Polish J. Chem., **78**, 451–456 (2004) **COMMUNICATION**

Syntheses and Characterization of Transition Metal Doped Molybdovanadophosphoric Heteropoly Compounds

by S.-B. Jing, Z.-J. Jin, W.-C. Zhu, Z.-L. Wang and G.-J. Wang*

College of Chemistry, Jilin University, Changchun 130023, P.R. China

(Received June 10th, 2003; revised manuscript December 8th, 2003)

Generally, heteropoly compounds exhibit a rich acid/base and redox chemistry, which makes them attractive for applications to biochemistry, analysis, catalysis, photochemistry and other areas [1–3]. When some coordinated metal atoms in the heterpoly anion are substituted for other metal atoms, the framework of the heteropoly anion is still maintained [4–6]. Although its physical and chemical properties are substantially changed, thus, its catalytic function can be enhanced [7–14]. Traditional synthesis method of the substituted heteropoly compounds often introduces much impurity into the products. The present paper reports an improved method of synthesizing the substituted heteropoly compounds, using fresh molybdovanadophosphoric heteropoly acid as precursor. In our work a series of pure transition metal substituted molybdovanadophosphoric heteropoly compounds $Na_6PMo_{10}VMO_{40}\cdot H_2O$ (M = Zn, Fe, Mn, Co, Ni, Cu) were prepared successfully and characterized by ICP, IR, DTA-TGA and cyclic voltammetry. Their thermal stability, oxidition-reduction behaviour and spectroscopic features were discussed in detail. It can be assumed that they exhibit a good thermal stability, oxidation-reduction behaviour and spectroscopic characteristics, and might be promising catalysts.

The molybdovanadophosphoric heteropoly acid with Keggin structure ($H_4PMo_{11}VO_{40}\cdot 32.5H_2O$) (abbreviated as $PMo_{11}V$) was synthesized according to [15]. Stechiometric amount of sulphate $ZSO_4\cdot H_2O$ ($Z = Fe^{2+}$, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) was added into a solution of $PMo_{11}V$. A solution of $NaHCO_3$ was added dropwise to adjust the pH value. The crystals of $Na_2SO_4\cdot 10H_2O$ were leached and the filtrate was placed in a desiccator for few days to obtain the crystals of the expected compounds $PMo_{10}VM$ (M = Zn, Fe, Mn, Co, Ni, Cu), which were collected and recrystallized. The products were analysed by ICP (OPTIMA 3300 DV, USA) and their molecular formulae were determined as $H_3Na_5PMo_{10}VMO_{40}\cdot nH_2O$ (M = Zn, Fe, Mn, Co, Ni, Cu).

*To whom correspondence should be addressed; e-mail: yeyutingzhu@mail.jlu.edu.cn

The characteristic peaks of the heteropolyanion at 700–1100 cm^{-1} were observed on the infrared spectra of the title compounds and $PMo_{11}V$ (Fig. 1), which indicate that the transition metal containing molybdovanadophosphoric heteropoly compounds $PMo_{10}VM$ remain the Keggin structure. When a molybdenum atom of $PMo_{11}V$ was substituted for other transition metal atom, the asymmetric stretching vibration υ_{as}(P–O) (1063 cm^{-1}) tends to split up, indicating that the symmetry of framework is changed. The splitting value $\Delta\upsilon$ was dependent on the type of transition metal atoms. The splitting value $\Delta\upsilon$ of $PMo_{10}VNi$ (65 cm^{-1}) was largest. It is reasonable to assume that the splitting value $\Delta\upsilon$ of the band υ_{as}(P–O) in the infrared spectrum might also be an index for identifying the heteropoly compounds. In addition, the asymmetric stretching vibrations υ_{as}(Mo–O) and υ_{as}(V–O) (the band of V–O is covered by the band of Mo–O), shifted towards low wavenumber for about 15 cm^{-1}, indicate that the transition metal atom can donate electron to Mo–O and as a result weakens the intensity of Mo–O.

