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Synthesis of reduced vanadium oxides in aqueous solutions

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Reduction of aqueous sodium and potassium vanadates with aqueous ABH_4 (A = Na and K) at ambient temperatures has been investigated systematically to obtain reduced vanadium oxides. Although the as-prepared samples do not show any discernible diffraction peaks, several binary crystalline oxides such as V_2O_3, V_3O_5, VO_2, and V_6O_{13}, as well as ternary oxides such as $Na_{0.33}V_2O_5$, $K_{0.23}V_2O_5$, and $K_2V_3O_8$ could be identified after annealing in evacuated sealed silica tubes at 580 °C. The volume and concentration of borohydrides as well as the reaction pH are found to influence the nature of the reaction products. Selected area diffraction of the as-prepared samples in transmission electron microscopy (TEM) indicates that they are nanocrystalline.

Vanadium exhibits a rich oxide chemistry with formal oxidation states ranging from 2+ to 5+. While the V^{2+} state is known only in the binary oxide VO, the other states V^{3+}, V^{4+} and V^{5+} are known both in binary and ternary oxides. In addition to the well known single-valent oxides, VO, V_2O_3, VO_2, and V_2O_5, vanadium also forms several other mixed-valent oxides such as V_3O_5, V_6O_{13}, V_4O_9, and V_3O_7, which are considered to have shear structures derived from rutile or ReO_3 structure.[1–6] The vanadium oxides are characterized by narrow 3d bands and the oxides having oxidation states <5+ exhibit interesting electronic properties.[2,3] For example, they exhibit semiconducting or metallic properties depending upon the V—V separation and V—O—V bond angles. A few oxides such as VO_2 and V_2O_3 show semiconductor-to-metal transitions as the temperature increases. Also, some vanadium oxides such as V_6O_{13} and a metastable form of VO_2, designated as $VO_2(B)$, are potential cathode hosts for rechargeable lithium batteries.[6–10] The metastable $VO_2(B)$ has also been considered as an anode host for rechargeable lithium cells with aqueous electrolytes.[6]

The binary vanadium oxides are generally made[4–7] by (i) a controlled reduction of the higher valent oxide V_2O_5 or NH_4VO_3 at higher temperatures with reducing gases such as H_2, SO_2 or NH_3 or in an inert atmosphere, (ii) reacting V_2O_5 and either V_2O_3 or V metal in evacuated sealed silica tubes at higher temperatures, or (iii) arc melting to obtain VO. However, the compositions of the $VO_{2+\delta}$ phases obtained by the reduction procedures and, in particular, the synthesis of the metastable $VO_2(B)$ are extremely sensitive to temperature. For example, reduction of V_2O_5 with H_2 at 350 °C for 3 days results in over-reduction to give V_2O_3 and at 320 °C for 3 days results in almost no reduction at all.[7] Also, the metastable $VO_2(B)$ begins to transform irreversibly to the thermodynamically more stable rutile phase at $T > 350$ °C. Our objective is to develop solution-based low temperature procedures to obtain reduced vanadium oxides.

Although the higher valent oxide V_2O_5 could be obtained in aqueous solutions by lowering the pH of the vanadate solutions down to about 1, methods to obtain the reduced vanadium oxides having valence states <5+ are rare or not known. Recently we showed[11,12] that alkali metal borohydrides such as $NaBH_4$ can be used as effective reducing agents to reduce oxo ions $(MO_4)^{n-}$ (M = V, Mo, W) in aqueous solutions to give binary oxides MO_2 or the ternary oxides $A_xM_yO_z$ (A = Na or K). We also identified the factors that influence the nature of the reduction products by investigating systematically the reduction of A_2MoO_4, A_2WO_4 and $AMnO_4$ with ABH_4 (A = Na or K) at ambient temperatures.[13–16] We present in this paper a systematic study of the reduction of sodium or potassium vanadates with sodium or potassium borohydride and a characterization of the reduction products.

