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Preparation of Nitrogenous Polysaccharide-Supported Ironporphyrins and Their Catalysis for the Aerobic Oxidation of Cyclohexane[1]

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Abstract—The coordinations of nitrogenous polysaccharide chitosan and chitin to chloro[tetraphenylporphinato]iron(III) have been investigated by means of the FTIR and UV–VIS analysis techniques, and the effect of their coordination on the aerobic oxidation of cyclohexane catalyzed by ironporphyrin has been studied. The new Fe–N coordination bonds between ironporphyrin and chitosan or chitin were found, and their coordination constants K, which were calculated by means of Langmuir's adsorption isotherm equation, were 9.68×10^{-4} and 6.80×10^{-4} L/mol, respectively, at equilibrium. It is shown that the coordination of the nitrogenous polysaccharide to ironporphyrin had an important influence on both the conversion and selectivity of the aerobic oxidation of cyclohexane catalyzed by ironporphyrin. The selectivity to the cyclohexanone and cyclohexanol production, the catalyst turnover, and the rate constants k of cyclohexane oxidation increased with increasing coordination constant K.

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The axial nitrogenous ligand was considered to be a key factor in controlling the catalytic activity of the cytochrome P-450 monooxygenase enzyme, and much effort has been made in the last two decades towards studying the effect of the axial nitrogenous ligand on the catalysis of metalloporphyrins for the oxidation of various substrates [1–4]. Collman, Gross, and others have provided experimental evidence of the marked influence of adding small nitrogenous molecules such as pyridine and imidazole into the metalloporphyrin catalyst systems on the activation of the catalyst and the product selectivity of catalytic olefin oxidation [5–11]. Gilmartin, Yassuko, and others have also found that there is an enhancement of the catalytic activation and the yield of products in the oxidation of alkane and olefin catalyzed by metalloporphyrins that were coordinated to pyridine- or imidazole-modified silica gel or resin [12–15]. However, according to our knowledge, there are very few reports about the coordination of the nitrogenous polysaccharides with metalloporphyrins and the effect of this coordination on the catalytic properties of metalloporphyrin for hydrocarbon oxidation processes.

In an earlier paper [16], we reported the preparation of partly deacetylated chitosan-supported ironporphyrin and its catalysis for the aerobic oxidation of cyclohexane in the absence of any coreductants and solvents, finding that the coordination between partly deacetylated chitosan and ironporphyrin increased the yields and selectivity of the aerobic oxidation of cyclohexane catalyzed by ironporphyrin. In order to investigate the reason why the nitrogenous biopolymers can enhance the catalytic ability of metalloporphyrins, we prepared both chitin-supported ironporphyrin and completely deacetylated chitosan-supported ironporphyrin and studied the Fe–N coordinate behavior between ironporphyrin and the nitrogenous group of polysaccharides; we also determined the corresponding coordinate constants K of the ironporphyrin with different nitrogenous polysaccharides by means of Langmuir's adsorption isotherm equation, and then investigated the effects of the coordination on the cyclohexane oxidation catalyzed by polysaccharide supported ironporphyrin.

EXPERIMENTAL

Instrument and reagents. IR spectra were recorded on a Perkin-Elmer Model 783 IR spectrophotometer. UV–Visible spectra were obtained with a Perkin-Elmer L-17 UV–Visible spectrometer. GC analysis of catalytic oxidation products was performed on a Shimadzu GC-16A chromatography. The reaction equipment is a MODEL 3KCF-10-500 ml high-pressure tank fitted with a magnetic stirrer and a MODEL CYS-1 digital oxygen detector.

All reagents and solvents used were analytical grade and were obtained commercially. Chloro[tetraphenylporphinato]iron(III) was synthesized according to the literature method [17, 18]. Chitosan was confirmed to be completely deacetylated by means of the IR analysis technique. No oxidation products were found in

[1] The text was submitted by the authors in English.

