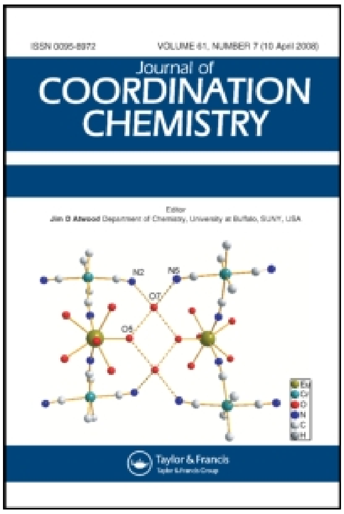

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PREPARATION AND CHARACTERIZATION OF TRISUBSTITUTED PEROXOTITANIUM HETEROPOLY COMPLEXES

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Triperoxotitanium-substituted tungstosilicates and tungstophosphates have been synthesized and characterized by elemental analysis, polarography, cyclic voltammetry, IR, UV, XPS and ^{183}W NMR spectroscopy. The catalytic activities of the complexes were studied.

Keywords: Keggin structure; Peroxotitanium; Trisubstituted; ^{183}W NMR; Catalysis

INTRODUCTION

In recent years, more attention has been drawn to catalytic activity and selectivity. Biological activity and physic-chemical properties of heteropoly complexes can be modulated by changing their chemical environment. The best method to do this at the moment is to replace some fragment atoms by transition metal atoms or lanthanide elements. Peroxymetal-containing heteropoly complexes (POHPC) with the Keggin structure are believed to have extensive prospects of application in organic syntheses and catalysis since they have high catalytic activities and selectivity in allyl epoxidation, oxidative dehydrogenation of alcohol and epoxide opening of *vic*-binary alcohols to carboxylic acids [1]. A more exciting prospect is their efficiency

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in anti-AIDS (HIV) tests [2]. At the same time, POHPC are believed to be a new type of oxygen atom shifting reagent. However, there are few reports on the synthesis and characterization of this kind of compound [3] so far.

This paper describes the synthesis by stereospecific reaction [4] and characterization of peroxotitanium-containing polyoxometalates with the Keggin structure, *i.e.*, α-$M_{10-m}H_m[SiW_9(TiO_2)_3O_{37}] \cdot xH_2O$ and α-$M_{9-m}H_m[PW_9(TiO_2)_3O_{37}] \cdot xH_2O$ (M = K, TBA), and a study of oxidizing catalytic activities of the complexes.

EXPERIMENTAL

Reagents and Apparatus

All reagents were of analytical grade. Instruments used were an ICP emission spectrometer, PE-3030 atomic absorption spectrometer, Nicolet 5DX IR spectrophotometer (KBr pellets), Beckman-DU8B UV spectrophotometer, ESCALB MK II photoelectron spectrograph, Unity-400 NMR spectrometer and 384B polarographic analyzer.

Syntheses

α-$Na_{10}SiW_9O_{34} \cdot 21H_2O$ and $Na_8HPW_9O_{34} \cdot 23H_2O$ were prepared according to the literature [5, 6].

α-$M_{10-m}H_m[SiW_9(TiO_2)_3O_{37}] \cdot xH_2O$ (M = K, TBA)

A 10 cm^3 solution of $Ti(SO_4)_2$ (1 g, 4.1 mmol) was added dropwise into a 30 cm^3 solution of α-$Na_{10}SiW_9O_{34} \cdot 21H_2O$ (4 g, 1.44 mmol) with stirring. The mixed solution was adjusted to pH 1.6 and heated on a water bath at 30°C for 1 h. 1 cm^3 of 30% H_2O_2 was added into the solution, stirred for a moment, then 10 g of KCI was added to the solution after cooling to room temperature. A yellow precipitate appeared immediately. The solid was collected and recrystallized from warm water (pH 2), yield 45%. A saturated TBABr solution was added into the solution of α-$K_9H[SiW_9(TiO_2)_3O_{37}] \cdot 12H_2O$ (1 mol dm^{-3}) and the tetraalkylammonium salt precipitated completely. The solid was then washed with ethanol and ether, and finally dried by air.

