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Wells–Dawson polyoxometelates $[HP_2W_{18-n}Mo_nO_{62}]Fe_{2.5}$, xH_2O; $n = 0$, 6: Synthesis, spectroscopic characterization and catalytic application for oxidation of dyes

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ABSTRACT

The synthesis, IR, ^{31}P NMR and cyclic voltammetry characterizations of new Wells–Dawson-type heteropolyanions that contain iron, $HFe_{2.5}P_2W_{18}O_{62}$, $23H_2O$ and $HFe_{2.5}P_2W_{12}Mo_6O_{62}$, 22 H_2O, are reported. The catalytic activity of these compounds was evaluated through the oxidation of methyl violet dye, by hydrogen peroxide. The influence of different parameters such as the initial pH, the initial H_2O_2 concentration, the catalyst mass, and the initial dye concentration have been studied.

1. Introduction

Polyoxometalates (POMs) constitute a diverse class of inorganic oxo-metal clusters composed of early transition metals in their highest oxidation state [1]. They have a great deal of structural diversity and various applications in different areas, including catalysis, material sciences, medicine, and biology. Several types have been characterized, and each of them is defined by the M/X ratio used in the polycondensation under acidic conditions. The two best-known heteropolyanions are the Keggin-type $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ [2] and the Wells–Dawson type $[(X^{n+})_2M_{18}O_{62}]^{(16-2n)-}$ [3] (Fig. 1).

Polyoxometalltes with Dawson structure may be promising catalysts in homogeneous and heterogeneous systems because their redox and acidic properties can be controlled at atomic and molecular levels. They are used not only in acid-catalyzed [4] reactions, but also in many oxidations of organic compounds [5,6]. Recently, the Dawson-type Fe(III)-substituted heteropolyanion $(\alpha_2P_2W_{12}Mo_5O_{61}Fe)^{7-}$ was successfully used as a catalyst for the oxidation of methyl orange dye (MO) by H_2O_2 in aqueous solution [7]. This compound was synthesized by addition of iron on the lacunary heteropolyanion $(\alpha_2P_2W_{12}Mo_5O_{62})^{10-}$ [8]. In this work, we have synthesized and characterized new heteropolyanions that contain iron $HFe_{2.5}P_2W_{18}O_{62}$, $23H_2O$ and $HFe_{2.5}P_2W_{12}Mo_6O_{62}$, $22H_2O$, by addition of Fe^{3+} ions to the Dawson acid forms $H_6P_2W_{18}O_{62}24H_2O$ or $H_6P_2W_{12}Mo_6O_{62}24H_2O$.

The catalytic activity of these compounds was evaluated through the oxidation of an aqueous dye, methyl violet (its structure is shown in Fig. 2) [9,10] by hydrogen peroxide.

Methyl violet (MV), of molecular formula $C_{24}H_{28}ClN_3$, is a triphenylmethane dye, soluble in water, ethanol,

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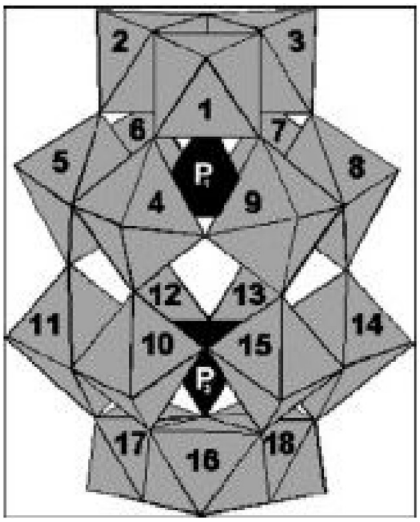

Fig. 1. Polyhedral representation of the polyanion Dawson structure.

methanol, diethylene glycol and dipropylene glycol. It is a dark green powder [11]. Methyl violets are the mixture of tetramethyl, pentamethyl, hexamethyl, and pararosanilines. These dyes are chiefly used in heterogray and printing inks. They impart a deep violet colour in paint and printing ink. They are also used to obtain shades of deep colours that can be applied for the dyeing of cotton, silk, paper, bamboo, weed, straw and leather. Methyl violet dye is widely used in analytical chemistry laboratories as a pH indicator to test pH ranges from 0 to 1.6. The toxic information reveals that the dye may cause hard skin and eye irritation – it means that in case of physical contact with the dye, this causes an irritation with redness and pain. The dye is harmful if it is swallowed. Also, the inhalation of methyl violet may cause an irritation to the respiratory tract, whereas its ingestion causes an irritation to gastrointestinal tract [12]. Therefore, it is necessary to remove it from the waste water. The influence of different parameters such as initial pH, initial H_2O_2 concentration, catalyst mass, and initial dye concentration has also been studied.