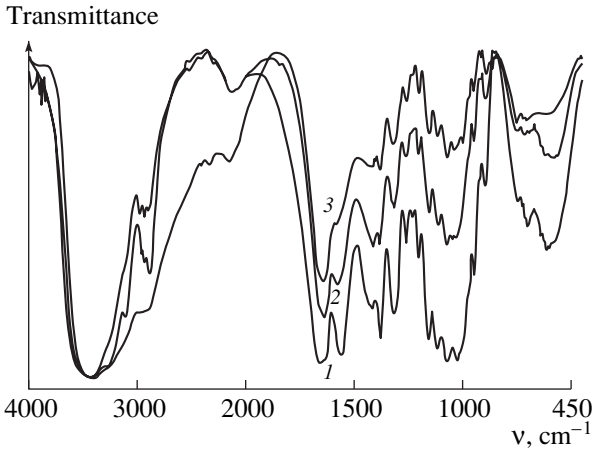

Fig. 1. IR spectra of chitosan (*1*), a mixture of chitosan and ironporphyrin (*2*), and a chitosan–ironporphyrin complex (*3*).

the raw material of cyclohexane with the use of GC analysis.

Preparation of Chitin and Chitosan-Supported Ironporphyrin Complexes

Chitin-supported ironporphyrin complexes. A mixture of 20 ml concentrated hydrochloric acid and 2 g chitin was stirred in a three-neck flask with a condensation tube and an electromagnetic stirrer at 25°C for 3 h; then, 200 ml of distilled water was added into this reaction system to form the colloidal solution; next, a 40% NaOH solution was slowly added until the pH value of the colloidal solution reached about 6.5. Moreover, 0.100 g chloro[tetraphenylporphinato]iron(III) dissolved in 100 ml chloroform was slowly dropped into the reaction system. After 2 h, the reaction was stopped, the reaction solution was filtered, and the filter cake was dried at 60°C and then repeatedly refluxed with $CHCl_3$ in a soxhlet apparatus until no chloro[tetraphenylporphinato]iron(III) was found in the solvent with the use of a UV–Visible spectrometer; 1.97 g brown solid product was obtained by means of drying the cake at 60°C. The filtrate was used to determine the amount of chloro[tetraphenylporphinato]iron(III) in the solid product. The amount of chloro[tetraphenylporphinato]iron(III) in 1 g chitin was determined to be 0.0264 mmol by means of the UV–VIS spectroscopy technique [19].

Chitosan-supported ironporphyrin complexes. A mixture of 100 ml diluted hydrochloric acid and 2 g completely deacetylated chitosan was stirred in a three-neck flask with a condensation tube and an electromagnetic stirrer at 25°C for 15 min. Then, 200 ml distilled water and 1% Na_2CO_3 solution were slowly added into the reaction liquid in turn until the reaction mixture became neutral. 1.80 g chitosan-supported ironporphyrin was obtained in the same way as the preparation of chitin-supported ironporphyrin. The amount of chloro[tetraphenylporphinato]iron(III) in 1 g chitosan was determined to be 0.0447 mmol by means of the UV–VIS spectroscopy technique [19].

Determination of the coordinate constants of the chitin and chitosan-supported ironporphyrin complexes. 0.020 g chitin was highly dispersed in 20 ml H_2O under violent stirring, and 10 ml given concentration of a chloroform solution of chloro[tetraphenylporphinato]iron was dropped into the system. After 2 h, the reaction was stopped and stilled for a while, the supernatant chloroform was taken out, and the corresponding equilibrium concentration of chloro[tetraphenylporphinato]iron was determined by means of the UV–VIS spectroscopy technique [19]. This procedure was repeated for different concentrations of the chloroform solution of chloro[tetraphenylporphinato]iron. By comparing the concentration of chloro[tetraphenylporphinato]iron in the original solution with the equilibrium concentration of chloro[tetraphenylporphinato]iron in the corresponding supernatant chloroform, the coordinate constant k between chitin and chloro[tetraphenylporphinato]iron can be evaluated by Langmuir's adsorption isotherm equation. The coordinate constant k between chitosan and chloro[tetraphenylporphinato]iron can be obtained through the same procedure.

