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Sandwich-type Cobalt Tungstophosphate: Synthesis, Characterization and Catalytic Activity

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Abstract

Sodium tungstophosphate, $Na_9[HPW_9O_{34}].7H_2O$ was synthesized by reaction in aqueous solution of sodium tungstate, phosphoric acid and acetic acid. It was used as a precursor for synthesis of sandwich-type cobalt tungstophosphate, $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2].20H_2O$ by reacting with cobalt chloride and potassium acetate. The potassium ion can be exchanged with tetrabutylammonium bromide. The characterization was carried out by means of elemental analysis, FT-IR, UV-vis diffuse reflectance spectroscopy (DR-UV-vis). The sandwich-type cobalt tungstophosphate was used to catalyze oxidation of cyclooctane with H_2O_2 as oxidant in absence and presence of phase transfer agent. The experimental results showed that with phase transfer agent, the sandwich-type cobalt tungstophosphate effectively catalyzed oxidation of cyclooctane, yielding high conversion and selectivity to cyclooctanone. The experiment with radical trap suggests the involvement of a free-radical mechanism.

Key Words : Sandwich-type cobalt tungstophosphate, Oxidation, Cyclooctane, Hydrogen peroxide
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Introduction

Polyoxometalates (POMs) represent a unique class of inorganic cage complexes. The Keggin-type POM is of special interest due to their ability to form lacunary (defect) derivatives via loss of one or more WO_6 units. This lacunary precursor can be viewed as inorganic ligands having vacant sites which contain terminal and basic oxygens that can coordinate to transition metal ions[1]. POMs were used in homogeneous oxidation with several oxidants, *t*-butyl hydroperoxide[2], hydrogen peroxide[3] and molecular oxygen[4]. Sandwich-type tungstophosphates derive from the union of two fragments with $[PW_9O_{34})]^{9-}$ composition. A tetranuclear arrangement of octahedra is joined by edges and connected to $(PW_9O_{34})^{9-}$ anionic unities through the corners. There are also two water molecules of constitution linked to the corners of both MO_6 octahedra in opposite positions as shown in Figure 1.

$K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2].20H_2O$ was previously synthesized with low yield (29%)[5] by reaction of a mixture containing HCl, Na_2HPO_4, Na_2WO_4 and $Co(NO_3)_2$ (molar ratio of 11:2:2:18) in water, heated at 100°C overnight. Then the reaction mixture was filtered and excess KCl was added to the filtrate, resulting in formation of precipitate. Oxidation of cyclooctane in the presence of $[(n\text{-}C_4H_9)_4N]_7H_3[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$, M = Co(II), Mn(II) and Fe(III) was reported.[6]

Continuing our research on the utilization of transition metal-substituted polyoxometalates as oxidation catalyst[7], this work reports synthesis of sandwich-type cobalt tungstophosphate and studies the catalytic reaction for the selective oxidation of cyclooctane using H_2O_2 as a clean oxidant.

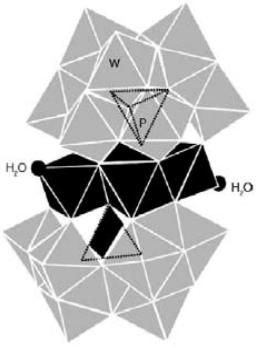

Figure 1. Structure of sandwich-type tungstophosphates.

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Materials and Experimantal Procedures

Materials

H_3PO_4, $Na_2WO_4.2H_2O$, $CoCl_2.3H_2O$, CH_3COOH, CH_3COOK, tetrabutylammonium bromide (TBABr), acetonitrile, 2, 6-di-*tert*-butyl-4- methylphenol and H_2O_2 (30 wt.% aqueous) are available commercially (Fluka and Lab-scan).

