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DEHYDRATION STUDIES OF TITANIUM MOLYBDATE

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Three chemically different samples (Ti : Mo ratios 1 : 2, 1 : 1 and 2 : 1) of titanium molybdate have been prepared by mixing the solutions of titanium(IV) chloride $\left(\frac{M}{40}\right)$, titanium sulphate $\left(\frac{M}{20}, \frac{M}{40}\right)$ and sodium molybdate $\left(\frac{M}{20}, \frac{M}{40}\right)$ in different volume ratios. Dehydration studies have been completed, which would seem to throw some light on the state of the water molecules present in the samples.

During the last twenty years ion exchange, especially on synthetic inorganic materials, has become one of the most useful ways to achieve important and analytically difficult separations. Recently, we have reported that the stability and ion exchange properties of amorphous molybdate [1] and antimonate [2] of titanium depend on the pH at which they are prepared and on concentrations as well as the mixing ratio of the starting reagents. The reversal of the sequence of K_d values for inorganic ions has been discussed in terms of size of cavities [2, 3]. It has also been reported that selectivity of hydrated tin(IV) oxide [4] depends on the degree of hydration. Therefore, to test the degree of hydration and to postulate a tentative structure of titanium molybdate, a thorough thermoanalytical study has been made for the three chemically different samples.

Experimental

Reagents: 15% titanium(IV) chloride solution (B.D.H.) and titanium(IV) sulphate solution (prepared by dissolving titanium dioxide in hot concentrated sulphuric acid containing ammonium sulphate), were used. All other reagents were of analytical grade.

Apparatus: An electric muffle furnace was used for heat treatments. For X-ray studies a Philips X-ray unit (Holland) with Philips camera and diffractometer was used. Thermogravimetry was carried out with a Stanton thermobalance.

Preparation

We have reported the synthesis and ion exchange properties of fourteen samples of titanium molybdate [1] under a range of conditions. Out of these samples we have now taken into account three chemically different samples; their method of preparation is given below.

Sample 1 was prepared by mixing $\frac{M}{40}$ titanium(IV) chloride solution with $\frac{M}{40}$ sodium molybdate solution with constant stirring in the volume ratio 1:1. A white precipitate appeared. Concentrated H_2SO_4 was added dropwise to this mixture with constant shaking till the final acid concentration was $0.18N$ H_2SO_4. Sample 2 was prepared by mixing the $\frac{M}{20}$ titanic sulphate solution with $\frac{M}{20}$ sodium molybdate solution in the volume ratio of 1:2 with constant stirring. A clear solution was obtained. Ammonia solution (sp. gr. 0.91) was added dropwise with constant shaking to this clear solution till the pH of aliquot was 2.

Samples 3 and 4 were obtained when $\frac{M}{40}$ titanium (IV) sulphate and sodium molybdate solutions were used in volume ratios of 1 : 1 and 2 : 1 respectively. The rest of the procedure was the same as for sample 1. The precipitates obtained in all the three cases were allowed to settle for 24 hrs, washed with distilled water by decantation, filtered and washed again with distilled water till the washing had a pH 6–7. The products so obtained were dried at 40°. They were immersed in demineralized water when they broke down to small particles. The particles were converted into hydrogen form by treatment with 2N HNO_3. The excess of the acid was washed out and the products dried at 40° were then ready for use.

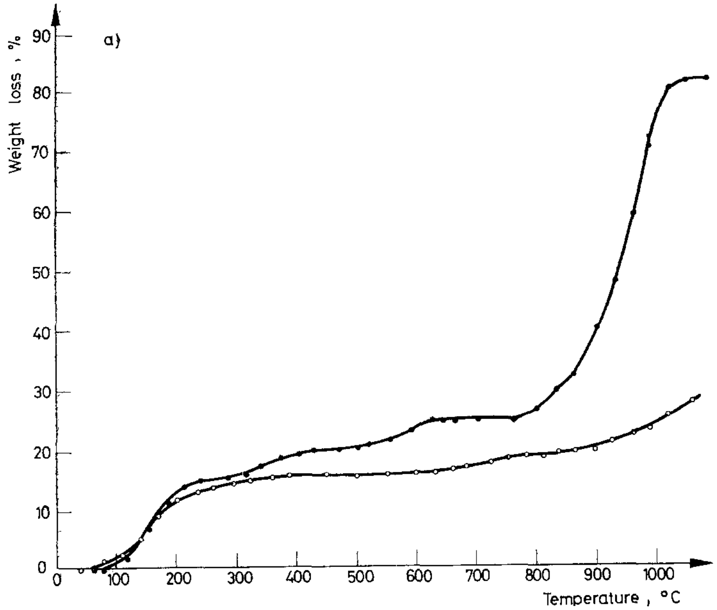

Fig. 1. Thermogravimetric curves of titanium molybdate
a) sample L.