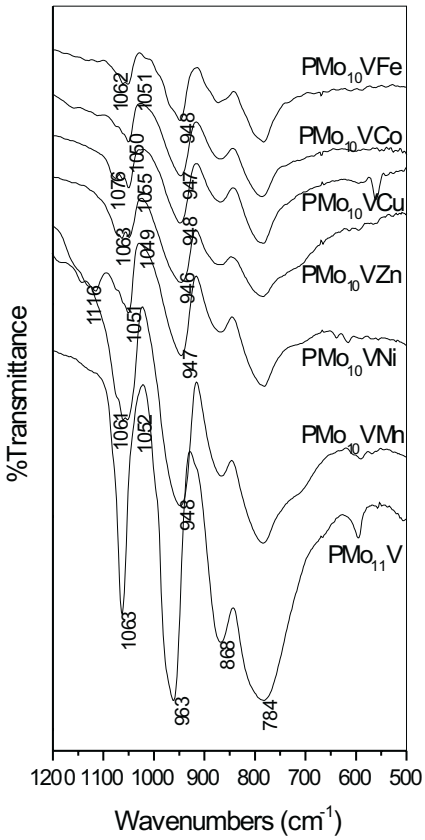

Figure 1. IR spectra of $PMo_{11}V$ and $PMo_{10}VM$.

TGA measurements were carried out to determine the number of molecules of crystallization water in the heteropoly compounds and the temperature, at which thermal decomposition of the samples takes place. All heteropoly compounds exhibit a good thermal stability (Table 1) and the temperature of exothermic peaks of this series of substituted compounds is lower than that of $PMo_{11}V$, which indicates that the addition of substituting metal cations lowers the thermal stability of the $PMo_{11}V$. In addition, the total weight loss of this series of compounds was 12–19%, which corresponds to the following formulae: $H_3Na_5PMo_{10}VFeO_{40}\cdot 14.5H_2O$, $H_3Na_5PMo_{10}VCoO_{40}\cdot 16.5H_2O$, $H_3Na_5PMo_{10}VCuO_{40}\cdot 18.5H_2O$, $H_3Na_5PMo_{10}VZnO_{40}\cdot 20.5H_2O$, $H_3Na_5PMo_{10}VNiO_{40}\cdot 21H_2O$, $H_3Na_5PMo_{10}VMnO_{40}\cdot 24H_2O$.

Table 1. The temperatures of exothermic peaks of $PMo_{11}V$ and $PMo_{10}VM$.

Heteropoly compounds	$PMo_{11}V$	$PMo_{10}VCu$	$PMo_{10}VNi$	$PMo_{10}VZn$	$PMo_{10}VCo$	$PMo_{10}VFe$	$PMo_{10}VMn$
T (K)	718	615	627	604	618	617	619

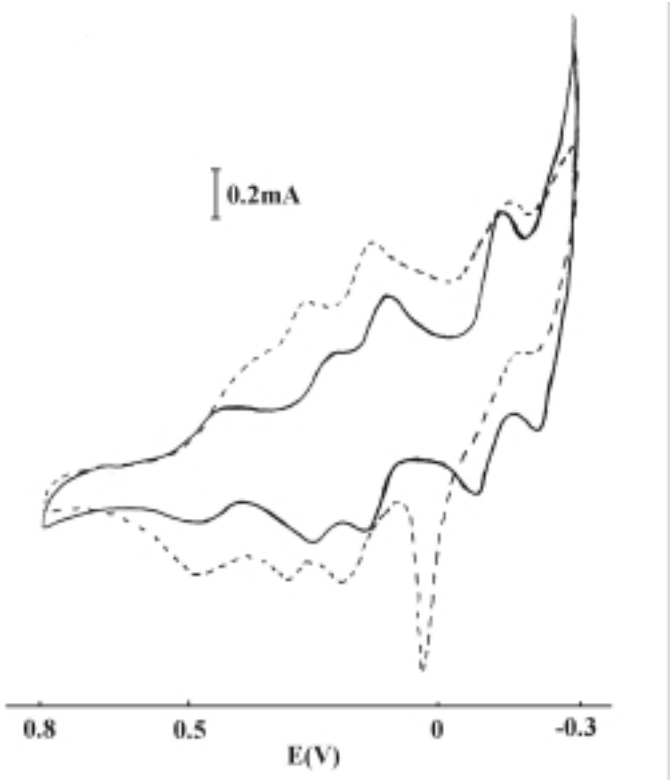

Figure 2. Cyclic voltammograms of $PMo_{11}V$ and $PMo_{10}VCu$ recorded using a platinum electrode in 50% (v/v) dioxane+water solutions with 0.1 mol/L H_2SO_4 as a supporting electrolyte. The concentration of the samples was 10^{-3} mol/L. A saturated calomel electrode (SCE) was employed as a reference electrode. The scan rate was 50 mV/s. — $PMo_{11}V$; ---- $PMo_{10}VCu$.

