

Hydrogen Adsorption on Zirconium Borate and Dioxide

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Zirconium borate is formed by dehydration of the trihydrate, $ZrO_2 \cdot B_2O_3 \cdot 3H_2O$, at 400° or above. The compound $ZrO_2 \cdot B_2O_3$ decomposes only slightly (2–3%) at 500 – 600° .

Neither $ZrO_2 \cdot B_2O_3$ nor ZrO_2 is reduced by hydrogen up to 600° , but some amount of the gas is adsorbed. The extent of adsorption has a negative temperature coefficient (physical adsorption in the crystal lattice). The extent of adsorption is relatively small with respect to chromium or manganese borates.

The behaviour of a number of metal borates in presence of hydrogen at a high temperature was reported earlier¹⁻⁴. Those of copper, nickel, cobalt, and silver were found to be reduced to the corresponding metal, releasing boron oxide. The reducibility was more or less of the same order as that for the corresponding oxide. In all the cases, however, the consumption of hydrogen was in excess of the theoretical requirement for reduction according to the equation:



The excess hydrogen was believed to undergo "activated adsorption".

Manganese and chromium borates⁵⁻⁶ were not reduced by hydrogen up to 600° , but large quantities of the gas were adsorbed. Both the borates tend to decompose at high temperatures. Both the compounds are paramagnetic and the susceptibilities are found to change with adsorption. It was possible on the basis of magnetic measurements to show that a part of the hydrogen was chemisorbed, but the major part of it was adsorbed in the lattice. In the present investigation, zirconium borate has been chosen as it is expected not to be reduced by hydrogen, and its electronic structure indicates little probability of chemisorption ($Zr^{4+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2 4p^6$) due to complete d -orbital and improbability of d - s promotion. For comparison, zirconium dioxide has also been taken for study.

Preparation of zirconium borate attracted the attention of a few investigators. Reference had been made on the preparation of colloidal zirconium borate⁷, but the substance was not isolated in the solid state. Andrieux⁸ electrolysed fused zirconium borate, but no reference was available on the synthesis and isolation of the material.

1. Deb and Khundkar, *this Journal*, 1956, **33**, 555.
2. Haq *et al.*, *Indian J. Appl. Chem.*, 1958, **21**, 81.
3. Jahan *et al.*, *this Journal*, 1961, **38**, 7.
4. Khundkar *et al.*, *ibid.*, 1962, **39**, 333.
5. *Idem*, *ibid.*, 1963, **40**, 9.
6. Khundkar *et al.*, *ibid.*, 1964, **41**, 439.
7. Prakash, *this Journal*, 1933, **9**, 193.
8. Colloq. intern. centr. rech. sci. (Paris) **29**, Electrolyse C7-40(1952).

Dry method of synthesis from the oxides appeared difficult as zirconium oxide had been known⁹ to be insoluble in fused boric oxide at temperatures up to even 1400°. Synthesis by the wet method was therefore adopted.

EXPERIMENTAL

Zirconium Borate

Preparation.— $\text{ZrO}_2 \cdot \text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was prepared by metathesis of zirconium nitrate solution with that of borax, with excess of the latter over the stoichiometric requirement. $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (B.D.H.) (13.4 g.) and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (AnalaR) (38.1 g.) were separately dissolved in minimum quantities of water. The zirconium nitrate solution was kept slightly acidic to avoid precipitation of basic compounds. The solutions were mixed together with constant stirring. The white gelatinous precipitate was filtered under suction, washed thoroughly with 5% and 1% boric acid solutions in turn, and finally with ethanol. The product was successively dried under suction, in a vacuum desiccator, and at 110° for 6 hr. in an electric oven.

Zirconium was determined gravimetrically by precipitation with mandelic acid from 20% HCl solution of the borate and igniting the precipitate to ZrO_2 ¹⁰. For the determination of boron, the zirconium was absorbed on Zeo-Karb 225 (H-form), after reducing the acidity, and the boric acid in the eluate was titrated with CO_2 -free NaOH solution in presence of mannitol¹¹. The composition of the borate, dried at 110°, corresponds to $\text{ZrO}_2 \cdot \text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. (Found: Zr, 36.29, 36.41; B, 9.10, 8.96. Calc. for $\text{ZrO}_2 \cdot \text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$: Zr, 36.96; B, 8.77%.)