Experimental

ABH_4 (A = Na or K; 0.25 or 2.5 M) solutions were prepared by dissolving the required amount of ABH_4 in dilute NaOH or KOH having a pH = 11–12. The initial pH of the borohydride solution has to be maintained high at 11–12 in order to suppress the hydrolysis of borohydride and prevent a rapid loss of hydrogen as the hydrolysis reaction below is facilitated by acidic conditions:[17]

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2 \qquad (1)$$

Sodium and potassium vanadate solutions (0.25 M) were prepared by dissolving the required amounts of V_2O_5 in dilute NaOH or KOH, respectively, having a pH = 11–12. The vanadate species formed will be $(VO_4)^{3-}$ in this pH range.[18] However, the $(VO_4)^{3-}$ species will tend to condense progressively as the pH is lowered to give $(V_2O_7)^{4-}$ around pH = 8, $(V_3O_9)^{3-}$ around pH = 7, and $(V_{10}O_{28})^{6-}$ around pH = 6. The decavanadate $(V_{10}O_{28})^{6-}$ ion is protonated to give $(HV_{10}O_{28})^{5-}$ and $(H_2V_{10}O_{28})^{4-}$ as the pH is lowered to 3.5. In highly acidic solutions, $(VO_2)^+$ ion is formed around pH = 2, and hydrated V_2O_5 is obtained as the pH is lowered further.

Reduction reactions were carried out at various pH values with a fixed amount (25 ml) of 0.25 M sodium or potassium vanadate and varying amounts of both 0.25 and 2.5 M ABH_4 solutions. First, the pH of the vanadate solution was lowered to a predetermined value by adding hydrochloric acid and kept under constant stirring on a magnetic stirrer. Then a known volume of the borohydride solution was added from a burette to the constantly stirring vanadate solution while maintaining the pH constant. The pH was maintained constant by adding hydrochloric acid as the pH tends to rise due to the formation of the basic AOH or ABO_2 during the reduction process [see reactions (2) and (3) later].

The solid formed after the addition of a required quantity of the borohydride was filtered, washed several times with water, and dried at around 100 °C. The samples were then characterized by X-ray powder diffraction and transmission electron microscopy (TEM). The samples were then annealed in evacuated sealed silica tubes at about 580 °C for about 4 days in order to obtain discernible X-ray diffraction patterns, and were then characterized.

Results and Discussion

Reduction of sodium vanadate with sodium borohydride

A series of experiments were first carried out at various pH values by reducing 25 ml of 0.25 M sodium vanadate with a constant amount (50 ml) of 0.25 and 2.5 M $NaBH_4$ (Table 1). While the reduction reactions at pH = 4–8 give solid products, those at pH $\leqslant$ 3 or pH $\geqslant$ 10 do not give solids. This could be due to the solubility of the reduction products in highly acidic or basic solutions or a poorer reducing power of borohydride in basic solutions. The as-prepared samples do not show any discernible peaks in the X-ray diffraction patterns (Fig. 1). So the as-prepared samples were annealed in evacuated sealed silica tubes at 580 °C. The products identified after annealing are given in Table 1 along with their percentage amounts estimated from X-ray diffraction intensities. The lattice parameters of the products agreed closely with those reported in the literature suggesting that the phases identified after annealing at 580 °C may not contain water or proton in the lattice.

Reduction with 0.25 M borohydride gives the sodium vanadium bronzes $Na_{0.33}V_2O_5$[19,20] and $Na_{1.8}V_2O_5$ at pH = 4, single phase $Na_{0.33}V_2O_5$ at pH = 6, and predominantly the unreduced phase $Na_4V_2O_7$ at pH = 8 (Table 1). This trend can be understood to be due to the decreasing reducing power arising from a decreasing ability of borohydrides to lose hydrogen with increasing pH. Reduction with 2.5 M borohydride, on the other hand, gives the binary oxides V_3O_5 and V_2O_3 at pH = 4, $Na_2V_5O_{13}$ and V_2O_3 at pH = 6, and a mixture of unreduced (Na_3VO_4) and reduced ($Na_{0.33}V_2O_5$ and V_2O_3) phases at pH = 8. This trend again is due to a decreasing reducing power with increasing pH. However, a ten-fold increase in the concentration of borohydride is able to access the more reduced binary oxides V_3O_5 and V_2O_3 at least at lower pH. Assuming, for simplicity, the $(VO_4)^{3-}$ ion as the species being reduced, the chemical reactions for the formation of $Na_xV_2O_5$ and the binary oxides V_2O_{5-y} can be given as follows:

$$2na_3VO_4 + 2NaBH_4 + (7-x)H_2O \rightarrow 2NaBO_2 + Na_xV_2O_5 + (6-x)NaOH + (8-0.5x)H_2 \quad (2)$$

$$2Na_3VO_4 + 2NaBH_4 + (7-y)H_2O \rightarrow 2NaBO_2 + V_2O_{5-y} + 6NaOH + (8-y)H_2 \quad (3)$$

