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Some More Findings on Tantalum Tungstate: A Crystalline Ion Exchange Material

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A new crystalline phase of tantalum tungstate through hydrofluoric acid medium abbreviated as TaW(HF) in this article has been synthesized. Its i.e.c. composition and other analyses i.e. TGA, DSC, Electrophotographs i.r. and X-ray have been reported. The *d* values, Miller indices (*h*, *k*, *l*) and unit cell constant (*a*) have been calculated. The analysis of these data shows that the phase belongs to FCC (face centered cubic) system.

INTRODUCTION

Being highly selective and resistant to heat and radiations, inorganic ion exchange materials have recently attained considerable importance in analytical and electrochemistry. A good number of these materials based on tin, titanium, niobium and tantalum etc. have been synthesized, characterised and investigated for their ion exchange properties and analytical applications in these laboratories.

Qureshi *et al.* have published their findings on tantalum arsenate[1,2], tantalum antimonate[3] and tantalum tungstate[4]. When the work was in progress on tantalum tungstate, Raveau *et al.*[5] have published some studies on the thermodynamics and kinetics of ion exchange on a different phase of tantalum tungstate. However, these materials could only be obtained in the amorphous state. The selectivity of exchanger depends on its composition and the method of its preparation. Numerous efforts have been made to explain the selectivity of inorganic ion exchangers for certain metal ions. However the selectivity sequence is not easy to predict. It is important to study crystalline phases because owing to their definite structure, a more exact interpretation of the ion exchange phenomenon may be achieved. The other merits of such material are that the surface area of crystalline preparations[6–9] occurs about 1000 times that of amorphous one and the tendency towards the hydrolysis decreases as one changes from amorphous to crystalline state. Therefore it was decided to synthesize a crystalline phase of it.

During the efforts to synthesize a crystalline tantalum tungstate, a number of methods have been tried. In this article we have presented the results on the synthesis of crystalline tantalum tungstate obtained by the

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slow evaporation of hydrofluoric acid solution. In addition to synthesis we have also mentioned its ion exchange capacity (I.E.C.) composition and other properties using thermogravimetric, differential scanning calorimetric, infrared and electrographic analyses. With the help of X-ray diffractogram the *d*-values, Miller indices (*h*, *k*, *l*) and unit cell constant (*a*) have been calculated.

EXPERIMENTAL

Tantalum pentachloride (Poole, Great Britain), sodium tungstate (B.D.H.), HF (38.40%) and all other reagents were of analaR grade. The following instruments were used during the investigations: a Bausch & Lomb Spectronic-20 Colorimeter, a Philips X-ray Unit, 900 & 950 Thermal Analyzers, Dupont 9900 DSC unit and 1R Spektromom-2000.

3.5823 gm of $TaCl_5$ was dissolved in 120 ml of conc. HCl and this solution was diluted to 5 litre with distilled water and a few ml of conc. HNO_3 was added. The resulting solution was heated for 6 hrs. gently. After heating for some time a gelatinous precipitate was obtained. The precipitate was kept in the mother liquor for 24 hrs., filtered and washed with demineralised water. The washed precipitate was dissolved in the least volume of HF acid and 3.29 g of sodium tungstate was also dissolved in the least volume of HF acid in polythene containers separately. Sodium tungstate in HF acid solution was mixed with $TaCl_5$-HF solution slowly with shaking. No precipitate occurred at the time of mixing. The mixture was kept for evaporation; on the 10th day the tantalum tungstate began to precipitate. The precipitation had been completed within 30 days followed by complete evaporation of HF acid. The product was yellow in colour. It was taken out and washed with DMW and acetone subsequently. The new synthesized tantalum tungstate which was prepared by slow evaporation of the HF solution is represented by TaW(HF) in this article.

Preparation of Hydrated Tantalum Pentoxide from Hydrofluoric Acid Solution

The tantalum pentachloride was hydrolysed as in the synthesis of tantalum tungstate and the precipitate obtained was dissolved in the least quantity of HF acid. The solution was allowed to evaporate. After complete evaporation of HF acid the product obtained is designated Ta_2O_5(HF).

Preparation of Na_2WO_4(HF)

3.29 g of Na_2WO_4 was dissolved in HF acid and the obtained solution was allowed to evaporate. The product obtained after complete evaporation is designated as Na_2WO_4(HF).

Composition

500 mg of TaW(HF) was thoroughly ground with 1.25 gm of KNO_3 and

1.25 gm of K_2CO_3. The mixture was heated in a platinum crucible at 760–800°C in a furnace till it melted. The melt was dissolved in magnesia solution. Tantalum was precipitated with tannin and determined gravimetrically[10] as tantalum pentoxide. The tungsten was determined by the sodium thiocyanate-stannous chloride method at 480 nm spectrophotometrically[11]. The mole ratio of Ta to W was found to be 2.568.

RESULTS AND DISCUSSION

TaW(HF), mole ratio Ta : W : : 2.568 : 1 shows 0.40 meg. g^{-1} ion exchange capacities for Na^+ and K^+ ions respectively. It is less compared to the earlier reported amorphous tantalum tungstate, mole ratio Ta : W: : 1 : 1.54. The decrease may be due to a decrease in W/Ta mole ratio as the anionic part dominates more in cation exchange capacity of the material.

Differential scanning calorimetric analysis of TaW(HF) seems to be a multireaction system. The removal of water of crystallisation completes upto 73.70°C. Then the removal of coordination water comes into picture. Its removal starts from 101.86°C and completes at 141.37°C. The remaining small peaks represent the phase transitions in regard of crystallinity etc.

