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Reduction of Aqueous Na_2WO_4 by $NaBH_4$ at Ambient Temperatures To Obtain Lower Valent Tungsten Oxides

C. Tsang, S. Y. Lai, and A. Manthiram*

Center for Materials Science & Engineering, ETC 9.104, The University of Texas at Austin,
Austin, Texas 78712

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A systematic investigation of the reduction of aqueous Na_2WO_4 with aqueous $NaBH_4$ at ambient temperatures reveals the formation of several lower valent tungsten oxides such as the tetragonal ($x < 0.38$) and cubic ($x > 0.43$) tungsten bronzes Na_xWO_3 and the binary oxides WO_2 and $W_{24}O_{68}$. The nature of the product formed is influenced both by the (i) reducing power of $NaBH_4$, which is controlled by the volume and concentration of the borohydride and the reaction pH, and (ii) the degree of condensation of the tungstate ions, which is controlled by the reaction pH. Although the reducing power of $NaBH_4$ increases with decreasing pH, an increasing degree of condensation of the tungstate tends to lower the degree of reduction in many instances. The as-prepared samples are amorphous as revealed by X-ray diffraction and crystallize around 450 °C as revealed by differential scanning calorimerty. The tungsten bronzes undergo interesting crystal-chemical changes with the temperature of heating.

Introduction

There is increasing interest to develop low-temperature procedures to synthesize complex inorganic materials.[1] The low-temperature methods such as sol−gel processing, ion exchange, and coprecipitation can offer several advantages over the conventional high-temperature methods. They can not only provide better homogeneity but also access metastable phases and unusual valence states. While several low-temperature techniques are available to synthesize higher valent transition metal oxides, methods to obtain reduced lower valent oxides in aqueous solutions are limited. We showed[2,3] recently that alkali metal borohydrides such as $NaBH_4$ can be employed as effective reducing agents in aqueous solutions to reduce the oxo ions $(MO_4)^{n-}$ (M = V, Mo, W) to give reduced transition metal oxides such as VO_2, MoO_2, $Na_xMo_6O_{17}$, and Na_xWO_3. The technique was found to give amorphous or nanocrystalline products that are often metastable. The amorphous (metastable) products crystallize around 300−500 °C to give the thermodynamically more stable crystalline products. The amorphous or nanocrystalline nature of the products makes several of the binary oxides attractive electrodes for rechargeable lithium batteries.[4,5]

Following the initial results, we also presented[6] a systematic investigation of the reduction of aqueous K_2MoO_4 with KBH_4 in order to identify the factors that influence the nature of the products. We found that the reaction pH, concentration, and amount of the reactants all play a complex role in controlling the reaction products. In this paper, we present a systematic investigation of the reduction of aqueous Na_2WO_4 with $NaBH_4$.

Experimental Section

Reduction of aqueous solutions of 0.25 M Na_2WO_4 was carried out with two different concentrations (0.25 and 2.5 M) of $NaBH_4$. The 0.25 M Na_2WO_4 solutions were prepared by dissolving the required quantity of Na_2WO_4 in deionized water; 0.25 and 2.5 M $NaBH_4$ solutions were prepared by dissolving the required quantities of $NaBH_4$ in dilute NaOH solution. The pH of the initial NaOH solution was kept at 11−12 in order to suppress the hydrolysis of borohydride as the hydrolysis reaction given below is facilitated by acidic conditions:[7]

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

Maintenance of a higher initial pH is essential to prevent a rapid loss of hydrogen and of the reducing power of borohydride. Reduction reactions were carried out at a given pH with a fixed volume of 0.25 M Na_2WO_4 taken in a beaker and by adding varying volumes of either 0.25 or 2.5 M $NaBH_4$ solutions from a burette. Reduction reactions were also carried out at various pH values by keeping the volumes of the sodium tungstate and sodium borohydride constant. Concentrated HCl was added to maintain the pH constant during the reduction process as the pH tends to increase during the addition of borohydride due to the formation of the basic $NaBO_2$ and NaOH (see eqs 2 and 4 later).

The solid formed after the complete addition of a specific amount of borohydride was filtered. The solid was soaked in methanol for ~3 h to dissolve any NaCl formed since washings with water was found to result in a partial loss of the solid due to its fine nature or partial solubility. The solid was then filtered, washed with methanol, and dried overnight at ambient temperature. The solid was then wrapped in aluminum foil and dried at 120 °C in an air oven for 2 h before characterization. The products were characterized by X-ray powder diffraction, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). DSC and TGA plots were recorded with a Perkin-Elmer Series 7 thermal analysis system in a flowing N_2 atmosphere (99.99% purity) at a heating rate of 10 °C/min. As the as-prepared samples were all found to be amorphous, the samples were also heated in an evacuated sealed silica tube at 600 °C to obtain crystalline phases and then characterized by X-ray powder diffraction; a few samples were also heated at 850 °C in order to understand the evolution of phases with synthesis temperature.