Value of $x = 0.33$ in reaction (2) will, for example, correspond to the formation of $Na_{0.33}V_2O_5$.Value of $y = 1$ and 2 in reaction (3) will, for example, correspond to the formation of the binary oxides VO_2 and V_2O_3 respectively. Similar reactions can be written for other products. Since the as-prepared samples do not show any X-ray diffraction peaks, it is of interest to know whether they are amorphous or nanocrystalline. Accordingly, we carried out selected area diffraction in TEM on some as-prepared samples. The TEM results reveal the presence of diffraction spots or rings indicating that both the binary oxides and the ternary sodium vanadium bronzes are nanocrystalline, as reported earlier for VO_2(B).[10]

Table 1 Reduction products obtained by reducing 25 ml of 0.25 M sodium vanadate with 50 ml of $NaBH_4$ at various pH values

sample no.	pH	concentration of $NaBH_4$/M	products identified[a]
1	4	0.25	$Na_{0.33}V_2O_5$(90); $Na_{1.8}V_2O_5$(10)
2	4	2.5	V_3O_5(35); V_2O_3(65)
3	6	0.25	$Na_{0.33}V_2O_5$(100)
4	6	2.5	$Na_2V_5O_{13}$(10); V_2O_3(90)
5	8	0.25	$Na_4V_2O_7$(90); $Na_{0.56}V_2O_5$(5); V_3O_5(5)
6	8	2.5	Na_3VO_4(70); $Na_{0.33}V_2O_5$(20); V_2O_3 (10)

[a] The numbers in parentheses refer to relative % of the products.

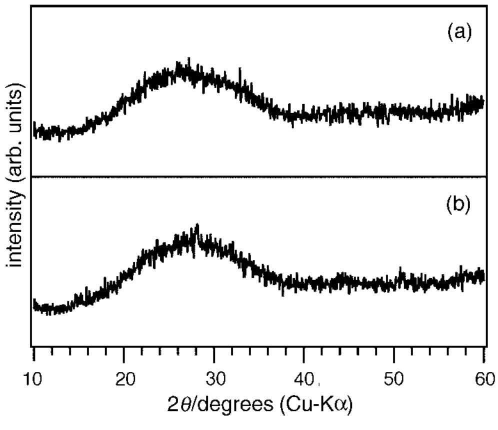

Fig. 1 X-Ray powder diffraction patterns of as-prepared samples: (a) sample 7 in Table 2, and (b) sample 17 in Table 3

As the pH range 4–6 is found to be promising to obtain reduced oxides, further experiments were carried out at both pH = 4 and 6 with varying volumes of both 0.25 and 2.5 M $NaBH_4$. As discussed in the Experimental section, the vanadate species that will be reduced around this pH range will be the decavanadates. The products identified and their percentages are given in Tables 2 and 3. The X-ray diffraction patterns for some representative samples are given in Fig. 2.

At pH = 4, the bronze $Na_{0.33}V_2O_5$ is formed predominantly with 0.25 M $NaBH_4$ while the more reduced binary oxides V_3O_5 and V_2O_3 are formed with 2.5 M $NaBH_4$. The amount of V_3O_5 decreases and V_2O_3 increases with increasing volume of 2.5 M $NaBH_4$ indicating that the reducing power increases with increasing volume of borohydride. Similarly, the secondary phases $Na_{1.8}V_2O_5$ and VO_2 having oxidation states of V lower than that in $Na_{0.33}V_2O_5$ begin to appear along with $Na_{0.33}V_2O_5$ as the volume of 0.25 M $NaBH_4$ increases. However, for the same amount (mmol) of $NaBH_4$, the 0.25 M borohydride gives the sodium bronze while the 2.5 M borohydride gives the binary oxides. This suggests that in addition to the amount (mmol) of borohydride, the overall concentration and content of the reaction medium may play a role in controlling the nature of the reduction products as we have seen before in other systems such as molybdates and tungstates.[13–15] For example, the concentration of the reaction medium may alter the degree of condensation of the vanadate ions to give the polyvanadates[18] and thereby influence the overall reducing power. The vanadates will become more and more difficult to reduce as the degree of condensation increases.