The Aerobic Oxidation of Cyclohexane Catalyzed by the Chitin and Chitosan-Supported Ironporphyrin Complexes

0.77 g of chitin-supported ironporphyrin (containing 0.0071 mmol ironporphyrin) and 350 ml cyclohexane were poured into a 500 ml high-pressure reactor and stirred and heated to 418 K. Then, air was continuously pumped into the reaction system, and the reaction pressure was kept at 0.8 MPa. The reaction mixture sampled was analyzed according to the literature [20]. The same procedure was also applied to the aerobic oxidation of cyclohexane catalyzed by chitosan-supported ironporphyrin complexes.

RESULTS AND DISCUSSION

Coordination of Chitin or Chitosan-Supported Ironporphyrin

Chitin or chitosan can coordinate with ironporphyrin to form chitin- or chitosan-supported ironporphyrin complexes. The color and solubility of chitin- or chitosan-supported ironporphyrins are different from that of chitin, chitosan, and ironporphyrin.

The IR spectra of chitin (*1*), a mixture of chitin and ironporphyrin (*2*), and a chitin–ironporphyrin complex (*3*) are shown in Fig. 1.

The characteristic IR absorption peak of the N–H of the amino group of chitosan is at 1599 cm^{-1}, and the characteristic IR absorption peak of the N–H of the amino group of chitosan-supported ironporphyrin com-

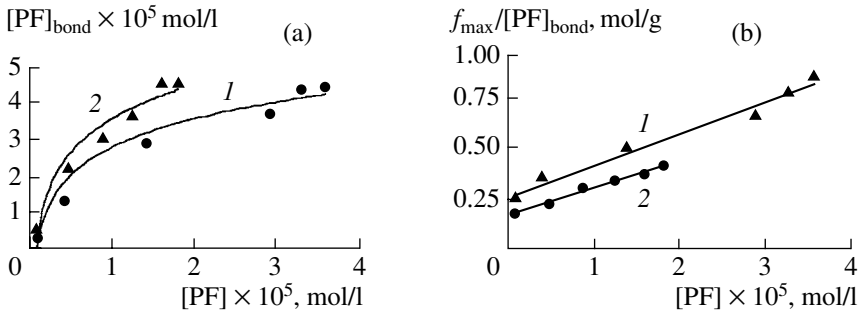

Fig. 2. (a) The relationships between the amount ($[PF]_{bond}$) of ironporphyrin adsorbed by (*1*) chitin or (*2*) chitosan and the equilibrium concentration ([PF]) of ironporphyrin in the supernatant chloroform. (b) The same on the Arrhenius coordinates.

plex was shifted to 1519 cm^{-1}. Similarly, the characteristic IR absorption peak of the N–H of the amino group of chitin–ironporphyrin complex was shifted from 1571 cm^{-1} of chitin to 1556 cm^{-1}. The change of the characteristic IR absorption peak of the N–H of the amino group showed that a new Fe–N coordinate bond had been formed between chitin or chitosan and ironporphyrin [21–23]. The characteristic IR absorption peak of the C=O of the amido group of chitin-supported ironporphyrin complex was shifted from 1631 cm^{-1} of chitin to 1659 cm^{-1} because of the coordination between chitin and ironporphyrin. This further proved the formation of an Fe–N coordinate bond between chitin and ironporphyrin.

The coordinate constants *K* of chitin and chitosan to ironporphyrin. The research [24, 25] shows that the coordination between macromolecules and metal complexes obey Langmuir's adsorption isotherm equation if the adsorption is a single-molecule-layer, and the amount of metal complexes adsorbed by macromolecules is related to the equilibrium concentration of metal complexes in the solution. Figure 2a shows the relationships between the amount ($[PF]_{bond}$) of ironporphyrin adsorbed by chitin or chitosan and the equilibrium concentration ([PF]) of ironporphyrin in the supernatant chloroform. It can be seen from Fig. 2a that the ironporphyrin amount ($[PF]_{bond}$) adsorbed by chitosan was more than that adsorbed by chitin under the same reaction conditions. This phenomenon evidenced that the adsorption force of chitosan to ironporphyrin was greater than that of chitin to ironporphyrin.

