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THERMAL CHARACTERIZATION OF HYDROUS TUNGSTEN OXIDES AND THEIR BEHAVIOR AS ION EXCHANGER

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Abstract

The preparation, and thermal characterization and ion exchanger behavior of hydrous tungsten oxides obtained from purified tungsten trioxide, by processing of a Brazilian scheelite ore were described. By an alkaline fusion of tungsten trioxide with an excess of sodium carbonate at 900°C an intermediate tungstate product is obtained. Acid lixiviation of the tungstate intermediary in different experimental conditions produces two different hydrous tungsten oxides I and II respectively. A third material was produced by thermal treatment of II, yielding the material IIA, a monohydrate species. The materials prepared were characterized by TG/DTG, X-ray diffractometry and by surface area measurements. Their ion exchange behavior was studied too, using Na^+ and K^+ ions as the exchanged species. The inorganic exchanger materials were partially regenerated and may be used consecutively.

Keywords: hydrous tungsten oxide, ion exchanger, thermal treatment

Introduction

Ion exchange procedures are of industrial and laboratorial interest and has been used to water demineralization and softness, materials recovery, metallic ions extraction, purification of laboratorial products and for biochemical and pharmaceutical applications [1].

The inorganic exchange materials were lesser utilized than the traditional organic resins, but their usage specially in radio-isotopes has grown considerably [2].

Different hydrous tungsten oxides have been prepared in different experimental conditions of temperature and concentration. Five or six different materials whose two species were frequently observed. Morley [3] describes the monohydrate form, $WO_3{\cdot}H_2O$ a crystalline yellow material and the dihydrate form, $WO_3{\cdot}2H_2O$, a white yellow amorphous material, when heated at 55–75°C loss water yelding the monohydrate form [4].

Hydrous tungsten oxides are stable in water, acetic, nitric aqueous solutions and in alcohols but soluble in alkaline and ammoniacal solutions and in hydrofluoridic

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acid. This materials presents an ambiguous behavior exchanging both anions and cations depending on the media. Thermal analysis studies for some tungstic acids were described in literature [5, 6] and were realized up to 750°C to avoid the volatilization of the WO_3. Ion exchange behavior of some cations were realized by some researches and were described by Chowdhury [7] involving separations of Zn^{2+}, Cu^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+} and Ni^{2+} from Mg^{2+} or Ni^{2+} and Mn^{2+} from Co^{2+}. According to literature [8] titration curves of hydrous tungsten oxide presents inflextion points showing exchange reactions at pH values up to 5 and at higher pH values occurs the dissolution of the inorganic exchangers due to formation of soluble tungstates.

Experimental

Material and methods

Tungsten oxide was prepared by purification of the Brazilian sheelite ore, in our Institution. Hydrous tungsten oxide (Synth-P.A.) was used as standard material.

Thermal analysis measurements (TG/DTG) were obtained in a Shimadzu thermal balance for TG analysis model TGA 50 between 20 and 800°C with a heat rate of 10°C min^{-1} in N_2 atmosphere.

X-ray diffractograms were obtained in a Philips equipment, model 1840 for 2θ values between 10 to 70°.

Surface area measurements were performed in FLOW SORB 2300 equipment of Micrometrics corporation, before the samples were degassed in the cell at 50°C for 3 h.

Sodium and potassium determinations were performed in a Micronal flame emission photometer, model B 262.

Hydrous tungsten oxides preparations

Preparation I

Purified tungsten trioxide, WO_3 was mixed with an excess of sodium carbonate in 1:6 ratio and melted in a Pt crucible at 900°C during 40 min resulting in a yellow melt (Na_2WO_4). An aqueous HCl 4.0 mol L^{-1} solution was heated near 100°C and added to the melted material producing a fine bright yellow solid and an incolor remaining solution with a pH 0.4.The material separated by centrifugation, was exhaustively washed with deionized H_2O, until eliminates residual sodium and chloride ions and dried at 100°C during 6 h.

Preparation II

Sodium tungstate melt was prepared as indicated in preparation I. An aqueous HCl 2.4 mol L^{-1} solution was added, drop to drop to the tungstate melt producing a white yellow solid and an incolor remaining acidic solution. The material was filtered in a cellulose nitrate membrane washed exhaustively with deionized H_2O until eliminates the residual sodium chloride ions and dried at 50°C during 48 h.

Preparation IIA

An amount of product of preparation II, after filtration and washing with deionized H_2O was heated at 100°C during 2 h resulting in a solid material with intense coloration yellow-green, that was named preparation IIA.