At pH = 6 also, the products become more and more reduced as the amount of 0.25 or 2.5 M $NaBH_4$ increases due to an increasing reducing power. However, the sodium bronzes are formed with both the 0.25 and 2.5 M $NaBH_4$ at least at lower volumes unlike at pH = 4. The binary oxides become predominant with both the 0.25 and 2.5 M $NaBH_4$ at larger volumes. Also, a slightly less reduced binary oxide VO_2 becomes accessible at pH = 6. The difference between the results at pH = 6 and 4 could be due to an interplay between an increasing degree of condensation of the vanadate ions at lower pH and a decreasing reducing power of borohydride at a higher pH. A more condensed ion with a lower Na/V ratio may give the binary oxides without sodium easily compared to a less condensed ion.

Reduction of potassium vanadate with potassium borohydride

Reduction of potassium vanadate with KBH_4 gave results that were in general similar to those obtained with sodium vanadate. However, the ternary phases obtained in the potassium vanadate system are different from those obtained in the sodium

Table 2 Reduction products obtained by reducing 25 ml of 0.25 M sodium vanadate with varying amounts of 0.25 and 2.5 M $NaBH_4$ at pH = 4

sample no.	concentration of $NaBH_4$/M	amount of $NaBH_4$ ml	mmol	product formed (%)[a] $Na_{0.33}V_2O_5$ (4.84)	$Na_{1.8}V_2O_5$ (4.1)	VO_2 (4.0)	V_3O_5 (3.33)	V_2O_3 (3.0)
7	0.25	40	10.0	100	—	—	—	—
8	0.25	50	12.5	90	10	—	—	—
9	0.25	150	37.5	90	—	10	—	—
10	2.5	5	12.5	—	—	—	95	5
11	2.5	25	62.5	—	—	—	90	10
12	2.5	50	125	—	—	—	35	65
13	2.5	100	250	—	—	—	30	70

[a]The average oxidation state of vanadium is given for each phase in parentheses.

Table 3 Reduction products obtained by reducing 25 ml of 0.25 M sodium vanadate with varying amounts of 0.25 and 2.5 M $NaBH_4$ at pH = 6

sample no.	concentration of $NaBH_4$/M	amount of $NaBH_4$ ml	mmol	product formed (%)[a] $Na_{0.33}V_2O_5$ (4.84)	$Na_2V_5O_{13}$ (4.8)	$Na_{0.56}V_2O_5$ (4.72)	VO_2 (4.0)	V_3O_5 (3.33)	V_2O_3 (3.0)
14	0.25	50	12.5	100	—	—	—	—	—
15	0.25	70	17.5	80	—	—	—	20	—
16	0.25	90	22.5	—	—	—	—	—	100
17	0.25	100	25.0	—	—	—	—	—	100
18	2.5	5	12.5	55	—	—	45	—	—
19	2.5	25	62.5	20	—	—	80	—	—
20	2.5	50	125	—	10	—	—	—	90
21	2.5	70	175	—	5	—	—	—	95
22	2.5	90	225	—	—	5	—	—	95

[a]The average oxidation state of vanadium is given for each phase in parentheses.

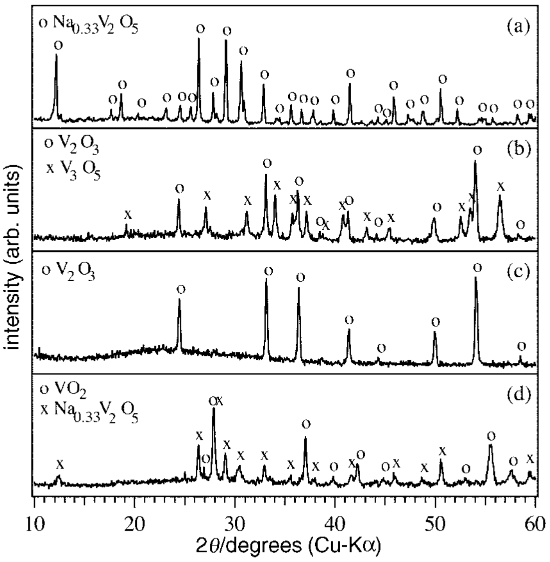

Fig. 2 X-Ray powder diffraction patterns of the products obtained after annealing in evacuated sealed silica tubes at 580 °C for about 4 days: (a) sample 7 in Table 2, (b) sample 12 in Table 2, (c) sample 17 in Table 3, and (d) sample 19 in Table 3