Synthesis

$Na_9[PW_9O_{34}].7H_2O$ (1)

The synthesis was modified from that in the literature by using CH_3COOH instead of HCl[8]. $Na_2WO_4.2H_2O$ (12 g, 36.4 mmol) was dissolved in 200 mL water. Then 85% H_3PO_4 (0.3 mL) was dropwise added and the mixture was stirred for 15 minutes. Addition of 17 M CH_3COOH (38.5 mmol) to final pH 7 produced white precipitates which were filtered and dried (5.26 g, 46% yield). (equation 1).

$$Na_2WO_4 + H_3PO_4 + CH_3COOH + H_2O \longrightarrow Na_9[PW_9O_{34}].7H_2O \qquad (1)$$

$K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2].20H_2O$ (2)

$CoCl_2$ (0.048 g, 0.2 mmol) and $Na_9[PW_9O_{34}].7H_2O$ (0.28 g, 0.1 mmol) solutions were added CH_3COOK buffer (10 mL) and then solution pH was adjusted to 5 with CH_3COOH, heated at 80°C for 1 hour. The violet crystals formed were filtered, washed with cold ethanol, and dried (1.1 g, 72% yield) (equation 2).

$$CoCl_2 + Na_9[PW_9O_{34}] + CH_3COOK \longrightarrow K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2].20H_2O \qquad (2)$$

Instrumentation

Elemental analysis (Co, W and P) was performed on an inductively coupled plasma emission ICP (Perkin Elmer Plasma 1000 Emission Spectrometer) and X-ray fluorescence (Philips model PW2400). FT-IR spectra were obtained using FT-IR Spectrophotometer (Nicolet 6700) as KBr disc. Diffuse reflectance spectroscopy spectrum was recorded with UV-vis (Shimadzu, UV-2550) spectrophotometer, using $BaSO_4$ as internal standard.

Oxidation reaction of cyclooctane

In a Parr reactor, cyclooctane and catalyst were added in acetonitrile followed by 30% H_2O_2. The reactions were carried out under air at refluxing temperature. After required reaction time, the reaction mixture was added 25% H_2SO_4 and the reaction products were extracted with diethyl ether. The organic layer was neutralized with saturated $NaHCO_3$ and dried over anhydrous Na_2SO_4. The products were analyzed with a gas chromatography (VARIAN, CP-3800) equipment with flame ionization detector and CP-sil8 capillary column (30 m, 0.25 mm) and *n*-octane was used as an internal standard. The chromatographic conditions were initial temperature : 50°C (2 minutes); temperature rate: 5°C/minute; final temperature: 250°C (1 minute); injector temperature: 220°C; detector temperature: 250°C. Cyclooctanone and cyclooctanol were identified by comparison with authentic standards. The percentage of each compound in the reaction mixture was estimated directly from the corresponding chromatographic peak areas. Blank experiments were also conducted in the absence of catalyst or oxidant. At the end of the oxidation reaction, cyclooctyl hydroperoxide was determined by treating the final reaction solution with an excess of PPh_3 before the GC analysis. PPh_3 reduces the cyclooctyl hydroperoxide and quantitatively to the corresponding cyclooctanol, giving triphenylphosphine oxide. The amount of cyclooctyl hydroperoxide was determined by comparing the concentrations of the cyclooctanone and of the cyclooctanol, measured before and after the treatment of the sample with PPh_3.[9]

Results and Discussion

Synthesis

Sandwich-type cobalt phosphotungstate can be prepared using the $Na_9[PW_9O_{34}].7H_2O$ as the primary reagent and then adding the cobalt chloride into the reaction system. The advantage of this method is that the target product can be controlled easily and directed to the sandwich-type structure.

Composition and Spectroscopic Characteristics

Composition and assignment of characteristic FT-IR bands of the synthesized complexes: precursor 1 and sandwich-type cobalt phosphotungstate 2 are shown in Table 2. A representative FT-IR spectrum of complex 2 is shown in Figure 2. The bands in the 10581065 cm^{-1} region are assigned to a PO_4 tetrahedral group. It was observed a splitting of this band due to lower symmetry of the PO_4 group. The stretching of the W-O_t bond (terminal bond of WO_6) appears in the 938-947 cm^{-1} region. The bands at 883-886 and 800-818 cm^{-1} are attributed to the remaining $(W\text{-}O\text{-}W)_c$ (bond of corner-shared octahedra) and $(W\text{-}O\text{-}W)_e$ (bond of edge-shared octahedra) stretching bonds, respectively.