Dehydration and Decomposition.—The borate was heated at different temperatures in the range of 200° to 600° for 4 hr. It was found that at 200° (Table I) two molecules of water were removed and at 400°, the product was completely dehydrated and conformed to the composition $\text{ZrO}_2 \cdot \text{B}_2\text{O}_3$. There was practically no decomposition of the borate up to 400°, as shown by the analysis for free boric oxide in methanol extract of the product. At 500° and 600° also, decomposition was only slight, being 2.49% and 3.09%, respectively. It was also noted that higher the temperature at which the borate was heated, the greater was the difficulty in dissolving it in the solutions of HCl. A 500°-heated product is insoluble in HCl (conc.) and even in aqua regia. The product dehydrated at 400° (viz., $\text{ZrO}_2 \cdot \text{B}_2\text{O}_3$) was used as the stock sample for the present investigation. Finely powdered ZrO_2 (E. Merck) was used as the oxide.

Adsorption.—The apparatus for the adsorption experiments was the same as used in the earlier investigations⁶. When the desired temperature was attained in the reaction zone, the system was evacuated and filled with pure dry hydrogen, the operation being repeated thrice; finally the inside pressure was adjusted to that of the atmospheric pressure with the help of an oil manometer. The sample (0.2 g.), contained in a platinum boat, was now

9. Thorpe, "Dictionary of Applied Chemistry", Vol. II, 4th ed., 1953, p. 46.

10. Vogel, "A Text Book of Quantitative Inorganic Analysis", 3rd ed., 1962, p. 549.

11. Martin and Hayes, *Anal. Chem.*, 1952, 24, 162.

pushed into the reaction zone (with the help of a solenoid) and the progress of the reaction was followed from that instance by noting the decrease in the volume of hydrogen from time to time.

TABLE I

Dehydration of zirconium borate trihydrate.
 $ZrO_2 \cdot B_2O_3 \cdot 3H_2O$ taken = 0.50 g. (containing 21.88% H_2O).
 Period of dehydration = 4 hr.

Temp.	Loss of wt.	Free B_2O_3 found in the product.	% ZrO_2 .	% B_2O_3 .	Composition.
200°	14.52%	0.22%	58.34	23.90	$ZrO_2 \cdot B_2O_3 \cdot H_2O$.
300°	19.88	0.23	60.82	36.70	..
400°	21.04	0.28	62.82	36.90	$ZrO_2 \cdot B_2O_3$
500°	22.04	2.49	Could not be determined for analysis		Apparently $ZrO_2 \cdot B_2O_3$
600°	22.17	3.09	Do		

TABLE II

Uptake of hydrogen by zirconium borate and oxide at diff. temp.
 $ZrO_2 \cdot B_2O_3$ taken = 0.20 g. ZrO_2 taken = 0.1256 g. Duration of expt. = 7 hr.

Temp.	H_2 uptake on Zr-borate.	% Free B_2O_3 in methanol extract of the product After H_2 uptake.	% Free B_2O_3 in methanol extract of the product After heating <i>in vacuo</i> .	H_2 uptake on ZrO_2 .
200°	17.3 ml	Trace	Trace	16.0 ml
300°	17.1	"	0.24	18.9
400°	14.9	"	0.20	15.7
500°	10.1	2.32	2.20	..
600°	5.7	3.08	3.10	4.7

The ZrO_2 samples were thoroughly degassed *in vacuo* in each experiment and cooled in the closed system at one side of the reaction tube before studying the hydrogen adsorption.

