Synthesis and ^{183}W NMR Characterization of α-$K_7GaW_{11}(TiO_2)O_{39}\cdot 11H_2O$ Heteropolyanion

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Abstract: The peroxotitanium-substituted heteropolytungstate α-$K_7GaW_{11}(TiO_2)O_{39}\cdot 11H_2O$ has been synthesized and characterized by elemental analysis, IR, UV, ^{183}W NMR and electrochemistry. ^{183}W NMR spectrum consists of six lines with intensity ratio 2:2:1:2:2:2, indicated that the TiO_2 occupied the empty octahedral site of the GaW_{11} anion forming a polyanion with Cs symmetry. The characteristic charge-transfer absorption band $O_2^{2-}\rightarrow Ti$ at 385 nm occurs in the UV spectrum. The polarographic reduction potential of O_2^{2-} at *ca.*+0.87 V has been found.

Keywords: Peroxotitanium gallatotungstate, Keggin structure, ^{183}W NMR.

In recent years, the research of peroxy polyoxometalates (POMs) has attracted increasing attention because of the two reasons. First, peroxy POMs are more active as oxygenation catalysts in some oxygen transfer reactions[1~5]. Second, recent research from our group and others has established that peroxy POMs are more active antiviral agents and less toxic both *in vitro* and *in vivo* than the parent metal-free POMs[6]. In order to entirely understand the properties and activities of peroxy POMs, we report here the synthesis and characterization of α-$K_7GaW_{11}(TiO_2)O_{39}\cdot 11H_2O$ heteropolyanion. It is the first peroxy titanium substituted gallatotungstate of this subclass. $K_9GaW_{11}O_{39}\cdot xH_2O$ (noted as GaW_{11}) was prepared following reference[7] and was identified by IR and polarogram.

Preparation of α-$K_7GaW_{11}(TiO_2)O_{39}\cdot 11H_2O$ (noted as $GaW_{11}TiO_2$): To an 40 mL aqueous solution of GaW_{11} (12 g, 3.72 mmol) was added 20 mL aqueous solution of $Ti(SO_4)_2$ (1g,4.20 mmol) dropwise. After the addition was completed, the solution was stirred for 1 h at 50°C, insoluble material was removed by filtration. To the filtrate 4 g KCl was added and stirring was continued for 5 min. Then 15 mL of 15% H_2O_2 was added, the solution changed to tangerine. After storing at 0°C for several days, the tangerine crystals appeared. The crystals were recrystallized from warm water (pH 2.0). Yield 34%. Anal. Calcd. (Found)% for α-$K_7GaW_{11}(TiO_2)O_{39}\cdot 11H_2O$: K 8.4 (8.3); W 61.9 (61.6); Ti 1.5 (1.5); H_2O 6.1 (6.2); O_2^{2-} 0.98 (0.94). IR (KBr, cm^{-1}): W-O_d 946, W-O_b-W 873, W-O_c-W 767, 669, Ga-O 650, O-Ga-O 450.

^{183}W NMR spectrum of $GaW_{11}TiO_2$ is a sharp six-line spectrum with chemical shifts -51.249, -83.230, -99.081, -118.180, -139.128 and -152.234 ppm and relative intensities of 2:2:1:2:2:2. This result strongly suggests that the TiO_2 group occupied the empty octahedral site of the GaW_{11} anion, forming a polyanion with Keggin structure.

Bands at 200 nm, 257 nm ($c=1\times10^{-5}$ mol/L, solvent H_2O), 385 nm ($c=1\times10^{-3}$mol/L, solvent H_2O) for α-$K_7GaW_{11}(TiO_2)O_{39}\cdot11H_2O$ were observed in UV spectra. Compared with GaW_{12} anion, the band at 257 nm is a characteristic band of a heteropolytungstate with Keggin structure, and should be assigned as an $O_b/O_c \rightarrow W$ charge transfer band. The band at 200 nm is an $O_d \rightarrow W$ charge transfer band. The band at 385 nm is the characteristic charge-transfer band of $O_2^{2-} \rightarrow Ti$.

Polarography was performed at pH 4.7 acetate buffer. The reduction processes of α-$GaW_{11}TiO_2$ anion involved the reduction of $O_2^{2-} \rightarrow O^{2-}$ at +0.87V, the reduction of $Ti^{4+} \rightarrow Ti^{3+}$ at –0.11 V and the reduction of $W^{6+} \rightarrow W^{5+}$ at -0.69V and –0.87V. The reduction of W^{6+} is similar to that of GaW_{11} anion, showing two-step two-electron reduction peaks.

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References

1. M. K. Harrup, G. S. Kim, C. L. Hill, *et al.*, *Inorg. Chem.*, **1998**, *37*, 5550.
2. T. Yamase, E. Ishikawa, Y. Asai, *et al*., *J. Mol. Catal A: Chem*, **1996**, *114*, 237.
3. L. Meng, J. F. Liu, *Chin.J.Catal.*, **1996**, *5*, 462.
4. Q. J. Shan, J. Gong, S. Q. Shi, L. Y. Qu, *Acta Chem. Sinica*, **1998**, *56*, 700.
5. M. W. Droege, R. G. Finke, *J.Mol.Catal*, **1991**, *69*, 323.
6. J. T. Rhule, C. L. Hill, D .A. Judd, *et al.*, *Chem Rev.*, **1998**, *98*, 327.
7. C. Brevard, R. Schimpf, G. Tourne, *et al.*, *J.Am.Chem.Soc.*, **1983**, *105*, 7059.

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