Table 1. Characteristics of synthesized complexes

Complex	%element Calc. (Found)			FT-IR (cm-1)			
	Co	W	P	P-O	W=Ot	(W-O-W)c	(W-O-W)e
1	0	64.5(64.0)	1.2(1.2)	1058, 1014	938	886	818
2	4.12(4.08)	57.87(56.38)	1.04(0.99)	1065,1037	947	883	800

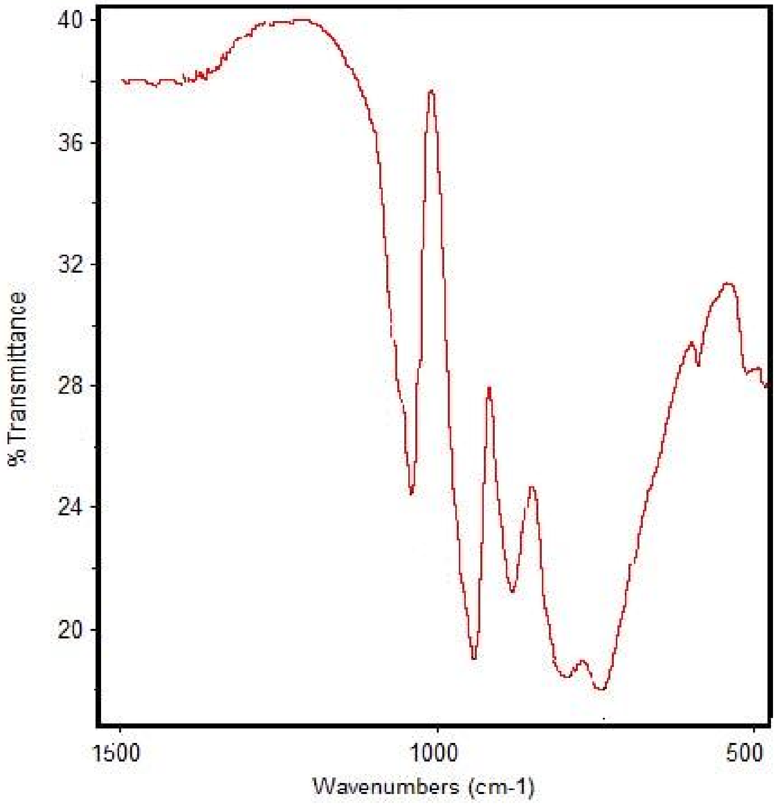


Figure 2. FT-IR spectrum of complex 2.

Figure 3 shows DRUV-vis spectrum of complex 2 in 200-750 nm region. Band at around 300 nm is assigned to the charge transfer $O^{2-} \rightarrow W^{6+}$ in an octahedral coordination. Bands of d-d electronic transition are observed. The spectrum of the complex 2 (Co^{2+}, d^7) presents a wide band at 560 nm typical of Co ion in an oxygen octahedral coordination.

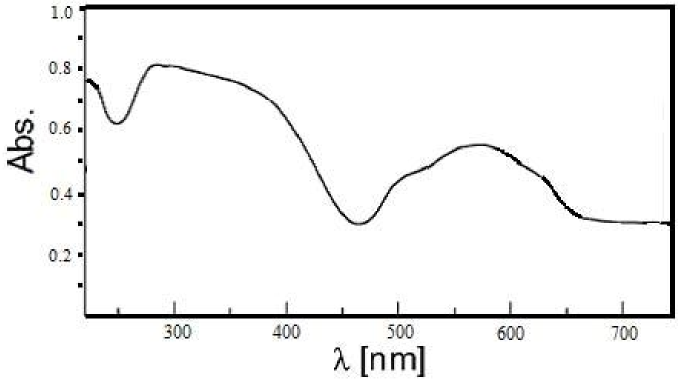
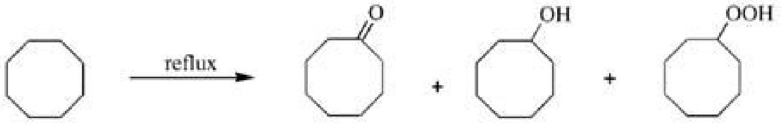


Figure 3. DRUV-vis spectrum of the complex 2.