The cyclic voltammogram of $PMo_{11}V$ has five steps (Fig. 2). The first step at the most positive potential is assigned to the reversible redox process of vanadium, the others to the reversible redox processes of molybdenum [16]. However, the redox waves of molybdenum in the substituted compounds appear at more positive potentials than those in $PMo_{11}V$ (Fig. 3), and the redox wave of vanadium in the substituted compounds shifts to a little more negative potential than that in $PMo_{11}V$ (Table 2). Based on these discussions, it can be assumed that the addition of substituent metal cation could just change the negative charge on the precursor ($PMo_{11}V$) [17] and the electron transfer in the transition metal atom could be easier than that in the molybdenum and vanadium atoms. Unlike other cyclic voltammogram of $PMo_{10}VM$, the cyclic voltammogram of $PMo_{10}VCu$ (Fig. 2) exhibits a very large current intensity and is chemically irreversible. This large stripping wave can be considered as a proof of the formation of a new copper-containing heteropolyanion from the precursor $PMo_{11}V$ [17].

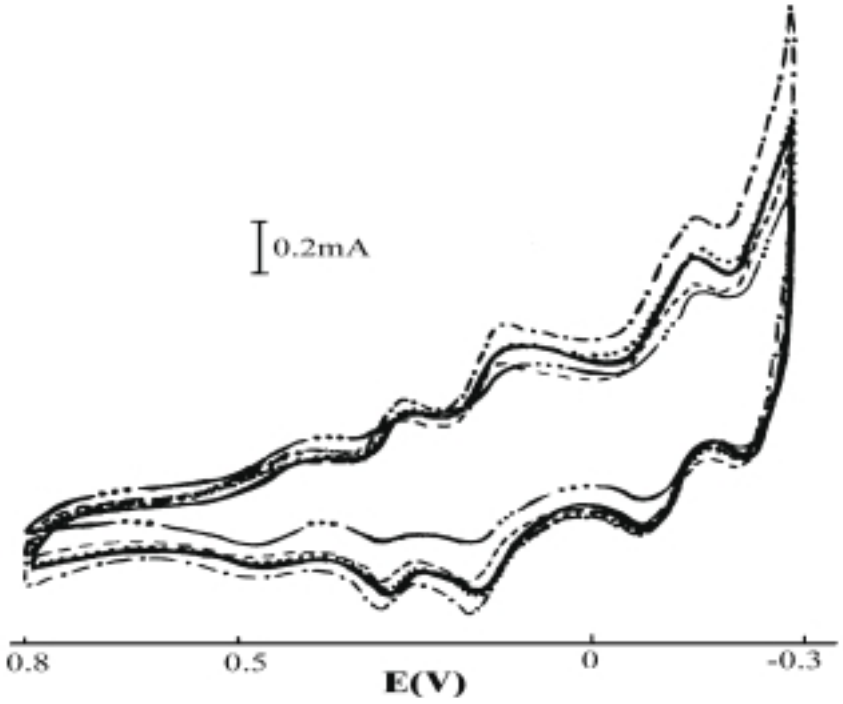

Figure 3. Cyclic voltammograms of $PMo_{11}VM$ (M = Zn, Fe, Mn, Co, Ni) recorded using a platinum electrode in 50% (v/v) dioxane+water solutions with 0.1 mol/L H_2SO_4 as a supporting electrolyte. The concentration of the samples was 10^{-3} mol/L. A saturated calomel electrode (SCE) was employed as a reference electrode. The scan rate was 50 mV/s. — $PMo_{11}VMn$; ----- $PMo_{11}VCo$; – ··· – $PMo_{11}VFe$; ····· $PMo_{11}VZn$; –·– $PMo_{11}VNi$.

Table 2. Voltammetric data for $PMo_{11}V$ and $PMo_{10}VM$. The scan rate was 50 mv/s.