In order to study the coordination relation between ironporphyrin and chitin or chitosan, we change Fig. 2a into Fig. 2b according to Langmuir's adsorption isotherm equation:

$$\frac{[PF]}{[PF]_{bond}} = \frac{1}{Kf_{max}} + \frac{[PF]}{f_{max}}. \quad (1)$$

The straight curves *1* and *2* in Fig. 2b were obtained by plotting the $[PF]/[PF]_{bond}$ with [PF]. The straight lines evidenced that the ironporphyrin adsorption by chitin or chitosan obeyed Langmuir's adsorption principle. This indicated that the coordination of chitosan or chitin to ironporphyrin was a single-molecule-layer chemical adsorption because of the formation of the Fe–N coordinate bond between chitosan or chitin and ironporphyrin.

The data of coordinate constant *K* were obtained in light of Eq. (1) and are listed in Table 1; the value of coordinate constant of chitosan to ironporphyrin is higher than the one of chitin to ironporphyrin. The result showed that the bond of coordinating chitosan to ironporphyrin is stronger than that of coordinating chitin to ironporphyrin.

Catalysis of Chitin-Supported Ironporphyrin and Chitosan-Supported Ironporphyrin for Cyclohexane Oxidation with Air

Chitin-supported ironporphyrin and chitosan-supported ironporphyrin to catalyze the aerobic oxidation of cyclohexane into cyclohexanone and cyclohexanol was performed in the same way as with ironporphyrin. Figure 3 shows how the mole fraction of cyclohexanone and cyclohexanol in the oxidation reaction system changed with reaction time. It shows that the linear relationships between the mole fraction of cyclohexanone and cyclohexanol and reaction time existed in the range of 0.5–1.5 h for chitosan–ironporphyrin and 1–2 h for chitin–ironporphyrin, respectively. The reaction rate constants (k_{one} and k_{ol}), respectively, were calculated and are listed in Table 1. The data indicated that the reaction rate constants (k_{one} and k_{ol}) in the presence of chitosan–ironporphyrin were greater than that in the presence of chitin–ironporphyrin for the cyclohexane oxidation reaction process with air. The greater

Table 1. Coordinate constant *K* between ironporphyrin and chitin and chitosan and the rate constants *k* of ketone and alcohol of cyclohexane oxidation catalyzed by chitin- and chitosan-supported ironporphyrin

	$K \times 10^4$, l/mol	k_{one}, h^{-1}	k_{ol}, h^{-1}
Chitosan–ironporphyrin	9.68	0.0407	0.0362
Chitin–ironporphyrin	6.80	0.0232	0.0222

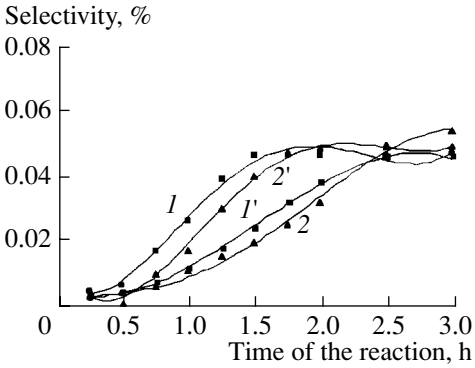

Fig. 3. Mole fraction (%) of cyclohexanone (*1*, *2*) and cyclohexanol (*1'*, *2'*) in the oxidation system as a function of reaction time (*t*) catalyzed by chitosan (*1*, *1'*) and chitin (*2*, *2'*) supported ironporphyrin, respectively.

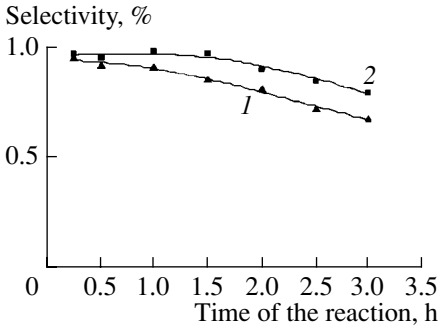

Fig. 4. Cyclohexanone and cyclohexanol selectivity (%) vs. reaction time (*t*): (*1*) chitin-supported ironporphyrin; (*2*) chitosan-supported ironporphyrin.

the coordination constant *K*, the greater was the reaction rate constant *k* of the cyclohexane oxidation with air.