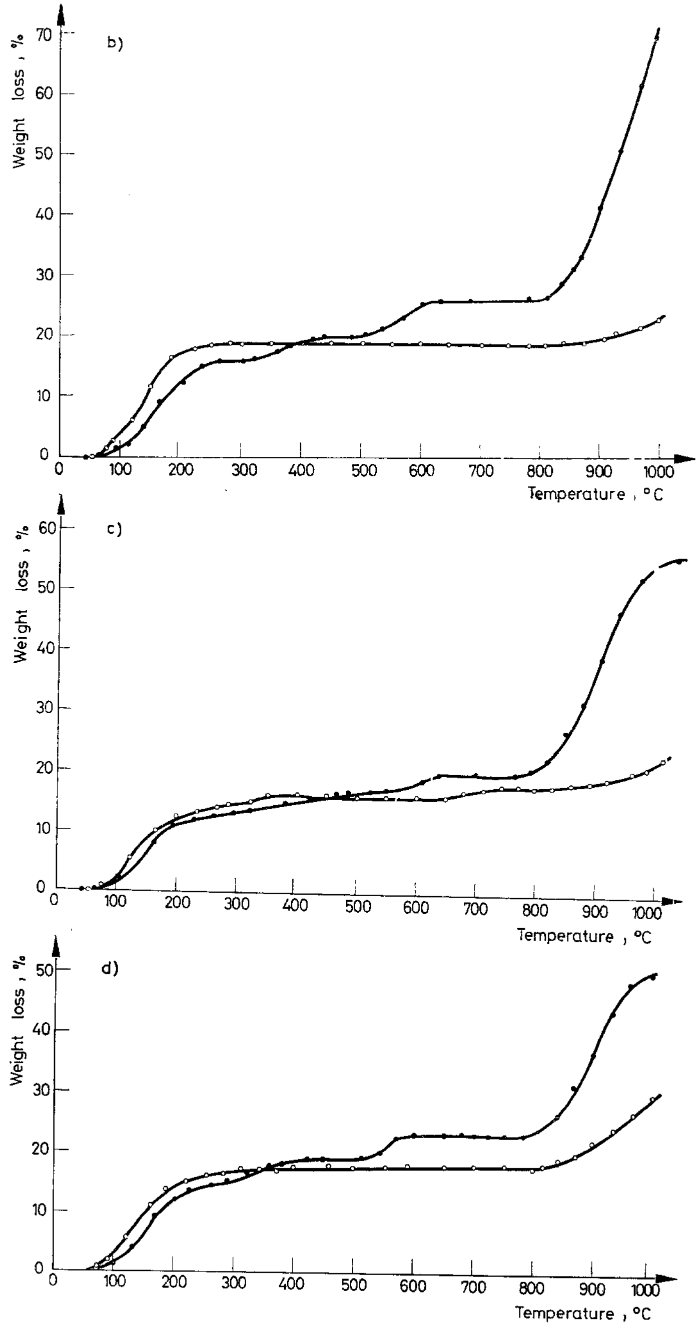

Fig. 1. Thermogravimetric curves of titanium molybdate. *b)* sample 2, *c)* sample 3, *d)* sample 4; ● sample in H-form; ○ sample in K-form

Chemical composition: Titanium and molybdenum were determined in the samples as reported in our previous paper [1]. The titanium to molybdenum ratio were found to be 1 : 1.94, 1 : 1.90, 1 : 1.11 and 1 : 0.50 for samples 1, 2, 3 and 4 respectively.

Ion exchange capacity: The ion exchange capacity of the samples was determined by saturation method [1]. The ion exchange capacity was found to be 1.60, 0.88, 0.95 and 0.93 mEq/g for samples 1, 2, 3 and 4 respectively.

Thermal treatment: 2 g of each sample were heated in an electrical muffle furnace for 15 hrs at 90–1000°. All the samples gave negative tests for molybdenum after this treatment. The results are given in Table 1.