Ion exchange behavior

Using Na^+ and K^+ as the exchanged species the behavior of the prepared hydrous tungsten oxides (I, II and IIA) and a commercial one (III) have been studied using two different procedures described below. The studies were performed in aqueous solution at pH 5.0 because the inorganic exchanger breaks down at more elevated pH values, mainly in the basic region (soluble tungstates were formed with alkaline metallic or ammonium ions).

Discontinuous or bath process

0.2000 g samples of each tungsten hydrous oxide preparation were added to 50.0 mL [MCl_n 0.05000+$M(OH)_n$ 0.05000] eq. L^{-1}, where $M^{+n}=K^+$ or Na^+, whose pH was previously adjusted to 5.0, by addition, drop to drop of enough HCl 2.0 mol L^{-1} aqueous solution in polyethylene flasks. The samples were stirred in a mechanical stirrer table at different times (between 0 and 24 h or 0 and 8 h, respectively for Na^+ or K^+ ions). The metallic ion concentration was measured before and after each agitation time by flame emission photometry.

Flow process (in column)

A similar procedure was developed using suitable glass columns with 5 mm internal diameters and 180 mm height, with a capillar open at the botton. The botton of the columns was packed with fiber glass material and with 0.2000 g of each hydrous tungsten oxide (Fig. 1). The aqueous exchange solution was pumped inside the prepared columns with a peristaltic pump at 0.5 and 3.3 mL min^{-1}, for Na^+ or K^+ ions respectively. The ion exchange solutions utilized were the same described in the discontinuous procedure. Differ-

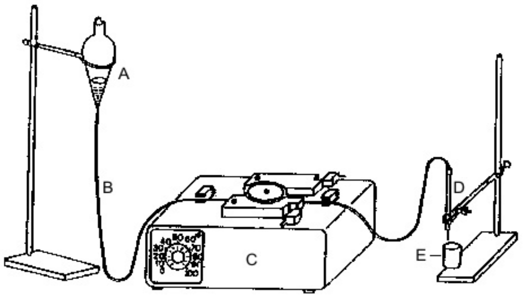

Fig. 1 System utilized for ion exchange experiments with columns: A – solution reservoir; B – polyethylene tube; C – peristaltic pump; D – packed ion exchange column and E – collector flask

ent pump rates were used based on the results obtained in discontinuous procedure for IEC values determination for Na^+ or K^+ ions, respectively.

Results and discussion

Characterization of the tungsten hydrous oxides

Thermal behavior for each one of the preparations was studied by recording the TG and DTG curves between 25 and 800°C, at a 10°C min^{-1} rate under nitrogen atmosphere using weighted samples between 5.00 and 10.00 mg.

Figures 2 and 3 show the TG and DTG curves obtained for the preparations I, II and IIA, III (a commercial material from Synth), respectively. The behavior difference of the preparation II (Fig. 2) when compared with the TG/DTG curves obtained for I and IIA (Figs 2 and 3) shows that compound II presents a higher hydration grade and a decomposition in two defined steps. TG/DTG curves show that the stoichiometry of preparation IIA, after heating at 100°C, is the same of the preparation I.

From the TG results the hydration grade was determined by the expression [9]:

$$18n=X[M+18n]/100$$

for M=molecular mass of anhydrous oxide; X=water loss percentual obtained in the TG analysis and n=hydration number.

