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Catalytic activity of monomeric and polymeric cobalt(II)–phthalocyanines in sulfide ion oxidation

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Abstract

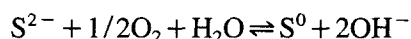
Polymeric cobalt(II)–phthalocyanine exhibited much higher specific catalytic activity in sulfide ion oxidation than the monomeric counterpart. Cobalt disproportionation, $2\text{Co}^{2+} \rightleftharpoons \text{Co}^{1+} + \text{Co}^{3+}$, was observed with the polymeric phthalocyanine in alkali medium. A concerted process of the oxidation and reduction steps over Co^{1+} and Co^{3+} active sites in the polymer gives rise to favourable conditions for an interstep energy compensation, thus lowering the activation energy of the reaction.

Keywords: Cobalt; Oxidation; Phthalocyanines; Sulfide ion

1. Introduction

The catalytic oxidation of sulfide ions has received considerable attention because of its importance for removing one hazardous pollutant from waste and natural waters [1]. Also, based on this reaction, it is possible to organize an effective manufacture of colloidal and finely dispersed sulfur.

The reaction of sulfide ion oxidation in alkali aqueous solutions



or



is an interesting model reaction. It proceeds under mild conditions and provides a possibility of mod-

elling some natural processes. Investigation of its mechanism also sheds light on some aspects of the mechanism of dioxygen activation on metal complexes which is an important problem of oxidative catalysis. This was the principal aim of the present work.

2. Experimental

2.1. Samples

Two cobalt(II)–phthalocyanine samples were the object of the present study: cobalt(II)–phthalocyanine (CoPc), supplied by Kodak, and cobalt(II)–polyphthalocyanine (CoPPc). The latter sample was prepared by condensation of phthalic anhydride and pyromellitic acid, 3:1 molar ratio, in the presence of CoCl_2 . Details of the preparation and purifying procedure are

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reported elsewhere [2]. Elemental analysis showed the following: N 19.80 (calculated for a dimer 21.60), Co 11.14 (calculated for a dimer 11.34), C 59.5, and H 1.9 wt%. The synthesized sample was also characterized by IR and UV–Vis spectroscopy. The viscosity of solutions containing 0.0108 g of phthalocyanine in 100 ml of dimethylformamide (DMF) was determined at 25°C by means of an Ostwald viscosimeter. Moreover, the relative viscosity, η_{rel} , expressed as the ratio of the time of flow for the solution to that of the solvent, was estimated. The relative viscosity of CoPc and CoPPc was 1.022 and 1.099, respectively, which is evidence for the formation of polymeric cobalt phthalocyanine.

2.2. Catalytic activity

The catalytic activity in reaction (1) was measured in a static system under continuous stirring by monitoring the volume of oxygen consumed at 20°C. Results were also checked with a chemical method by determining the converted amount of sulfide ions. The reaction proceeded to elementary sulfur with over 97% selectivity. Only very small amounts of thiosulfate were found in the reaction products. A Na_2S aqueous solution of 20 g/l concentration, 15 ml for each run, and 0.02 g of pure CoPc or CoPPc were used (the initial $\text{mol}_{\text{S}^{2-}}/\text{g-at.}_{\text{Co}}$ was 110). The catalytic activity was evaluated by the rate (W) of reaction (1), $W = \text{mol}_{\text{S}^{2-}}/\text{g-at.}_{\text{Co}} \text{ min}$, which was determined from the slope of the kinetic curve in its linear part. For example, the conversion degree at 50°C for 30 min was 89 and 38% for CoPPc and CoPc, respectively. On the basis of the kinetic curves at various temperatures, $\log W$ was plotted against $1/T$.

2.3. Electronic spectra

Electronic spectra of DMF solutions of CoPc and CoPPc in the ultraviolet and visible regions were recorded on a Hewlett Packard HP 89500 spectrometer. Modified quartz cells were utilized which facilitated purging with different gases,

admission of reagents and simulation of conditions in the catalytic reactor. Reflectance spectra of silica-supported CoPPc samples were acquired on a Beckman UV/VIS/IR 5270 instrument equipped with a diffuse reflectance attachment. These samples were prepared by adsorption from DMF solution.

3. Results and discussion

Data on the synthesized cobalt(II)–polyphthalocyanine indicate that the predominant fraction corresponded to a dimer. The following lines are focused on the catalytic activity of the CoPc monomer and CoPPc dimer.

Fig. 1 shows the kinetic curves of S^{2-} oxidation by air over powdered CoPc and CoPPc samples in aqueous solution at 20 and 50°C. The results indicate convincingly that the polymeric sample manifested considerably higher catalytic activity than the monomeric one. Examination of the temperature dependence of the reaction rate (Fig. 2) gave clear evidence that the activation energy of reaction (1) on the polymeric sample was lower than that with the monomeric sample. Thus, the data presented in Fig. 2 showed values of 11.1 and 7.0 kcal/mol for CoPc and CoPPc, respectively, for the plot of $\log W$ against $1/T$.