DISCUSSION

The uptake of hydrogen on 0.20 g. samples of the borate was studied at different temperatures between 200° and 600°. Progress of hydrogen uptake at different temperatures has been shown by curves in Fig. 1. At 200°, hydrogen uptake starts from the beginning, but gradually slows down and finally becomes immeasurably slow in about 6-7 hr. In 7 hr., the total uptake is 17.3 ml, there being two phases in the process of adsorption at this temperature. At 300°, the initial uptake is somewhat higher than that at 200° and equilibrium is reached earlier. In 6 hr., total uptake is 17.1 ml. At 400°, the same trend is followed and the total uptake is 14.9 ml in 6 hr. Above this temperature, adsorption becomes increasingly slower: 10.10 ml at 500° and 5.70 ml at 600°.

For comparison, similar adsorption study was made with 0.1256 g. of ZrO_2 (equivalent to 0.20 g. $ZrO_2 \cdot B_2O_3$). The progress of hydrogen uptake at different temperatures with time are shown in Fig. 2. At 200° , the uptake is initially high, but it falls off gradually; equilibrium is attained in 6 hr., the total uptake being 16.0 ml. The same trend is followed at 300° and 400° , but the volume of hydrogen consumed at 300° is slightly higher (18.9 ml).

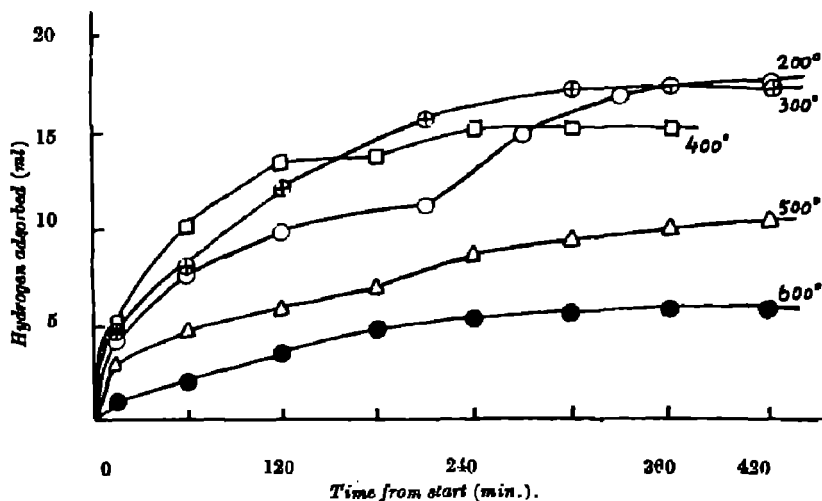


FIG. 1. Adsorption of H^+ on $ZrO_2 \cdot B_2O_3$ at diff. temp.

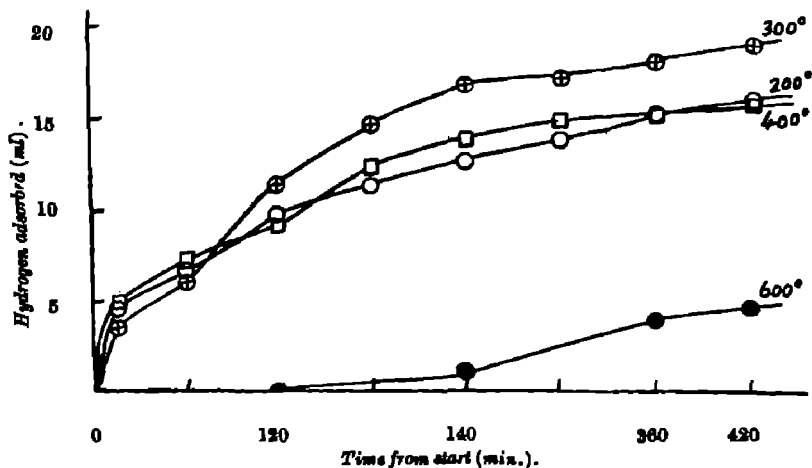


FIG. 2. Adsorption of H^+ on ZrO_2 at diff. temp.