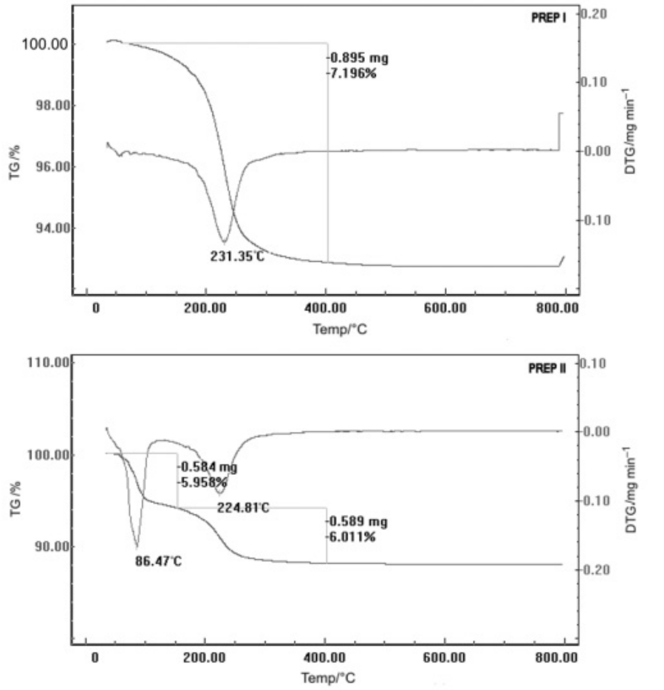

Fig. 2 TG/DTG curves obtained for preparations I and II

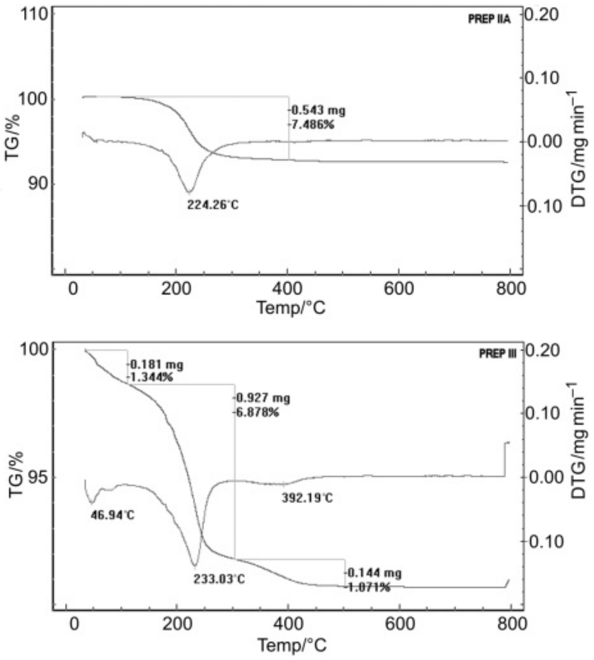

Fig. 3 TG/DTG curves obtained for preparations IIA and III

Table 1 The analysis results and stoichiometric formulas determined for hydrous tungsten oxides

Preparation	Temperature range/°C	Water loss/%		Stoichiometry
I	25–400	7.20	7.20	$WO_3{\cdot}1.0H_2O$
II	25–300	5.96		
	300–400	6.01	13.16	$WO_3{\cdot}2.0H_2O$
IIA	25–400	7.49	7.49	$WO_3{\cdot}1.0H_2O$
III	25–100	1.34		
	100–300	6.88		
	300–500	1.07	9.29	$WO_3{\cdot}1.3H_2O$

Table 1 shows the chemical composition obtained from the thermogravimetric results. X-ray diffractograms for all four studied materials were obtained from scanning the samples between 2θ values from 5 to 80°. Crystalline forms of all hydrous tungsten oxides were obtained by X-ray diffraction (Table 2). Surface area measurements, were determined by BET methodology and their results obtained described in Table 2. These values are low and agree with their crystalline structures.

From the patterns obtained the '*d*' values from each diffractogram were calculated from the expression following and compared with those of two ASTM Standard materials. Table 3 shows the 'd' values calculated by X-ray diffractograms using the Bragg law expression:

$$\lambda=2d\sin\theta$$

where λ=1.54178 for CuK and 2θ=incidence angle.

These results show that the materials I and IIA agree with the ASTM standard 18–1420, (monohydrate) and the material II with the ASTM standard 18–1418, the dihydrate hydrous tungsten oxide. These results agree with the thermal analysis results.

Table 2 Surface area measurements and X-ray characteristics

Preparation	Surface area/m^2 g^{-1}	Structure
I	21	crystalline
II	11	crystalline
IIA	7	crystalline
III	24	crystalline

Table 3 X-ray comparative determined 'd' values calculated from the diffractograms

Material	d/Å ($100I/I_0$)						
I	5.380 (54)	3.480 (100)	2.683 (10)	2.622 (17)	2.564 (27)	1.852 (11)	1.834 (13)
IIA	5.370 (100)	3.480 (40)	2.683 (18)	2.629 (4)	2.564 (14)	1.855 (9)	1.834 (5)
ASTM standard 18–1420	5.370 (75)	3.490 (100)	2.687 (10)	2.826 (12)	2.570 (25)	1.854 (10)	1.837 (14)
II	6.960 (100)	3.770 (30)	3.700 (30)	3.470 (30)	3.310 (40)	3.260 (40)	2.648 (14)
ASTM standard 18–1418	6.930 (100)	3.750 (26)	3.690 (26)	3.450 (49)	3.300 (49)	3.250 (38)	2.644 (12)

Ion exchange behavior

The ion exchange capacities (IEC) of each one of the prepared hydrous tungsten oxides was studied using two different procedures described below. The regeneration and reutilization of the exchanger were studied too.

For the bath or discontinuous process is possible to determine the IEC for each ion studied at different stirring times. According to description in the methodology stirring times between 0.25 and 8 h for Na^+ and 0.25 and 24 h for K^+ ions were utilized. The IEC values for Na^+ and K^+ were obtained at 4 and 8 h, respectively (Table 4). The results obtained show that Na^+ was the most effectively exchanged cation for all materials.