TABLE I Chemical analysis data for the products (wt. %)

	Analysis found(calc.)							
Complex	*W*	*Ti*	*K*	*H_2O*	*C*	*H*	*N*	*O_2^{2-}*
α-$K_9H[SiW_9(TiO_2)_3O_{37}] \cdot 12H_2O$	53.51	4.62	11.53	6.90				3.01
	(53.67)	(4.66)	(11.41)	(7.00)				(3.11)
α-$TBA_7H_3[SiW_9(TiO_2)_3O_{37}]$	39.78	3.52			31.72	6.12	2.49	2.14
	(39.26)	(3.41)			(31.89)	(6.05)	(2.32)	(2.28)
α-$K_9[PW_9(TiO_2)_3O_{37}] \cdot 6H_2O$	55.63	4.91	11.78	3.61				3.18
	(55.57)	(4.82)	(11.82)	(3.63)				(3.22)
α-$TBA_6H_3[PW_9(TiO_2)_3O_{37}]$	41.59	3.59			28.86	5.54	2.14	2.29
	(41.62)	(3.61)			(28.98)	(5.50)	(2.11)	(2.41)

α-$M_{9-m}H_m[PW_9(TiO_2)_3O_{37}] \cdot xH_2O$ (M = K, TBA)

There were prepared by using the same method as mentioned above. Analytical data are given in Table I.

RESULTS AND DISCUSSION

Polarography and Cyclic Voltammetry

All data were obtained in a 1 mol dm^{-3} HAc-NaAc buffer solution of pH 4.7 at 298 K using a polarographic analyzer equipped with an Hg/Hg_2Cl_2-CI^- electrode and a Pt counter electrode. The concentration of the HPC was 1.0×10^{-3} mol dm^{-3}. Experiments were carried out under an N_2 atmosphere (See Tabs. II and III). The polarography of the POHPC have four waves. Generally, if the substituted atoms are not reduced, the half-wave potentials of the heteropolyanions will be similar to those of their precursors. If the substituted atoms are reduced, the number of reduction waves will be changed [7]. The first and the second reduced waves are the reduction waves of O_2^{-2} and Ti^{4+}, respectively, and the third and the forth ones are reduction waves of W^{6+}. Oxidation ability of the POHPC is stronger than that of the HPC because of having O_2^{-2} in the POHPC. The cyclic voltammetric data show that the first and the second reduction

TABLE II Polarographic data for the complexes (V)

Complex	*Wave* I	*Wave* II	*Wave* III	*Wave* IV
α-$K_9H[SiW_9(TiO_2)_3O_{37}] \cdot 12H_2O$	−0.184	−0.528	−0.844	−1.024
α-$K_9[PW_9(TiO_2)_3O_{37}] \cdot 6H_2O$	−0.180	−0.478	−0.792	−0.936

TABLE III Cyclic voltammetric data for the complexes (mV)

	Speed	*Peak* I			*Peak* II			*Peak* III			*Peak* IV		
Complex	(mV/s)	*Epc*	*Epa*	ΔEp	*Epc*	*Epa*	ΔEp	*Epc*	*Epa*	ΔEp	*Epc*	*Epa*	ΔEp
$SiW_9(TiO_2)_3-K$	50	−258			−582	−578	4	−906	−826	80	−1058	−1024	34
	100	−273			−583	−514	9	−907	−827	80	−1060	−1021	39
	200	−290			−586	−571	15	−906	−826	79	−1068	−1024	44
	300	−365			−593	−568	25	−906	−826	80	−1068	−1024	44
$PW_9(TiO_2)_3-K$	50	−252			−580	−560	20	−864	−807	57	−985	−915	50
	100	−259			−582	−550	32	−863	−804	59	−987	−936	51
	200	−256			−584	−558	26	−862	−804	58	−989	−939	50
	300	−257			−583	−555	28	−862	−804	58	−989	−938	51

peaks are irreversible and the last two peaks are *quasi*-reversible. Controlled-potential electrolysis show that the first reduction wave, the reduction wave of O_2^{-2}, is a 2e process and the second reduction wave, the reduction wave of Ti^{4+}, is a 1e process.

Spectroscopic Studies

The inner-shell electron binding energies of α-$K_9H[SiW_9(TiO_2)_3O_{37}] \cdot 12H_2O$ are as following: $W_{4f7/2}$, 35.8 eV; K_{2p}, 292.7 eV; Si_{2p}, 102.2 eV; Ti_{2p}, 458.7 eV; $O_{1s}(O^{2-})$, 530.7 eV; $O_{1s}(O_2^{-2})$, 532.7 eV; for α-$K_9[PW_9(TiO_2)_3O_{37}] \cdot 6H_2O$: $W_{4f7/2}$, 35.4 eV; K_{2p}, 293.0 eV; P_{2p}, 133.7 eV; Ti_{2p},458.6 eV; $O_{1s}(O^{2-})$, 530.7 eV; $O_{1s}(O_2^{-2})$, 532.5 eV. The oxygen peak of the POHPC are not symmetric and are split in part. Devolution analysis gives two kinds of environment of oxygen atoms, *i.e.*, O^{2-} and O_2^{-2}.