We suggest the following interpretation of the observed differences between the catalytic activ-

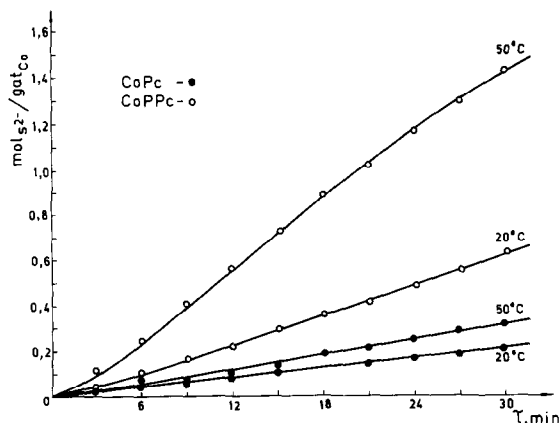


Fig. 1. Kinetic curves of sulfide ion catalytic oxidation over cobalt(II)–phthalocyanine and cobalt(II)–polyphthalocyanine.

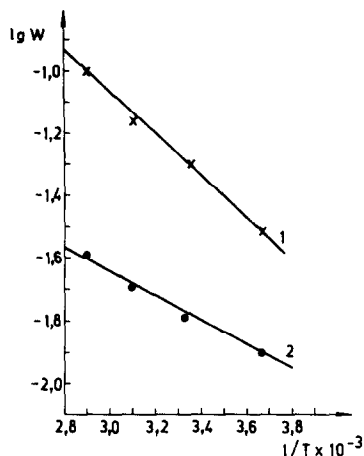


Fig. 2. Temperature dependence of the rate of sulfide ion catalytic oxidation.

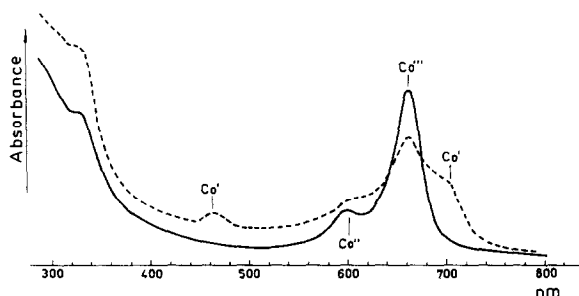


Fig. 3. Electronic spectra of Co(II)-polyphthalocyanine (dashed curve) and Co(II)-phthalocyanine (full curve) in DMF with NaOH added under argon: $[\text{CoPPc}] = 7.2 \times 10^{-2} \text{ g dm}^{-3}$, $[\text{CoPc}] = 6.2 \times 10^{-2} \text{ g dm}^{-3}$. The NaOH:CoPPc ratio was 1.4:1 by weight.

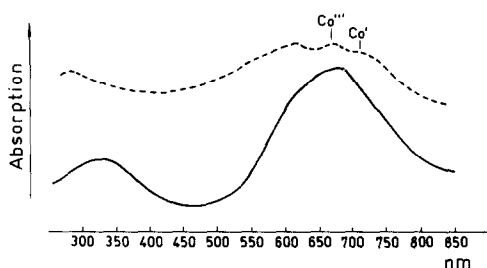


Fig. 4. Reflectance spectra of 5 wt% CoPPc deposited on silica: in air at atmospheric pressure (—) and after treatment with 2% aqueous solution of NaOH and evacuation (---).

ity and the temperature dependence of the reaction rate of sulfide ion oxidation over monomeric and polymeric phthalocyanines.

It has been found for bridged binuclear cobalt(II)-phthalocyanines, dissolved in a

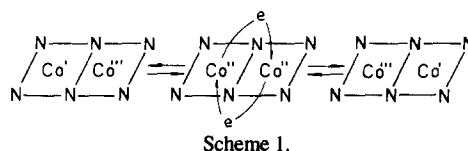
weakly coordinating solvent, that the addition of hydroxyl ions causes disproportionation to Co(I)- and Co(III)-phthalocyanines [3]. An electronic coupling occurs either through space or through an electron-transferring bridge. The conjugated system of the bridge polymer facilitates the electron transfer between the active sites. An inter-layer electron coupling in the solid is also possible.

A similar phenomenon was observed with the cobalt(II)-polyphthalocyanine sample. Fig. 3 presents electronic spectra of CoPc and CoPPc samples in DMF solution with NaOH added in argon atmosphere. The spectrum of CoPc is typical of the commercial product [4]. Well resolved bands characteristic of the Co^{1+} and Co^{3+} states in cobalt(II)-polyphthalocyanines [3,4] were observed in the spectrum of CoPPc. This is a reliable indicator of disproportionation processes with the participation of the polymeric sample.

This type of disproportionation was also established on the surface of solid CoPPc. Fig. 4 shows the reflectance spectrum of 5 wt% CoPPc deposited on silica. Absorption at 670 nm due to Co^{3+} was observed with that sample in air. After treatment with 2 wt% aqueous solution of NaOH and evacuation in a special cell, a band attributed to Co^{1+} also appeared.