Table 4 IEC results obtained for each prepared material by the discontinuous and in column process

Preparation	IEC/millieq. g^{-1}			
	Discontinuous		Flow process	
	K^+	Na^+	K^+	Na^+
I	0.212(2)	0.850(2)	0.212(3)	0.850(2)
II	0.304(3)	0.929(3)	0.304(3)	0.929(3)
IIA	0.202(3)	0.861(3)	0.202(3)	0.861(3)
III	0.226(6)	0.410(6)	0.222(6)	0.475(6)

Reversibility of the exchange and regeneration of the hydrous exchangers

The ion exchange behavior was studied for Na^+ and K^+, by a discontinuous or in column procedures. In both cases all prepared materials show suitable exchange properties with good ion exchange capacities, IEC values. The reversibility of the exchange and regeneration of the inorganic exchanger and their use in consecutive operations were studied too (Table 5). The materials were partially regenerated in all cases (Fig. 4) but it is possible to employ the same inorganic exchanger in consecutive ion exchange procedure after a regeneration step. The sodium ion exchange is more efficient in terms of IEC value for all three materials prepared and for the commercial inorganic material studied (Table 4).

Table 5 Successive exchange and regeneration steps IEC values for the column process

Preparation	IEC/milieq. g^{-1}							
	Na^+				K^+			
	I	II	IIA	III	I	II	IIA	III
1st	0.880	0.948	0.948	0.600	0.215	0.292	0.215	0.292
2nd	0.608	0.744	0.744	0.375	0.189	0.267	0.163	0.192
3rd	0.540	0.608	0.608	0.300	0.189	0.267	0.163	0.192
4th	0.540	0.608	0.608	0.300	0.189	0.267	0.163	0.192
5th	0.540	0.608	0.608	0.300	0.189	0.267	0.137	0.192
6th	0.540	0.540	0.540	0.200	0.189	0.267	0.137	0.192

Conclusions

All hydrous tungsten oxides (I, II, IIA and III) obtained present crystalline structures. Its crystalline forms show low surface area measurement results 7 to 24 m^2 g^{-1}. Their physicochemical properties and their ion exchange behavior in terms of IEC values determined in aqueous solution of alkaline metals (Na^+ and K^+) show that those inor-

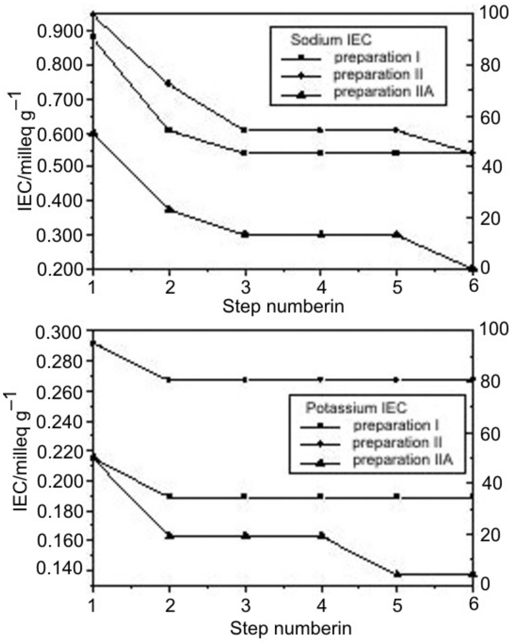

Fig. 4 Reversibility study for ion exchange experiments in column for Na^+ and K^+ ions

ganic compounds can be considered as promising ion exchanger materials. This inorganic exchanger may be regenerated partially and utilized again in successive steps.

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References

1 K. Dorfner, 'Ion exchangers', Gruyter, New York 1991.
2 M. Qureshi and K. G. Varshney, 'Inorganic Ion Exchangers in Chemical Analysis', CRC Press, Boca-Raton, Ann Arbor, Boston 1991.
3 A. M. Morley, J. Chem. Soc., 2 (1930) 1987.
4 S. W. H. Yil and C. T. Wang, 'Tungsten sources, metallurgy, properties and applications', Plenum Press, New York 1979.
5 M. L. Fredman, 'The tungstic acids', Contribution from Refractory Metals Laboratory, General Electric Co., 81 (1959) 3834.
6 N. H. Furman, 'Standard Methods of Chemical Analysis, 6th Ed., R. E. Krieger Publ. Co., Hutington, New York 1975, Vol. 1.
7 N. D. Chowdhury and A. K. De, Chromatographia, 11 (1978) 586.
8 A. Clearfield, 'Inorganic Ion Exchange Materials', CRC Press, Boca-Raton, Florida, 1982, Vol. 1, p. 163.
9 C. Airoldi and S. F. Oliveira, J. Braz. Chem. Soc., 3 (1992) 47.