vanadate system. For example, the potassium vanadate system gives ternary oxides such as $K_{0.23}V_2O_5$ and $K_2V_3O_8$. Also, the binary oxide V_6O_{13} could be obtained in addition to VO_2, V_3O_5 and V_2O_3. The experimental conditions to obtain some of these phases are given in Table 4. The X-ray diffraction patterns obtained after annealing the reduction products in evacuated sealed silica tubes at 580 °C are given in Fig. 3 for some representative samples.

Although the X-ray pattern given in Fig. 3(b) for VO_2 corresponds to the thermodynamically more stable monoclinic rutile form, the pattern recorded with samples heated below 350 °C corresponds to the metastable VO_2(B).[10] Thus single phase VO_2(B) could be easily obtained by the solution-based borohydride method unlike the literature procedures.[6,7] In addition, the VO_2(B) obtained by the borohydride method shows superior performance as an electrode in lithium cells.[10] While the VO_2(B) prepared by the literature methods inserts about 0.5 lithium per vanadium,[6,7] the VO_2(B) prepared by our solution-based approach inserts reversibly about 1.0 Li per V with a larger capacity of about 325 mA h g^{-1} and excellent cyclability. We believe that the smaller particle size achieved by the solution-based approach and the accompanying microstructure play critical roles in giving better electrode properties.

Table 4 Reduction products obtained by reducing 25 ml of 0.25 M potassium vanadate with potassium borohydride

sample no.	pH	concentration of KBH_4/M	amount of KBH_4 ml	mmol	products identified[a]
23	3.5	0.25	5	1.25	$K_{0.23}V_2O_5$(75); VO_2(25)
24	3.5	0.25	85	21.3	VO_2(100)
25	3.5	0.25	100	25.0	V_2O_3(100)
26	3.5	2.5	100	250	V_3O_5(30); V_2O_3(70)
27	6	2.5	10	25	$K_2V_3O_8$(100)
28	6	2.5	25	62.5	$K_{0.51}V_2O_5$(80); $K_2V_3O_8$(20)
29	6	2.5	150	375	V_6O_{13}(90); V_2O_3(10)
30	9	0.25	50	12.5	$K_2V_3O_8$(100)

[a]The numbers in paraentheses refer to relative % of the products.

Conclusions

The reduction of sodium and potassium vanadates with sodium and potassium borohydrides have been studied systematically in aqueous solutions by varying the volume and concentration of the borohydrides as well as the reaction pH. Several binary

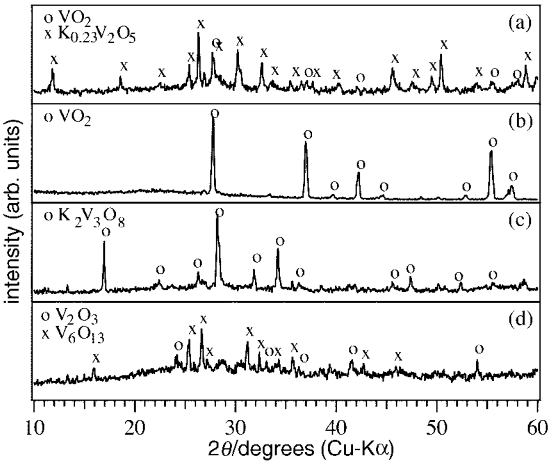

Fig. 3 X-Ray powder diffraction patterns of the products obtained after annealing in evacuated sealed silica tubes at 580 °C for about 4 days: (a) sample 23 in Table 4, (b) sample 24 in Table 4, (c) sample 27 in Table 4, and (d) sample 29 in Table 4

oxides such as V_2O_3, V_3O_5, VO_2 and V_6O_{13} as well as ternary sodium vanadium and potassium vanadium oxides have been obtained by this process. The oxides are nanocrystalline and may become attractive as electrode hosts for rechargeable lithium batteries since the smaller particle size can give faster lithium-ion diffusion and better performance. A finer control of the reaction conditions in the future may lead not only to the accessibility of some additional phases but also to single phase products in some cases.

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