The phenomenon discussed above was used as a basis of probable explanation of the experimentally observed higher catalytic activity and lower temperature dependence of the rate of reaction (1) for CoPPc in comparison with CoPc. In the particular case the disproportionation can be expressed by the dynamic equilibrium (Scheme 1)

Sufficiently substantiated concepts of thiols oxidation over cobalt phthalocyanines can be found in the literature [5–9]. Thiols contain the –SH functional group which shows some analogy with the oxidation of SH^- . The basic features of



Scheme 1.

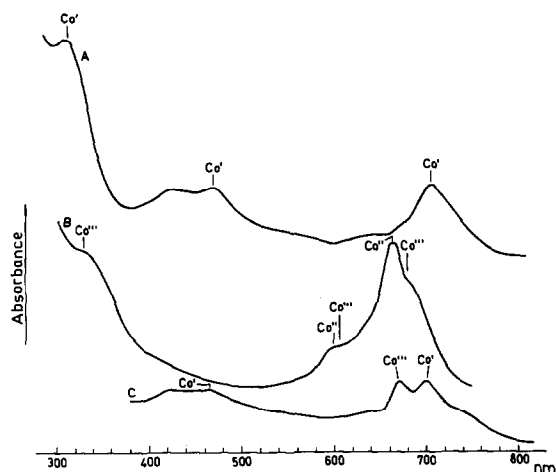


Fig. 5. Spectra of CoPPc in DMF: (A) in the presence of Na_2S under argon ($[\text{CoPPc}] = 9.0 \times 10^{-2} \text{ g dm}^{-3}$, $[\text{Na}_2\text{S}] = 3.3 \times 10^{-1} \text{ g dm}^{-3}$); (B) in air ($[\text{CoPPc}] = 1.1 \times 10^{-1} \text{ g dm}^{-3}$); (C) under conditions simulating reaction (1), presence of Na_2S and air bubbling ($[\text{CoPPc}] = 1.1 \times 10^{-2} \text{ g dm}^{-3}$, $[\text{Na}_2\text{S}] = 0.6 \times 10^{-1} \text{ g dm}^{-3}$).

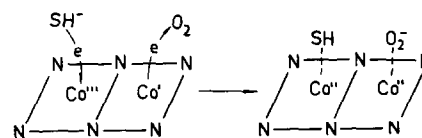
the reaction mechanism involve nucleophilic coordination of thiolate to the cobalt ion and addition of dioxygen with the formation of a superoxo complex. The respective oxidation states of cobalt are formed during these steps as a result of electron transfer.

The oxidation and reduction steps of reaction (1) were simulated separately by recording the electronic spectra of the reaction mixture in DMF solution. Fig. 5-A presents the spectrum of Co(II)-polyphthalocyanine dissolved in DMF upon addition of sodium sulfide in argon. One can arrive at the conclusion of cobalt reduction to Co^{1+} . Purging the CoPPc solution with air caused the formation of significant amounts of Co^{3+} in the phthalocyanine (Fig. 5-B). On modelling the conditions of reaction (1) by purging a solution of CoPPc and Na_2S in DMF with air, the spectrum acquired demonstrated the occurrence of Co^{1+} and Co^{3+} states (Fig. 5-C). This spectrum is very close to the one shown in Fig. 3 which elucidates the disproportionation in CoPPc.

Results obtained in a homogeneous phase can be used for interpretation of processes on the solid surface. The observed disproportionation (Scheme 1) and the data on cobalt oxidation states

distribution under working conditions (Fig. 5-C) can be used to propose the following mechanism of sulfide ion oxidation. The oxidation and reduction steps of reaction (1), i.e., dioxygen and SH^- coordination, respectively, may take place simultaneously on cobalt ions of two neighbouring CoPPc nuclei (Scheme 2)

The high specific catalytic activity of the polymeric samples can be explained by the possibility of a concerted process of the oxidation and reduction steps over adjacent active sites. These sites give rise to favourable conditions for an effective interstep energy compensation in the rate-determining reaction step [10]. For example, the heat evolved at the exothermal step can be used for the rate-determining endothermal step. The net result is consistent with lowering of the activation energy of the reaction (Fig. 6), which is determined by the energy barrier of the endothermal step: $E = E_{\text{red}} - \alpha Q_{\text{ox}}$, where α is the degree of interstep energy compensation. The properties and structure of the catalyst are of particular importance in this case [11] because they create favourable conditions for an interstep energy compensation.



Scheme 2.

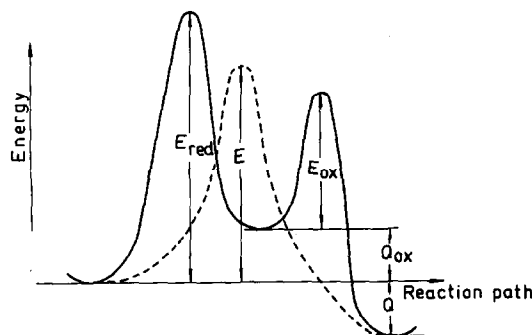


Fig. 6. Energy diagram of redox reactions: with (---) or without (—) interstep compensation.

Acknowledgements

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