Heteropoly compounds	E_{pc}(v)	E_{pa}(v)	ΔE_p (mv)	$E_{1/2}$(v)	Heteropoly compounds	E_{pc}(v)	E_{pa}(v)	ΔE_p (mv)	$E_{1/2}$(v)
$PMo_{11}V$	0.425	0.490	65	0.458		–0.150	–0.060	90	–0.105
	0.210	0.255	45	0.233		–0.280	–0.205	75	–0.248
	0.100	0.145	45	0.123	$PMo_{10}VFe$	0.420	0.485	65	0.453
	–0.130	–0.080	50	–0.105		0.270	0.300	30	0.285
	–0.270	–0.205	65	–0.238		0.100	0.160	60	0.130
$PMo_{10}VNi$	0.420	0.490	70	0.455		–0.160	–0.080	80	–0.120
	0.265	0.300	35	0.283		–0.280	–0.210	70	–0.245
	0.125	0.170	45	0.148	$PMo_{10}VMn$	0.420	0.480	60	0.450
	–0.150	–0.070	80	–0.110		0.260	0.290	30	0.275
	–0.285	–0.210	75	–0.248		0.115	0.165	50	0.140
$PMo_{10}VZn$	0.410	0.470	60	0.440		–0.145	–0.075	70	–0.110
	0.260	0.300	40	0.280		–0.280	–0.215	65	–0.248
	0.115	0.165	50	0.140	$PMo_{10}VCu$	0.420	0.490	70	0.455
	–0.150	–0.070	80	–0.110		0.265	0.300	35	0.283
	–0.290	–0.215	75	–0.253		0.135	0.190	55	0.163
$PMo_{10}VCo$	0.430	0.490	60	0.460		–0.150	0.020	170	–0.065
	0.270	0.310	40	0.290		–0.280	–0.210	70	–0.245
	0.130	0.175	45	0.153					

REFERENCES

1. Schuchardt U., Cardoso D., Sercheli R., Pereira R., Cruz R.S., Guerreiro M.C., Mandelli D., Spinacé E.V. and Pires E.L., *Appl. Catal. A: Gen*., **211**, 1 (2001).
2. Baronetti G., Brand L., Sedran U. and Thomas H., *Appl. Catal. A: Gen*., **172**, 265 (1998).
3. Strukul G. (ed.), *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Acad. Publ., Netherlands 1992, p. 253.
4. Neumann R. and Dahan M., *Polyhedron*, **17**(20), 3557 (1998).
5. Li M.X., Jin S.L., Liu H.Z., Xie G.Y., Chen M.Q., Xu Z. and You X.Z., *Polyhedron*, **17**(21), 3721 (1998).
6. Mizuno N., *Catal. Surv. Japan*., **4**(2), 149 (2000).
7. Zhang H.B., Zheng J.W. and Zhang Y.Z., *J. Electroanal. Chem*., **317**, 169 (1991).
8. Simões M.M.Q., Conceição C.M.M., Gamelas J.A.F., Domingues P.M.D.N., Cavaleiro A.M.V., Cavaleiro J.A.S., Ferrer-Correia A.J.V. and Johnstone R.A.W., *J. Mol. Catal. A: Chem*., **144**, 461 (1999).
9. Neumann R., Khenkin A.M., Juwiler D. and Miller H., *J. Mol. Catal. A: Chem*., **117**, 169 (1997).
10. Ali B.E., El-Ghanam A.M. and Fettouhi M., *J. Mol. Catal. A: Chem*., **165**, 283 (2001).
11. Süss-Fink G., Gonzalez L. and Shul'pin G.B., *Appl. Catal. A: Gen*., **217**, 111 (2001).
12. Cramarossa M.R., Forti L., Fedotov M.A., Detusheva L.G., Likholobov V.A., Kuznetsova L.I., Semin G.L., Cavani F. and Trfirò F., *J. Mol. Catal. A: Chem*., **127**, 85 (1997).
13. Knapp C., Ui T., Nagai K. and Mizuno N., *Catal. Today*, **71**, 111 (2001).
14. Zhang H.P., Zhang X.M., Ding Y., Yan L., Ren T. and Suo J.S., *New J. Chem*., **26**(4), 376 (2002).
15. Tsigdinos G.A. and Hallada C.J., *Inorg. Chem*., **7**(3), 437 (1968).
16. Zhang H.B., Wu T.H., Yan X.B., Leng Y.C. and Li S.J., *Chem. J. Chin. Univ*., **11**(10), 1096 (1990).
17. Keita B., Girard F., Nadjo L., Cotant R., Canny J. and Richet M., *J. Electroanal. Chem*., **478**, 76 (1999).