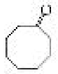
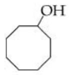
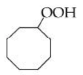
Oxidation of Cyclooctane

The oxidation of cyclooctane was carried out in acetonitrile solvent using H_2O_2 as an oxidant. The results are summarized in Table 2. For the catalyzed reactions, oxidized products detected are cyclooctanol, cyclooctanone and small amount of cyclooctyl hydroperoxide (equation 3).



(3)

Table 2. Oxidation of cyclooctane using complex 2 as catalyst (Cyclooctane 0.65 mL, 5 mmol, catalyst 0.75 μmol, 7.5 mL CH_3CN at reflux temperature)

Entry	Catalyst	H2O2/cyclooctane molar ratio	Time (h)	Conversion (%)	Selectivity (%)		
							
1	-	4	9	0	0	0	0
2	2	0	9	0	0	0	0
3	2	4	9	15	61	24	15
4	2+TBABr[a]	4	9	50	81	3	16
5	2+TBABr[a]	6	9	72	81	9	10
6	2+TBABr[a]	8	9	78	83	8	9
7	2+TBABr[a]	8	12	87	83	10	7
8	2+TBABr[a,b]	8	12	0	0	0	0

[a] Add TBABr (2.58 mg, 8.0 μmol)

[b] Add 2,6-di-*tert*-butyl-4-methylphenol as a radical scavenger (5 mmol)

The experimental results show that in the absence of catalyst and oxidant (entries 1 and 2), no reaction occurred. The complex 2 gave low conversion and selectivity at H_2O_2/cyclooctane molar ratio = 4. This might be due to low solubility of the complex in cyclooctane.

In the presence of tetrabutylammonium bromide (TBABr) as a phase transfer agent, enhancement in both conversion and selectivity can be obtained, 15% conversion with 61%selectivity compared to 50% conversion with 81% selectivity (entry 3 vs 4). This results from higher solubility of the complex in the reaction medium. These values were further increased when a larger amount of oxidant was used. With increasing in the H_2O_2/cyclooctane molar ratio to 6 and 8, conversion increased to 72 and 78%, respectively (entries 5 and 6). For the selectivity, it can be observed that the yield of cyclooctyl hydroperoxide decreased while yield of cyclooctanone was simultaneously increased. This is similar to that reported previously.[3] At longer time (12 hours in entry 7) conversion of cyclooctane can be further increased to 87% with constant %selectivity. Compared to the $[(n\mathrm{C_4H_9})_4\mathrm{N}]_7\mathrm{H_3}[\mathrm{Co_4(H_2O)_2(PW_9O_{34})_2}]$ which was reported to yield 92% conversion and 83:13:4% selectivity to cyclooctanone : cyclooctanol : cyclooctyl hydroperoxide under reaction condition (cyclooctane/ catalyst molar ratio = 666, H_2O_2/cyclooctane molar ratio = 9.8, using CH_3CN as solvent at reflux temperature in 12 h)[6], this work shows that the $\mathrm{K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2].20H_2O}$ in the presence of $(n\text{-}\mathrm{C_4H_9})_4\mathrm{NBr}$ as phase transfer agent, can also catalyze the oxidation reaction of cyclooctane without need to synthesize the tetrabutylammonium salt.

When the oxidation was performed in the presence of radical scavenger (2,6-di-*tert*butyl-4-methylphenol) (entry 8). No oxidized products were found. This suggested the involvement of a free-radical mechanism. The activation of H_2O_2 may occur simultaneously at W and Co. The metal-catalyzed hemolytic decomposition of H_2O_2 to radicals $HO^\bullet$ and $HOO^\bullet$ can account for the formation of alkyl radical $R^\bullet$ upon H-abstraction from the substrate RH by $HO^\bullet$. Reaction of alkyl radical $R^\bullet$ with metal-peroxide resulted in final oxidized products, cyclooctanone and cyclooctanol.

Conclusions

The sandwich-type cobalt tungstophosphate, $\mathrm{K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2].20H_2O}$ was successfully synthesized and characterized. It was shown to catalyze oxidation of cyclooctane using environmental friendly oxidant, H_2O_2 in acetonitrile solvent. Higher conversion and selectivity to cyclooctanone can be achieved from this catalyst in the presence of phase transfer agent, tetrabutylammonium bromide which is due to higher homogeneity of the reaction.

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