At 600° , there is an induction period of about 2 hr. After this the adsorption is also slowed down, being 4.70 ml in 6 hr. Total hydrogen uptake appears to be more or less similar to that on zirconium borate (Table II). In Fig. 3 are shown the equilibrium adsorption of hydrogen on zirconium borate and zirconium dioxide at different temperatures. For the borate $ZrO_2 \cdot B_2O_3$, the adsorption has a negative temperature coefficient from 200°

upwards. For ZrO_2 , the adsorption passes through a maximum at 300° , after which this also shows a negative temperature coefficient.

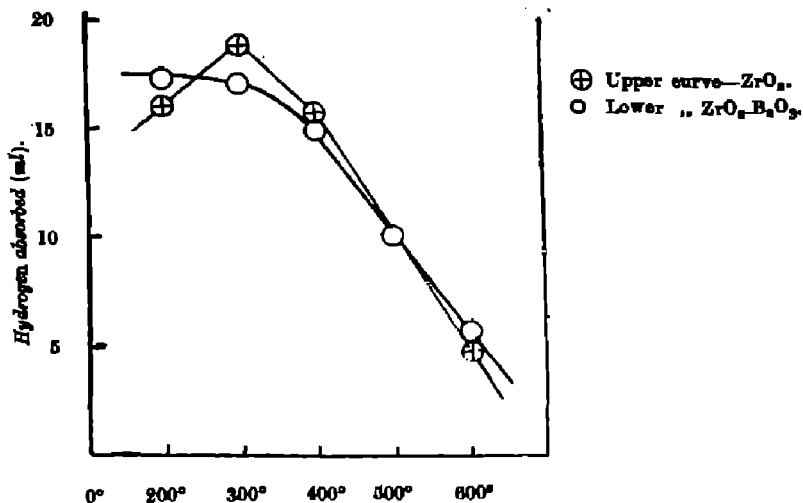


FIG. 3. Variation of H^+ adsorption with temp.

The adsorption on different borates and oxides has been compared in Table III. The results for manganese and chromium compounds have been quoted from earlier work^{1,6}. In the case of manganese borate, the positive temperature coefficient of adsorption indicates the prominence of chemisorption. Chemisorption involves the formation of surface bonds with d -orbitals (either originally unfilled or made so through d - s promotion) in the case of transition metals, their oxides and, by analogy, their borates. In the case of chromium borate, although chemisorption became more prominent with increase of temperature, the proportion of physical adsorption being more, the overall effect was a negative temperature coefficient for the uptake of hydrogen. In the case of chromium sesquioxide, the overall effect was maximum at 500° , after which it showed a decreasing tendency. In the case of zirconium borate, the electronic structure does not indicate any vacant d -orbital and the probability of d - s promotion is also small. Incidentally, in the case of zirconium borate and also of the dioxide, the uptake is more or less by physical adsorption inside the crystal lattice. This explains the negative temperature coefficient of the adsorption. The maximum at 300° in the case of the zirconium dioxide may be due to kinetic factor.

TABLE III

Comparison of hydrogen adsorbed on diff. borates and oxides.

Borates taken = 0.20 g. in each case.

Substance taken.	Hydrogen adsorbed at		
	300° .	500° .	600° .
MnB_4O_7	29.2 ml	45.5 ml	53.3 ml
$Cr_2O_3 \cdot 8B_2O_3$	30.2	35.6	14.0
Cr_2O_3 (0.08 g.)	43.9	58.8	55.6
$ZrO_2 \cdot B_2O_3$	17.1	10.1	5.7
ZrO_2 (0.1256 g.)	18.9	..	4.7

Decomposition of zirconium borate is negligible up to 400° and only 2-3% at 500-600°, as determined by the values of free B_2O_3 in methanol extract of the products of heating *in vacuo*; a comparison of these values with those of the products obtained after hydrogen adsorption (Table II) will clearly show that no boric oxide is released due to any reduction of the zirconium borate up to 600°. ZrO_2 has a high free energy of formation and it is not reduced by hydrogen even at 2000° under high pressure. The non-reducibility of the borate has been shown by our present experiments.

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