Table 1

Heat treatment of titanium molybdates

	Sample 1	Sample 3	Sample 4
Material left after heat treatment, %	19.30	30.03	40.00
TiO_2 according to the structures proposed, %	18.40	28.00	37.30

Thermogravimetry: Samples 1,2,3 and 4 were dried at 40°. 200 mg of each sample in the hydrogen and potassium forms were analysed thermogravimetrically at a heating rate of 6°/min. The results obtained are reported in Figs 1a, 1b, 1c and 1d. Thermogravimetry at the rate of 4°/min for the hydrogen form of all the samples gave identical results with those for the same samples at a heating rate of 6°/min.

X-ray studies: All the four samples were dried at 40° and were studied by X-ray diffraction (Powder method) using Cu Kα radiation with Nickel filter for ten hours. No line was observed in any photograph. Sample 2 was dried at different temperatures and the lines were observed as given below:

No line at 100°, two lines at 245°, 3.506 (Sb) 1.854 (VVW); an additional line at 325° 1.657 (m.w.b.); the same three lines at 420°; seven more lines at 500° 6.965 (w), 3.795 (m.b.), 3.253 (vs), 2.65 (w), 2.326 (m.w.b.); 1.894 (m.w.b.) and 1.728 (m.w.) and eight more lines at 600° 2.517 (VVW), 1.685 (VVW), 1.628 (VW), 1.597 (VW), 1.547 (VW), 1.476 (VVW), 1.445 (VVW) and 1.344 (VVW). The relative intensities of the lines based on visual estimation are given in parenthesis preceded by the corresponding *d*-values in Å. Sample 3 dried at 600° was studied quantitatively with a diffractometer. It was found that the pattern of lines observed is identical with those for titanium dioxide brookite (ASTM card No. 3–0380) and molybdenum trioxide (ASTM card No. 5–0508).

Results and discussion

The X-ray studies show that the formation of molybdenum trioxide and titanium dioxide is facilitated as the drying temperature of titanium molybdate increases. This process is completed up to 600°. It seems that it may be due to loss of water which is incorporated either in the form of OH groups or H_2O as such within the exchanger (titanium molybdate). This behaviour of titanium molybdate is entirely different from that of phosphate [5,] and arsenate [6] of zirconium and titanium but resembles that of hydrous oxides [7] of zirconium, titanium, thorium and to other amorphous inorganic ion exchangers prepared in our laboratory.

At temperatures higher than 600° volatilization of molybdenum trioxide occurs (Table 1) which is responsible for the complete loss of molybdenum. On the basis of these observations and those reported in our earlier paper [1] we may say that titanium molybdate is a combination of hydrated oxides of titanium and molybdenum in a gel form structure. These hydrated oxides form a network structure with different size of cavities or surface area responsible for the selectivity of the exchanger towards the inorganic ions. The size of cavities or surface area seems to be dependent of the degree of hydration of these oxides [4]. To decide how these water molecules are attached to oxides of titanium and molybdenum, thermoanalytical results are used. Thermogravimetric curves of four samples of titanium molybdate (Figs 1a, b, c and d) are generally similar. The total per cent weight loss up to 600° in hydrogen form is always higher than that in potassium form. Hence we may say that water incorporated within the titanium molybdate is in two different forms: (i) in the form of OH groups whose hydrogen can be exchanged by any other cations; (ii) in the form of free water molecules which do not play any role in ion exchange but are responsible for the cavity size. With the help of per cent weight loss up to 600° in the potassium and in the hydrogen form, the following calculations are made:

Sample 1 (Fig. 1a)
$TiO_2(MoO_3)_{1.94}$ M.W. = 359.14

Water molecules whose hydrogen is exchangeable = Total per cent weight loss in hydrogen form – total per cent weight loss in potassium up to 600° = 9%

$$\text{m} \frac{1800\,n}{359.14 + 18n} = 9, \text{ where } n \text{ is number of water molecules}$$

$$n = 1.98$$

$TiO_2(MoO_3)_{1.94}(H_2O)_{1.98}$ M.W. = 394.78

water molecules whose hydrogen is unexchangeable = Total weight loss in potassium form up to 600° = 15%

$$\frac{1800\,n}{394.78 - 18n} = 15$$

$$n = 3.87$$

Now the empirical formula is $TiO_2(MoO_3)_{1.94}(H_2O)_{1.98}$ 3.87 H_2O

Ion exchange capacity per dry gram of the exchanger

$$= \frac{1.98 \times 2 \times 10^3}{464.44} = 8.50 \text{ mEq/g.}$$

In this way calculations have been made also for the remaining three samples. Results are recorded in Table 2.

