %.

Results and Discussion

Preliminary experiments demonstrated that catalyst samples which exhibited activity in liquid-phase hydrogenation

reactions were the ones with the mass ratio of the heterogenized metal porphyrinates less than 1 %. This is explained by the blocking of the carrier pores with porphyrin crystals when their content is high. When the system was preliminary saturated with hydrogen, in no case the adsorption of hydrogen was observed.

The catalysts did not change their chemical composition in the course of the reaction, which is confirmed by the absence of their transformation products when the heterogenized catalysts were washed away from the carrier surface after the process and analyzed by HPLC and UV-Vis spectroscopy (Figure 1).

Kinetic curves for the hydrogenation of 4-nitrophenol on all the catalyst types have a definite signature with areas of zero (white dots) and first order for high and low concentrations of the substrate, correspondingly (Figure 2). As the monitoring analysis for OsOEP/SiO₂ shows, the reaction proceeds to amines as the final products, while in the PdOEP/SiO₂ systems insignificant amounts of the intermediate products – azoxy- and azophenols – of homogeneous nitro group hydrogenation were (Table 2, Figure 3). In the latter case, condensation mechanism of hydrogenation is supposedly realized.

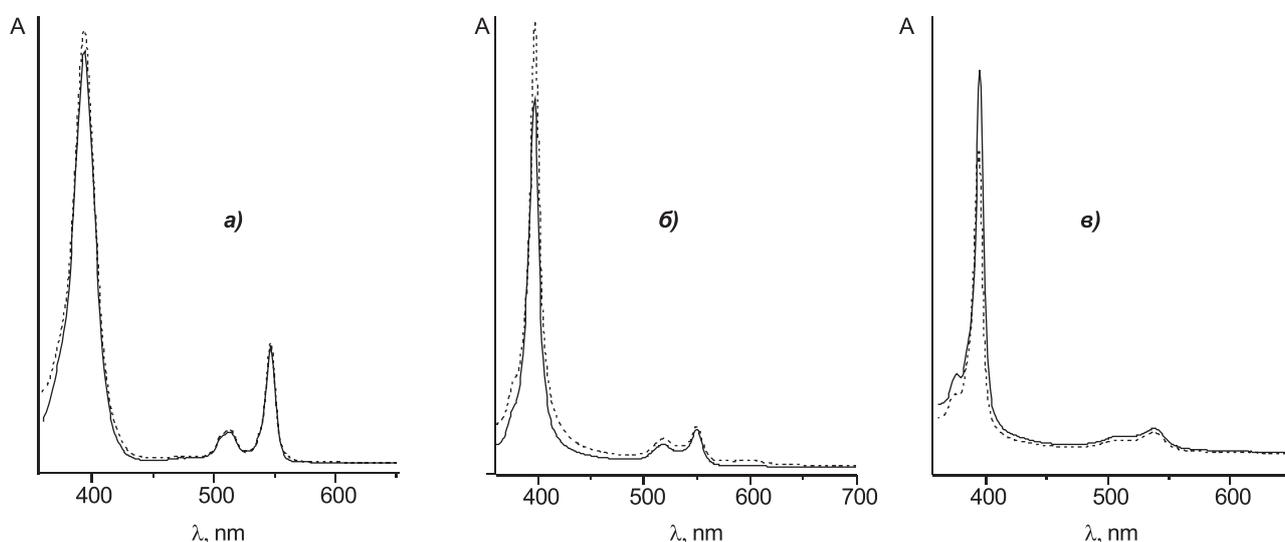


Figure 1. Electronic absorption spectra of metal porphyrinates before (—) and after (---) the course of the hydrogenation of 4-nitrophenol: a) PdOEP/SiO₂, b) RuOEP/SiO₂, c) OsOEP/SiO₂.

