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Polymer-metal complex based on copper(II) acetate and polyvinyl alcohol: thermodynamic and catalytic properties

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Abstract

In this work we obtained a polymer-metal complex by mixing aqueous solution of copper(II) acetate with PVA at a certain ratio, pH of the solution and temperature. The composition of the complex compound was determined by potentiometric and conductometric titration. The possibility of a complex formation was proved by calculating thermodynamic characteristics. The stability constant of the polymer-metal complex was calculated on the basis of the modified Bjerrum's method. The metal-polymer complex was synthesized in the ratio 1:2. IR spectroscopy and scanning electron microscopy (SEM) confirmed the coordination of polymeric PVA ligand to copper and allowed evaluating the morphology and features of the complex surface. The catalytic activity of the synthesized compound was evaluated in the oxidation reaction of elemental phosphorus (P_4) by oxygen in aqueous-organic media under mild conditions. Quantitative analysis of phosphoric acid was made by photocolorimetric method. We found that the oxidation process of P_4 in the presence of the complex $Cu(PVA)_2(OAc)_2$ in aqueous-organic media is characterized with the maximum absorption rate, in comparison with $Cu(OAc)_2 \cdot H_2O$ oxidation process with P_4, and yields up to 97% of the products. The process of oxidation of yellow phosphorus by oxygen in the presence of the copper(II)-PVA complex proceeds through key reactions of two-electron reduction of the catalyst P_4 with the formation of intermediate phosphorus-containing products P^{3+} and the stages of catalyst regeneration by oxygen. Twenty-electron oxidation of P_4 to the phosphorus-containing P^{5+} products involves 10 two-electron redox reactions and a number of complexation or hydrolysis stages.

Keywords

copper(II) acetate
polyvinyl alcohol
polymer-metal complex
thermodynamic characteristics
catalysis
oxidation
white phosphorus

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1. Introduction

The development of oxidation processes is essential in today's chemistry and industry [1–4]. Many oxidative techniques have been known to exist in natural life, and a lot of them have been used in various applications the industry, from wastewater treatment to cellulose or lignin bleaching [5–8]. Among these applications, oxidizing processes in the detergent industry, called bleaching, are particularly preferred for removing dyes [9–11].

In general, the stability and selectivity of homogeneous catalysts are strongly related to their molecular structure. Given the steric, electronic and conformational properties, suitable ligands must be designed for metal complexes that function as effective catalysts. These ligands must also be flexible against oxidation and be electron donors in order to achieve high oxidation states of the active metal. Most of them are heat-sensitive substances and generally deteriorate above 150 °C [12–14].

Furthermore, the consideration of steric, electronic and conformational properties is necessary for the design of suitable ligands for metal complexes that will serve as effective catalysts.

Under heat treatment, polymers such as polyvinyl alcohol (PVA), polyvinyl chloride (PVC), polystyrene (PS), etc., which have saturated main molecular chains and side