The results of TGA of TaW(HF) and Na_2WO_4(HF) are presented in Table 1. These results indicate a high thermal stability. In the lower

TABLE 1
THERMOGRAVIMETRIC ANALYSIS RESULTS OF TaW(HF) AND Na_2WO_4(HF)

Temp. (°C)	TaW(HF)—% loss	Na_2WO_4(HF)—% loss
50	0.762	0.756
100	2.284	1.512
150	5.334	2.268
200	6.096	3.024
250	8.382	3.024
300	9.144	3.780
350	9.906	4.536
400	11.230	6.048
450	12.954	6.804
500	15.240	9.828
550	19.812	12.852
600	22.098	13.608
650	23.060	13.608
700	23.622	13.680
750	24.384	15.120
800	25.908	18.90
850	26.12	23.94
900	26.67	30.996
950	27.432	37.80
1000	27.432	37.80

TABLE 2
d SPACING VALUES

TaW(HF)		Na_2WO_4(HF)		Ta_2O_5ASTM–(21–1198)		Na_2WO_4(BDH) ASTM–(12–17)	
d (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0
6.8041	100	6.801	100	8.92	6	5.28	90
5.1510	17	6.402	28	4.42	6	3.23	95
4.3496	19	4.866	46	3.78	60	2.753	100
4.1486	14	4.067	61	3.77	70	2.282	6
3.8306	24	4.524	59	3.76	50	2.094	20
3.6745	56	4.015	53	3.63	50	1.8642	40
3.4241	46	—	—	—	—	1.7574	40
3.2406	80	3.861	74	3.59	6	1.6142	35
3.0763	14	3.765	71	3.36	70	1.5430	20
2.6195	25	3.396	37	3.36	80	1.4435	25
		3.300	86	3.35	70	1.3921	14
		3.205	73	3.32	20	1.3177	2
2.5974	25	2.956	31	3.06	25	1.2786	10
2.5197	23	2.711	11	3.05	25	1.2202	20
2.4402	16	2.665	19	3.04	25	1.1887	20
2.4275	14	2.519	22	3.02	16	1.1412	6
2.2962	16	2.478	22	2.979	100	1.1154	4
2.2629	16	2.365	24	2.763	6	1.0759	10
2.0741	14	2.273	22	2.751	6	1.0542	10
1.9513	25	2.220	22	2.457	65	1.0206	4
1.8798	13	2.129	19	2.454	75	—	—
1.7892	20	2.100	13	2.436	60	—	—
1.7262	16	2.828	11	2.433	60	—	—
1.6543	14	1.987	10	—	—	—	—
1.4029	12	1.946	2	—	—	—	—

temperature range TaW(HF) loses more than Na_2WO_4(HF). It might be due to the presence of higher content of water of coordination and crystallization, which hints more and more hydroxogroups. These groups mainly form tungstic acid which on heat treatment gets converted into tungstic oxide. At higher temperature TaW(HF) shows weight less than Na_2WO_4(HF). It is entirely due to the thermal inertness of tantalum oxide.

The IR spectrum of TaW(HF) shows broad peaks at 3300 cm^{-1}, 1620 cm^{-1} and 1260 cm^{-1} which correspond to weak hydroxo stretching vibrations (O–H), deformation vibrations of interstitial water and hydroxyl groups and deformation vibration of M–OH bonds respectively.

Electron photographs of TaW(HF) at the magnification of 5,200 and 10,400 were taken. The electrophotograph of 5,200 magnification indicates the crystalline nature of the material.

X-ray diffractograms of TaW(HF) and Na_2WO_4(HF) were taken from their powder samples. The *d* values have been calculated from the

TABLE 3
MILLER INDICES IN TaW(HF) CRYSTALS

Values	*d* values (Å)	*hkl*
30°	6.8041	220
17°12′	5.1510	220
20°24′	4.3496	311
21°24′	4.1486	222
23°12′	3.8306	400
24°12′	3.6745	331
26°	3.4241	420
27°31′	3.2406	422
29°	3.0763	511, 333
34°12′	2.6195	440
34°30′	2.5974	531
35°36	2.5197	600, 442
36°48	2.4402	620
37°	2.4275	533
39°12′	2.2962	622
39°48′	2.2629	444
43°36′	2.0741	711, 551
46°30′	1.9513	640
49°30′	1.8798	642
51°	1.7892	731, 553
53°	1.7262	800
55°30′	1.6543	733

measured values and these calculated d values alongwith d values of Ta_2O_5 and $Na_2WO_4.2H_2O$ (obtained from their ASTM Card's No. 21–1198 and 12–77 respectively) are presented in Table 2. Hydrated tantalum (HF) shows no line in X-ray diffractogram.

The sudy of Table 2 at a glance hints that TaW(HF) is a crystalline material and it is quite different from Ta_2O_5, $Na_2WO_4.2H_2O$ and Na_2WO_4(HF). A few *d* values appear to be common between TaW(HF) and Na_2WO_4(HF); this similarity among *d* values may be due the presence of common phase of tungstic acid.

The X-ray diffraction pattern of TaW(HF) has been analysed for the Miller indices (*h*, *k*, *l*) and unit cell constant (*a*). Miller indices have been calculated from measured and corresponding *a* values. They are shown in Table 3. The pattern of these indices reveals that the crystal of TaW(HF) belongs to a face centered cubic (fcc) system. The unit cell constant (*a*) of the crystal lattice is 15.11 Å.

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