

found to be about 5% (0.034 meq/g) and 9% (0.056 meq/g) respectively, whereas the weak acid sites constitute about 85% (0.27+0.29 meq/g) as shown in Table 1. Impregnation of pure alumina with 0.5% by weight of lithium ion brings down the strong and medium acids by about 70 and 40% respectively, at the same time it increases the weak acids by 15%. Lithium ion content >0.5% eliminates completely the strong and medium acid sites, while the amount of weak acid sites shows a continuous increase. In other words lithium ion addition seems to modify the strong acid sites into weak acid sites, keeping the total acidity constant (Table 1). Herman Pines⁵ has also observed a similar effect on the addition of sodium ion to alumina catalyst.

On the other hand modification of pure alumina with 2% hydrofluoric acid enhances significantly the strong and medium acids by 370% (0.160 meq/g) and 340% (0.260 meq/g) respectively, whereas the enhancement in the case of weak acids is only about 78% (Table 1). Increase of hydrofluoric acid beyond 2% seems to have no effect on weak acids but the strong and medium acids continue to increase with hydrofluoric acid. It is to be noted that unlike lithium ion which keeps the total acidity constant, hydrofluoric acid increases the total acidity.

The author thanks Dr G. S. Laddha for facilities and encouragement.

References

- HIRSCHLER, A. E. & SCHNEIDER, A., *J. chem. Engng Data*, **6** (1961), 313.
- BENESI, H. A., *J. phys. Chem.*, **61** (1957), 970.
- PINES, H. & HAAG, W. O., *J. Am. chem. Soc.*, **83** (1961), 2847.
- MACIVER, D. S., BRIDGES, J. M. & RYMER, G. T., *J. phys. Chem.*, **66** (1962), 871.
- PINES, H. & CHEN, G. T., *J. Am. chem. Soc.*, **82** (1960), 2471.

Physico-chemical Properties of Sodium Tungstate Catalyst

P. K. SINHAMAHAPATRA* & S. SINHAMAHAPATRA†

Department of Chemistry, Faculty of Science
Banaras Hindu University, Varanasi 221005

Received 9 September 1976; accepted 13 December 1976

Thermal characteristics of sodium tungstate, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ have been investigated by DTA and TG, and various transition products analysed by chemical analysis, IR, X-ray diffraction, surface acidity and magnetic susceptibility techniques. This tungstate undergoes endothermic changes at 150°, 600° and 700° which are assigned to dehydration, crystal transformation and melting, respectively. The compound does not undergo any decomposition till melting. The pure tungstate as well as its transition products are diamagnetic and do not contain acid sites.

*Present address: Catalyst Section, Indian Institute of Petroleum, P.O. I.I.P., Mohkampur, Dehra Dun 248005. (To whom correspondence to be made.)

†Present address: Oil Technology Division, Department of Applied Chemistry, University College of Science & Technology, Calcutta 700009.

SODIUM tungstate has been used as a catalyst in the isomerization of iodides by hydrogen peroxide¹, decomposition of hydrogen peroxide², dehydration of formamide³ to hydrogen cyanide at 250-510°, tridymite formation from quartz⁴, vinyl acetate production⁵ and in the decomposition of benzil by hydrogen peroxide⁶. As the activity of a catalyst depends mainly on its physicochemical properties, it is worthwhile to study some of the properties of sodium tungstate. The present note deals with thermal analysis (DTA and TG), infrared (IR), X-ray diffraction (XRD), surface acidity and magnetic susceptibility of sodium tungstate as well as of its thermal transition products.

DTA and TG of sodium tungstate were carried out as reported earlier⁷. IR spectra and XRD patterns of the pure sample as well as of its thermal transition products obtained by calcining the compound at 250°, 660° and 710° in air for 2 hr in each case, were obtained by the methods described earlier⁸. Magnetic susceptibilities of these samples were measured by Faraday method at 24° using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant. The surface acidic strength of the samples was measured using *n*-butylamine and H_0 indicators⁹. Na^+ and W^{6+} in solution were estimated by conventional methods. The amount of water was determined using Coleman carbon-hydrogen analyser.

The composition of the catalyst, as reported, is $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.