2. Experimental part

2.1. Preparation and characterization of catalysts

The heteropolyanions precursors $H_6P_2W_{18}O_{62}$ $24H_2O$ and $H_6P_2W_{12}Mo_6O_{62}$ $24H_2O$, as well as their acids forms, were synthesized according to the published procedures [13,14], and their purity was confirmed by infrared and NMR ^{31}P spectroscopies. IR spectra were recorded on KBr pellets using a spectrophotometer Shimadzu FTIR-8400s. ^{31}P NMR spectra were recorded on a Bruker 2000 apparatus operating at 110 MHz in the Fourier-transform mode. The ^{31}P shifts were measured in a 10^{-3} M solution of polyanions in a D_2O solution and were referenced to H_3PO_4 85%.

Cyclic voltammetry experiments were performed on an EDAQ e-corder 401 potentiostat. All experiments were carried out using a three-electrode cell configuration with

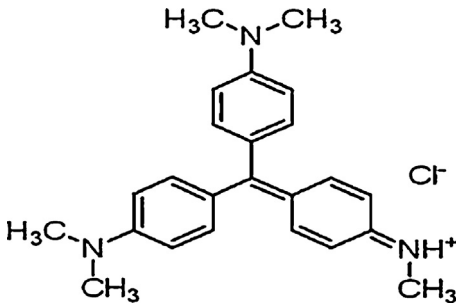

Fig. 2. Chemical structure of methyl violet.

a glassy carbon working electrode, a saturated calomel reference electrode (SCE), and a platinum auxiliary electrode.

All experimental solutions were de-aerated thoroughly by bubbling pure N_2 into the solutions for 10 min. All cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1}. All experiments were performed at room temperature.

$HFe_{1,5}P_2W_{18}O_{61}$ $23H_2O$ (1): 5 g (1.088 mmol) of $H_6P_2W_{18}O_{62}$ were dissolved in 20 ml of water at room temperature and 0.767 g of solid $FeCl_2$, $6H_2O$ (3.26 mmol) was then added. The mixture was then stirred for 10 min. A yellow powder of (**1**) was obtained after five days by slow evaporation. IR (KBr pellet, cm^{-1}): 1092(s), 1025(w), 960(s), 909(s).NMR of **(1)**: ^{31}P $\delta = -12.43$ ppm. Anal. calcd. (found): P 1.27 (1.20); W 68.10 (62.05); Fe 1.72 (2.01).

$HFe_{1,5}P_2W_{12}Mo_6O_{61}22H_2O$ (2): 5 g (1.2 mmol) of $H_6P_2W_{12}Mo_6O_{62}$ were dissolved in 20 ml of water at room temperature and 0,541 g (3.56 mmol) of solid $FeCl_2$ $6H_2O$ was then added. The mixture was stirred for 10 min. A dark yellow powder of **(2)** was obtained after five days by slow evaporation. IR (KBr pellet, cm^{-1}): 1084(s), 1025(w), 953(s), 912(s). NMR of (2): ^{31}P $\delta = -8.82$ ppm. Anal. calcd. (found): P 2.13(1.87); W 76.08(74.03); Mo 19.80(18.70); Fe 1.92(3.01).

2.2. Procedure for catalytic oxidations

2.2.1. Reagents

Methyl violet (MV) was supplied by Merck. H_2O_2 was purchased from Aldrich. All other reagents (NaOH or H_2SO_4) used in this study were of analytical grade.

2.2.2. Procedure – analysis

The initial concentration of the MV solution was 10 mg/L for all experiments, except for those carried out to examine the effect of the initial dye concentration. In all experiments, 100 mL of MV solution containing the appropriate quantity of catalyst and H_2O_2 was magnetically stirred at room temperature.

The pH of the reaction was adjusted by using 0.1 N H_2SO_4 or NaOH aqueous solutions.

The MV concentration was measured by a Jenway UV–vis spectrophotometer. The wavelength that corresponds to the maximum absorbance is $\lambda_{max} = 585$ nm. The resolutions of the wavelength and the bandwidth were 1 nm and 0.5 nm. The cell used during the experiments was made of 1-cm-thick quartz.