IR frequencies including assignments are listed in Table IV. Characteristic bands of the Keggin structure are in the range 400 – 1100 cm^{-1}. However, IR spectra of the POHPC show additional weak bands at 875 cm^{-1} and 490 cm^{-1}; the former is characteristic of the peroxide group and the latter is characteristic of the peroxotitanium group [7].

Characteristic electronic absorption bands of the Keggin structure appear at about 200 and 260 nm. An additional band at ca. 330 nm was observed and has been attributed to the charge-transfer $O_2^{-2} \rightarrow Ti$ [8].

^{183}W NMR chemical shifts of the complexes are with respect to an external standard of 2 mol dm^{-3} Na_2WO_4 solution in D_2O at pH 6. The complexes show a sharp two-line spectrum with a ratio of 1 : 2 in relative intensity, respectively, *i.e.*, $SiW_9(TiO_2)_3$ – K, – 126.9 and – 142.3 ppm; $PW_9(TiO_2)_3$ – K, – 110.4 and – 127.7 ppm; These results prove that each molecule has two different groups of W atoms, *i.e.*, W atoms connected with titanium atoms and the W atoms not connected with titanium atoms. This should be compared with SiW_{12}(– 103.8 ppm) and PW_{12}(– 99.4 ppm). The δ values of the W atoms in $SiW_9(TiO_2)_3$ and $PW_9(TiO_2)_3$ are all shifted towards a higher field.

TABLE IV Characteristic IR data for the complexes (cm^{-1})

HPC	$\nu_{as(W—Od)}$	$\nu_{as(x—Oa)}$*	$\nu_{as(W—Ob—W)}$	$\nu_{as(W—Oc—W)}$		$\nu_{—o—o—}$	$\nu_{Ti—O—O}$
$SiW_9(TiO_2)_3$ – K	955	899		783	720	873	495
$SiW_9(TiO_2)_3$ – TBA	953	896		797	719	878	494
$PW_9(TiO_2)_3$ – K	957	1056	802	726		870	483
$PW_9(TiO_2)_3$ – TBA	948	1055	810	720		872	480

* X = Si, P.

TABLE V Oxidative product distribution of the cyclohexene expoxidation (%)

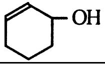
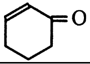
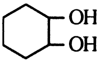
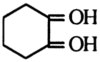
Catalyst products					*Other*
$SiW_9(TiO_2)_3-K$	16.64	27.76	29.67	9.54	16.39
$PW_9(TiO_2)_3-K$	5.8	7.37	50.86	12.46	23.51

TABLE VI Yields of the maleic anhydride epoxidation

Catalyst	*Conv.* (%)	*Catalysts**	*Conv.* (%)
$SiW_9(TiO_2)_3-K$	89.98	$SiW_{11}(TiO_2)-K$	73.86
$SiW_9(TiO_2)_3-TBA$	92.04	$SiW_{11}(TiO_2)-TBA$	86.36

* See Ref. [10].

Catalytic Activity

The catalysis of the complexes were examined based on a model reaction concerning the epoxidation of cyclohexene (50 mmol) by H_2O_2 (30%, 50 mmol) in 1.2-dichloroethane (5 cm^3) and H_2O (5 cm^3). The experiment conditions were catalyst 0.07 mmol; reaction temperature 340 K; reaction time 5 h. The products were determined by HP5988A GC-MS and results are shown in Table V. Results indicate that the catalytic activity of complexes with a central silicon atom is higher than that of complexes with a central phosphorus atom. These results parallel similar observations for the WO_4^{2-}-aqueous H_2O_2 catalyst system [9].

Catalytic maleic anhydride epoxidation using $SiW_9(TiO_2)_3$ as catalyst precursor was studied as a model reaction. The experimental condition were as previously described [10] and the epoxidation product was proved according to IR, ^1H NMR and liquid chromatography. Results are shown in Table VI. The catalytic activity of heteropoly complexes with $(TiO_2)_3$ is higher than that of heteropoly complexes with (TiO_2). As to the complexes with identical anions, the bigger the cation ions are, the greater its activity is, due to increased phase transfer ability. In a word, changing counter ion and the number of substituted TiO_2 groups may improve the catalytic activity of heteropoly complexes. These results reveal an encouraging applied prospect of peroxoheteropoly complexes.

Acknowledgments

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