DTA and TG curves of sodium tungstate are shown in Fig. 1. The DTA curve shows one endothermic peak at 150° (range 100-220°) followed by two sharp endothermic changes at 600° and 700°. The TG curve represents a gradual weight loss starting from 100° and ending at 220°, the total weight loss being 11.6%, corresponding to the

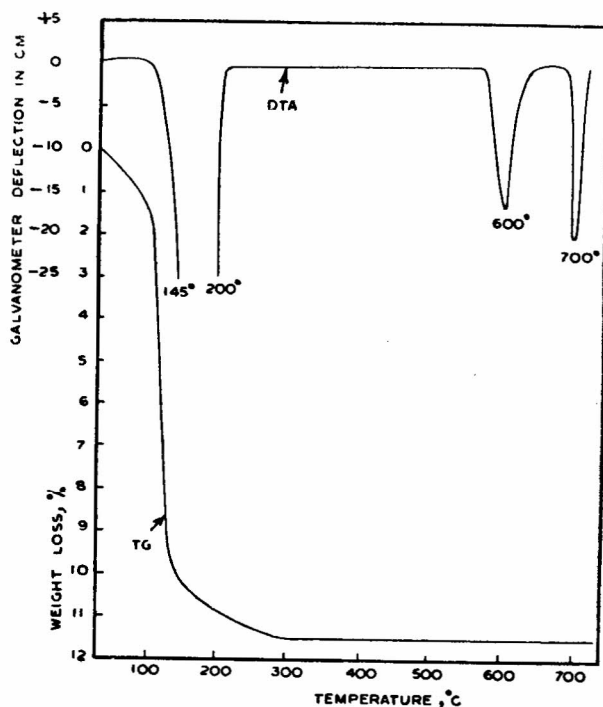
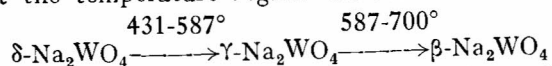


Fig. 1 — DTA and TGA of sodium tungstate dihydrate

removal of two molecules of water. Therefore, the endothermic peak at 150° in DTA curve is due to the loss of two molecules of water thereby giving anhydrous sodium tungstate. The TG curve neither indicates the possibility of formation of any intermediate stage during dehydration nor exhibits any significant weight-change in the temperature range 220-750°. Hence, the endothermic changes at 600° and 700° are due to some processes which do not accompany any weight change.

The pure sample exhibits IR bands at 930 and 800 cm⁻¹ which may be assigned to the νW-O of normal tungstates¹⁰. The other bands appearing at 3300-1600 cm⁻¹ region are due to symmetric and antisymmetric νO-H and δH-O-H of lattice water¹¹⁻¹³. The tungstate appears to be completely dehydrated at 250° as indicated by the absence of characteristic bands due to water molecules. Therefore, the endothermic change at 150° is clearly due to dehydration. The significant observation at and after 250° is that the band at 800 cm⁻¹ shifts to 830 cm⁻¹ with enhanced intensity followed by the disappearance of the 930 cm⁻¹ band. Thus, the strong band of ST 250 (sodium tungstate calcined at 250°) sample at 800 cm⁻¹ may be expected to be coupled with frequency, characteristic of water. As the IR bands of the samples ST 660 and ST 710 are almost the same as those of ST 250, it can be suggested that the endothermic changes after 250° are not due to decomposition of the tungstate rather due to phase changes. The last endothermic peak at 700° is, however, due to melting.

The pure sample exhibits a well defined XRD pattern with characteristic lines at $d=6.95, 6.0, 5.3, 4.2, 3.6, 3.3, 3.17, 2.98, 2.17, 2.12$ Å, etc. On comparison with the d -values given in ASTM Card No. 1-011 for the standard patterns of sodium orthotungstate(VI) dihydrate it is seen that the sample is pure Na₂WO₄ · 2H₂O. XRD patterns of the catalyst are little changed at and after 250° with the registration of strong lines at $d=5.25, 3.21, 3.16, 2.75$ Å, etc. The d -values of the ST 250, ST 660 and ST 710 samples compare excellently with those reported in the ASTM Card No. 5-0247 for Na₂WO₄ ($d=5.19, 3.18, 2.72$ Å, etc.), indicating that the endothermic change at 150° is due to dehydration and those after 250° are due to crystal transformation. Earlier workers also found sodium tungstate to undergo the following phase changes at the temperature region 431-700°:



The present studies, however, reveal that sodium tungstate does not undergo any phase change in the temperature range 431-570°. The temperature range at which phase changes take place, seems to be 570-700°. Magnetic measurements indicate that the pure sodium tungstate as well as its thermal transition products are diamagnetic. Surface acidity measurements reveal that this tungstate does not have surface acidic sites at any stage of thermal treatment. This study also rules out the possibility of the decomposition reaction Na₂WO₄ → Na₂O + WO₃, till the melting of the tungstate as WO₃ is known to have a good number of surface acidic sites.

References

1. YATSIMIRSKII, K. B. & MOROZOVA, R. P., *Kinetika & Kataliz*, **4** (1963), 574.
2. SPITALSKII, E. & FUNCK, A., *Z. physik. Chem.*, **126** (1927), 1.
3. FELLOWS, L. & MELLERS, E. V., *Brit. Pat.* 584,598 (1947).
4. INUZUKA, H., *J. Japan Assoc. mineral petrol., econo. Geol.*, **26** (1947), 200; *Chem. Abstr.*, **42** (1948), 65i.
5. Imperial Chemical Industries Ltd, *Netherland Pat.* 413,733 (1965).
6. KWART, H. & WEGEMER, N. J., *J. Am. chem. Soc.*, **87** (1965), 511.
7. BHATTACHARYYA, S. K., RAMACHANDRAN, V. S. & GHOSH, J. C., *Adv. Catal.*, **9** (1957), 114.
8. SINHAMAHAPATRA, P. K. & BHATTACHARYYA, S. K., *J. thermal Anal.*, **8** (1975), 45; SINHAMAHAPATRA, P. K. & BHATTACHARYYA, S. K., *Chem. Era*, **XII** (3) (1976), 79.
9. HIRSCHLER, A. E. & SCHNEIDER, A., *J. chem. Engng Data*, **6** (1961), 313.
10. NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (John Wiley, New York), 1963, 159.
11. GAMO, I., *Bull. chem. Soc. Japan*, **34** (1961), 760, 765, 1430, 1433.
12. ZECCHINA, A., COLUCCIA, S., GUGLIELMINOTTI, E. & GHIOTTI, G., *J. phys. Chem.*, **75** (1971), 2774.
13. DOUGLAS, R. M., *Acta Crystallogr.*, **10** (1959), 423.
14. MELLOR, J. W., *A comprehensive treatise on inorganic and theoretical chemistry*, Vol. II (Longmans, Green, London), 1931, 774.

Thermal Decomposition of Gamma-irradiated Barium Bromate

S. D. BHATTAMISRA & S. R. MOHANTY

Nuclear Chemistry Laboratory, Utkal University
Bhubaneswar 751004

Received 20 September 1976; accepted 29 November 1976

The effect of gamma-irradiation of barium bromate is to shorten the induction period and increase the rates of its decomposition in the linear, acceleratory, and decay stages. The activation energy of the linear reaction decreases under irradiation and that of the acceleratory stage increases whereas the activation energy of the decay stage remains unaffected.

DUKE and Shute¹ found that the decomposition of potassium bromate catalysed by bromide ion in fused alkali nitrates was first order with respect to both bromate and bromide. Jach^{2,3} has shown that whereas the isothermal decomposition of sodium bromate followed a contracting envelope formula that of potassium bromate occurred according to a first order rate law. Both these substances undergo fusion when sufficient bromide accumulates during the course of the decomposition because of which a discontinuity occurs in the Arrhenius plots. The discontinuity is removed by γ-irradiation in the case of potassium bromate. The present work deals with the influence of irradiation on the isothermal decomposition of barium bromate which takes place throughout in the solid condition.

AR grade barium bromate, dried⁴ at 170°, was irradiated in sealed glass ampoules with ⁶⁰Co γ-rays to various doses up to 420 Mrad at room tem-