The saturation ion exchange capacity determined experimentally is lower than theoretical ion exchange capacity (Table 2), owing to the fact that the samples are amorphous in which case replacement of all hydrogen atoms by other cations is not possible.

Table 2

Thermogravimetric results

Sample	Composition	Molecular weight	Water molecules in the form of OH groups	Water molecules in the form of H_2O	Ion exchange capacity mEq/g.
1	$TiO_2(MoO_3)_{1.94}$	359.14	1.98	3.87	8.50
2	$TiO_2(MoO_3)_{1.90}$	353.40	1.48	4.95	6.35
3	TiO_2MoO_3	206.23	0.48	2.27	3.70
4	$TiO_2(MoO_3)_{0.5}$	151.87	0.44	1.88	4.54

These calculations show that all the four samples contain different amount of free water as well as water containing replaceable hydrogen ions. The varying amount of water seems to be responsible for the change in the ion exchange properties and the stability of the exchanger. The pH titration curves for all the four samples show a monofunctional behaviour similar to other amorphous inorganic ion exchangers. On the basis of these observations and the reported [8] species of titanium and molybdenum the following tentative structure (similar to hydrated antimony pentoxide [9] and titanium antimonate [2]) for titanium molybdate (Sample 3) may be postulated (see page 377).

Similar structures may be drawn for the rest of the samples. Hence it is clear that the size of the cavity within the exchanger depends on the composition and water of hydration.

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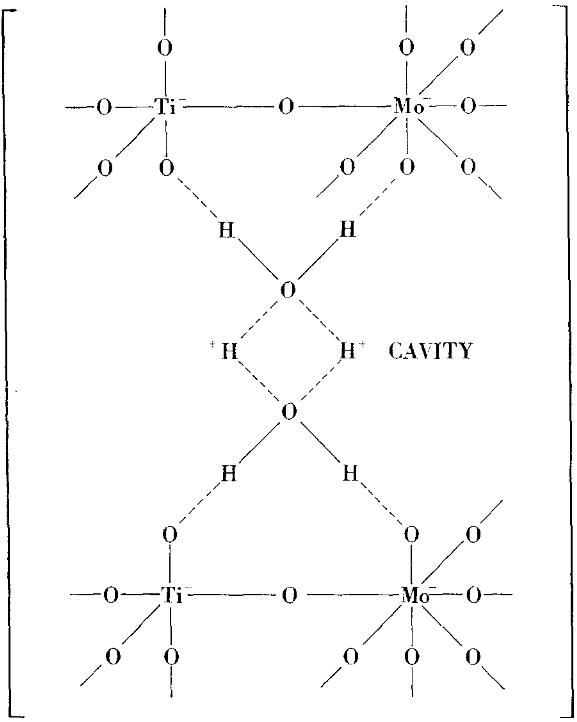

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RÉSUMÉ — Préparation de trois échantillons différents de molybdate de titane (rapport Ti : Mo = 1 : 2, 1 : 1 et 2 : 1) par mélange en proportions variables de solutions de chlorure de titane(IV) (M/40), de sulfate de titane (M/20, M/40) et de molybdate de sodium (M/20, M/40). Obtention de renseignements sur l'état des molécules d'eau présentes dans l'échantillon à partir de l'étude de la déshydratation.

ZUSAMMENFASSUNG — Drei chemisch verschiedene Titanmolybdat-Präparate wurden durch Mischen von Titan(IV)chlorid- (M/40), Titansulfat- (M/20, M/40) und Natriummolybdatlösungen (M/20, M/40) in verschiedenen Volumenverhältnissen hergestellt. Das Ti : Mo Verhältnis betrug 1 : 2, 1 : 1, 2 : 1. Mit den Präparaten wurden Dehydrationsversuche unternommen, um den Zustand der Wassermoleküle in den Proben zu bestimmen.

Резюме — Приготовлено три химически различных образца молибдата титана (Ti : Mo/1 : 2, 1 : 1 и 2 : 1) путем смешения растворов хлорида титана (IV) (M/40), сульфата титана (M/20, M/40) и молибдата натрия (M/20, M/40) в разных объемных соотношениях. Изучен процесс дегидратации с целью выяснения положения молекул воды, содержащейся в образцах.