Figure 4 shows the changes of selectivity of cyclohexanone and cyclohexanol with reaction time. It can be seen from Fig. 4 that the selectivity of cyclohexanone and cyclohexanol decreased with the increase of the reaction times and that the selectivity of cyclohexanone and cyclohexanol in the presence of chitosan-supported ironporphyrin was higher than that in the presence of chitin-supported ironporphyrin in the course of cyclohexane oxidation.

Table 2 displays the cyclohexane conversion and the catalyst turnover iron of the aerobic oxidation of cyclohexane catalyzed by the chitin, chitosan, unsupported ironporphyrin, chitin-supported ironporphyrin, and chitosan-supported ironporphyrin, respectively. The data in Table 2 show that chitin and chitosan could not catalyze the aerobic oxidation of cyclohexane, and the unsupported ironporphyrin and supported ironporphyrin could catalyze the aerobic oxidation of cyclohexane. Compared with ironporphyrin, the cyclohexane conversion and the catalyst turnover increased five times by chitosan–ironporphyrin and three times by chitin–ironporphyrin. Here, the chitosan–ironporphyrin, which had a greater coordination constant *K*, also possessed better catalytic power for the cyclohexane oxidation with air.

Table 2. The results of cyclohexane oxidations catalyzed by chitosan- and chitin-supported ironporphyrin and ironporphyrin with air*

	Conversion, %	Turnover**
Chitosan–ironporphyrin	8.76	39328
Chitin–ironporphyrin	5.01	21760
Ironporphyrin	1.81	8076
Chitin	0	–
Chitosan	0	–

* Reaction conditions: TPPFeCl, 0.0071 mmol; cyclohexane, 350 ml; temperature, 418 K; pressure, 0.8 MPa; reaction time, 1.5 h.

** Referred to one mole of iron atom.

The above result evidenced that the coordination between nitrogenous polysaccharides and ironporphyrin increased the catalytic power of ironporphyrin for the aerobic oxidation of cyclohexane, and the stronger the coordination was between nitrogenous polysaccharides and ironporphyrin, the greater were the reaction rates, the cyclohexane conversion, and the catalyst turnover for the aerobic cyclohexane oxidation catalyzed by nitrogenous polysaccharide-supported ironporphyrin.

Primary Analysis of the Effect of Nitrogenous Polysaccharides on the Catalysis of Ironporphyrin for Cyclohexane Oxidation with Air

It is frequently suggested that the active intermediate in hydrocarbon oxidation catalyzed by metalloporphyrins is a high-valence metal–oxygen complex [26]. An appropriate metal–oxygen bond force is beneficial to the activity of the oxygen atom of the high-valence metal–oxygen complex. Previous research [27–31] has proved that the coordination of the nitrogenous ligands to ironporphyrin can increase the catalytic power of ironporphyrin, because the nitrogenous ligands can lengthen and weaken the M–O bond in the high-valence metal–oxygen complex by means of donating an electron into the M–O antibonding orbital. Thus, it is possible that the formation of the Fe–N bond between nitrogenous polysaccharides and ironporphyrin benefits the donation of an electron from a nitrogen atom into the Fe–O antibonding orbital to activate the oxygen atom of the high-valence metal–oxygen complex. Thus, chitosan-supported ironporphyrin and chitin-supported ironporphyrin have greater catalytic power for the aerobic oxidation of cyclohexane than unsupported ironporphyrin.

There are amido groups in chitin molecules and amino groups in chitosan molecules. The N atom of the amino group of chitosan has a higher electron density than that of the amido group of chitin. The coordination of amino in chitosan to ironporphyrin is stronger than that of amido in chitin to ironporphyrin. On the one hand, the high-valence Fe–O complex formed by chitosan-supported ironporphyrin has a greater activity than that by chitin-supported ironporphyrin, because the N atom of chitosan is of greater benefit in lengthening and weakening the Fe–O bond of the high-valence Fe–O complex by means of donating an electron into the Fe–O antibonding orbital. On the other hand, the stronger the adsorbtion of ironporphyrin by chitosan, the less it was degraded by air under the reaction conditions. Therefore, the catalytic efficiency of chitosan–ironporphyrin for cyclohexane oxidation was better than that of chitin–ironporphyrin.

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