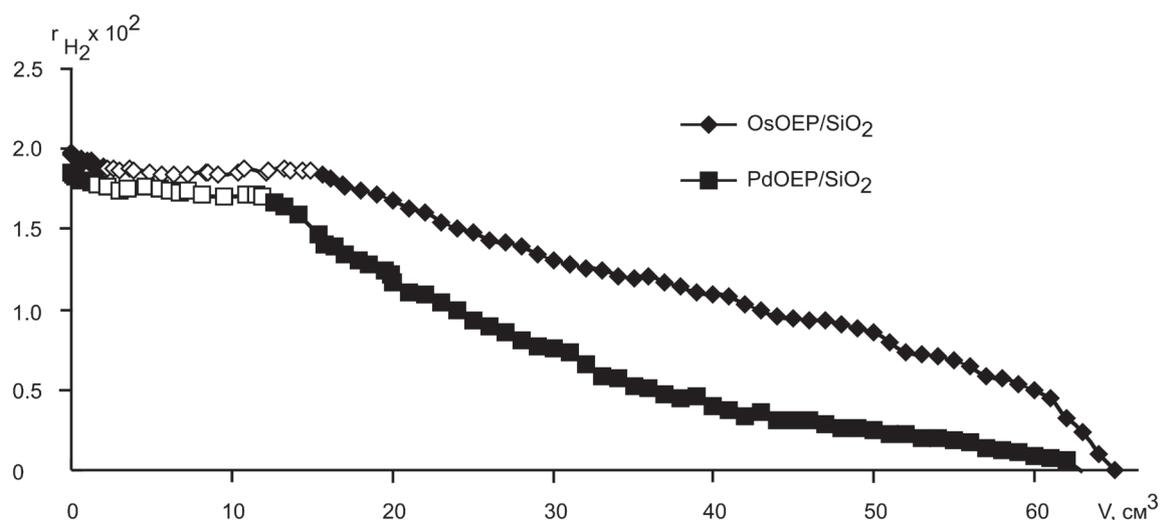


Figure 2. Kinetic curves for the hydrogenation of 4-nitrophenol in water at 303 K on PdOEP/SiO₂ and OsOEP/SiO₂ catalysts.

Table 2. Quantitative analysis of the liquid phase for the hydrogenation of 4-nitrophenol on OsOEP/SiO₂ and PdOEP/SiO₂.

Time, min	Composition of the hydrogenate	Concentration of 4-aminophenol in solution, mol/L	Conversion, %
	OsOEP/SiO ₂		
5	4-nitrophenol	<10 ⁻⁶	0
1200	4-nitrophenol, 4-aminophenol	0.0031	30
2160	4-nitrophenol, 4-aminophenol	0.0062	60
2540	4-aminophenol	0.0093	99
	PdOEP/SiO ₂		
5	4-nitrophenol	<10 ⁻⁶	0
960	4-nitrophenol, 4-aminophenol, traces of intermediates	0.0024	20
1960	4-nitrophenol, 4-aminophenol, traces of intermediates	0.0057	54
2460	4-nitrophenol, 4-aminophenol, traces of intermediates	0.0078	75
3000	4-aminophenol, traces of non-identified intermediates	0.0093	99

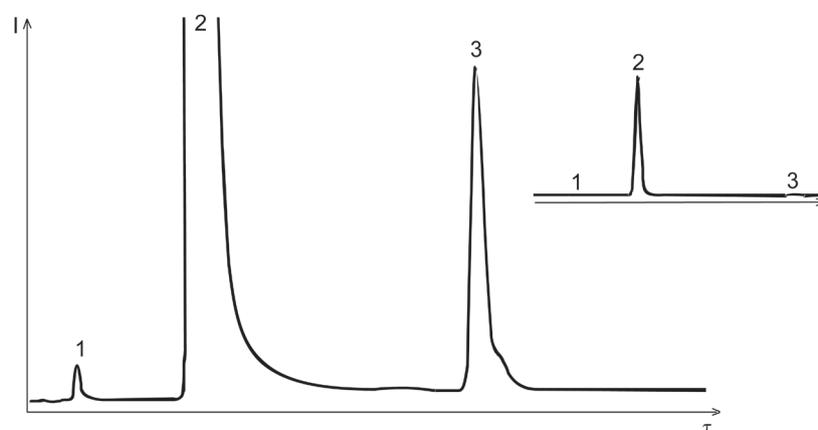


Figure 3. Hydrogenate chromatograms at 2500 min reaction time for hydrogenation of 4-nitrophenol on PdOEP/SiO₂ at 303 K: 1 – water; 2 – 4-aminophenol; 3 – 4-nitrophenol.

Table 3. Activity parameters of the catalysts for the model substrates hydrogenation at atmospheric pressure and 303 K.

Substrate	$r_{H_2}^0$, cm ³ (H ₂)/min g(MeOEP/SiO ₂)	$r_{H_2}^{1500}$, cm ³ (H ₂)/min g(MeOEP/SiO ₂)	$r_{H_2}^{2500}$, cm ³ (H ₂)/min g(MeOEP/SiO ₂)	$k_{H_2}^{0-500}$, s ⁻¹	Reaction time, min
PdOEP/SiO ₂					
acetone	0.035±0.007	0.026±0.005	0.030±0.006	0.047±0.002	1500±20
4-nitrophenol	0.020±0.004	0.011±0.002	0.0020±0.0004	0.050±0.002	3000±20
nitrobenzene	zero activity				
RuOEP/SiO ₂					
4-nitrophenol	0.042±0.004	0.032±0.004	0.010±0.002	0.047±0.002	2500±20
nitrobenzene	zero activity				
OsOEP/SiO ₂					
4-nitrophenol	0.021±0.004	0.017±0.004	0.010±0.002	0.055±0.002	2540±20
nitrobenzene	zero activity				

The results of the kinetic experiment allow to calculate the parameters of catalytic activity of the studied catalyst samples (Table 2). The activity was characterized by the observed reaction rate constant of first order on the basis of the substrate and of zero order on the basis of hydrogen.

The collected data demonstrate that the studied catalyst samples exhibit catalytic activity for the reduction of nitro group but are almost completely inactive towards carbon-carbon double bonds. In all cases the observed reaction rates (r_{H_2}) do not exceed 5 cm³(H₂)/(min·g(MeOEP/SiO₂)), and thus the reaction can be considered to proceed in the kinetic area while diffusion steps do not influence the observed reaction rate,^[15,18] so it is not practical to calculate reaction rates and constants for the reactions on the catalyst surface and the catalytic activity can be characterized solely by the observed kinetic parameters.

Hydrogenation of all the chosen model compounds except for sodium maleate is known to proceed via a number of subsequent and parallel steps.^[15,18,19] However the stoichiometry of the nitro group hydrogenation calculated with respect to the absorbed hydrogen was close to 2.9±0.1 for all systems, which conforms to selective hydrogenation into the corresponding amines. This is confirmed by the absence of significant amounts of intermediates in the hydrogenates (Table 2). The observed rates of hydrogenation calculated on the basis of changes in the concentrations of the model compounds were close to ones calculated using hydrogen adsorption rates. This demonstrates that the substrates do not react with the catalysts, for that would result in a significant drop of the catalytic activity.

The reaction rates and constants for the PdOEP/SiO₂ system decrease considerably when it is repeatedly used. Consumption of hydrogen is observed in this case when the system is preliminary saturated, in contrast to primary experiments. This might be caused by trace remnants of adsorbed 4-nitrophenol and its derivatives on the catalyst surface. The structure of the catalyst remains intact.

On the basis of the collected data we assert that metal porphyrinates, heterogenized on silica gel possess catalytic activity in liquid-phase hydrogenation reactions. It was demonstrated that the activity and selectivity of such systems

can be adjusted by variations of the central metal cation and the porphyrin ligand. This evidence allows to perform a guided search of catalysts with a desired set of properties. Furthermore, we demonstrated a considerable influence on the catalytic activity of the heterogenized porphyrins of the nature of substituents in nitrobenzenes. For instance, PdOEP/SiO₂ had zero catalytic activity in the reduction of nitrobenzene, while 4-nitrophenol was reduced by the same system to 4-aminophenol. This testifies the selectivity of the PdOEP/SiO₂ system in hydrogenation reactions of nitro compounds.

The measurements of the reaction rates were conducted at different temperatures and with varied rates of stirring of the reaction mixtures. It was found in the course of the study that the rates of hydrogenation insignificantly depend on the temperature and do not depend on the stirring rate. Therefore we conclude internal diffusion to be the limiting reaction step. Thus the hydrogenation reactions supposedly proceed via the condensation mechanism: first, adsorption of all the reactants occurs, followed by their migration to the active sites of the porphyrin where the chemical reaction takes place, resulting in the formation of intermediates, which is confirmed by chromatographic monitoring of the liquid phase. The resulting observed rate of hydrogenation is thus determined in the first place by the structure of the carrier (silica gel) and to a lesser extent by the nature of the metal in the complex. However, the ionic radius of the metal determines the tolerance of the system to contamination with reaction intermediates which decreases the hydrogenation. Hereby the less pronounced decrease of the reaction rate for OsOEP/SiO₂ compared to PdOEP/SiO₂ can be explained.

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