Results and Discussion

Influence of $NaBH_4$ Amount on the Reduction Products. First, a series of experiments were carried out at a constant pH

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Table 1. Reduction of 200 mL of 0.25 M Na_2WO_4 (50 mmol of Na_2WO_4) with Varying Amounts of 2.5 M $NaBH_4$ at pH = 6

sample no.	amounts of $NaBH_4$ mL	amounts of $NaBH_4$ mmol	% products formed: tetragonal Na_xWO_3[a]	% products formed: cubic Na_xWO_3
1	50	125		100 ($x = 0.62$)
2	150	375		100 ($x = 0.58$)
3	300	750	33	67 ($x = 0.54$)
4	350	875	50	50 ($x = 0.45$)
5	400	1000	100	

[a] Tetragonal phase has $x < 0.38$.

Table 2. Reduction of 200 mL of 0.25 M Na_2WO_4 (50 mmol of Na_2WO_4) with Varying Amounts of 2.5 M $NaBH_4$ at pH = 4

amounts of $NaBH_4$ mL	amounts of $NaBH_4$ mmol	% products formed: tetragonal Na_xWO_3[a]	% products formed: cubic Na_xWO_3[b]
15	37.5	38	62
35	87.5	61	39
50	125	69	31
100	250	71	29
200	500	71	29
400	1000	64	36
600	1500	62	38

[a] Tetragonal phase has $x < 0.38$. [b] Cubic phase has $x = 0.50 \pm 0.03$.

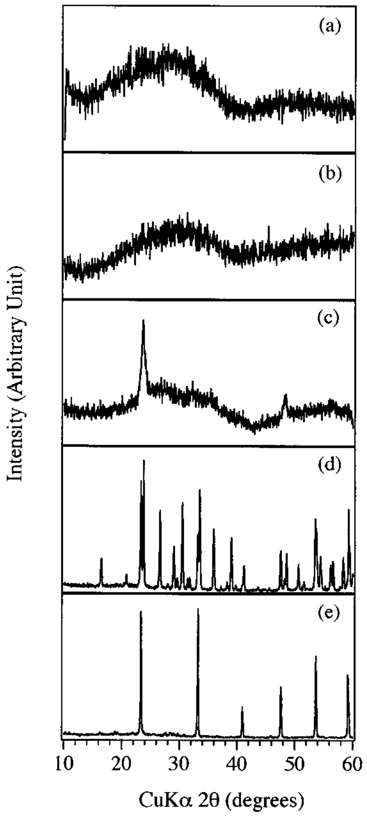

Figure 1. X-ray powder diffraction patterns of the product obtained by reducing 200 mL of 0.25 M Na_2WO_4 with 400 mL of 2.5 M $NaBH_4$ at pH = 6 (sample 5 in Table 1): (a) as-prepared sample (amorphous), (b) after heating to 400 °C in DSC (amorphous), (c) after heating to 490 °C in DSC (metastable and possibly ReO_3 type), (d) after heating to 600 °C in DSC (tetragonal tungsten bronze Na_xWO_3), and (e) after heating in an evacuated sealed silica tube at 850 °C (cubic tungsten bronze Na_xWO_3).

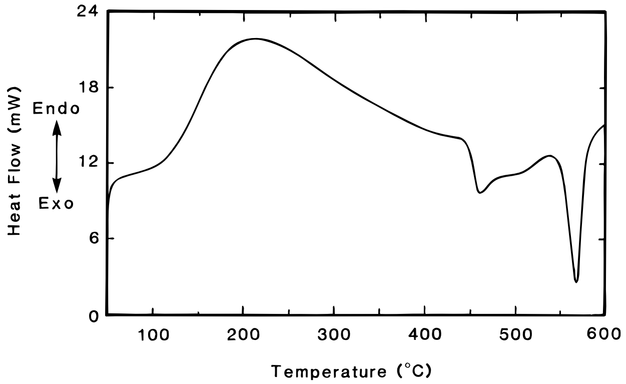

Figure 2. DSC plot recorded in N_2 atmosphere with a heating rate of 10 °C/min for the as-prepared sample 5 in Table 1.

with varying amounts of 2.5 M $NaBH_4$. The results obtained with 200 mL of 0.25 M Na_2WO_4 at pH = 6 and 4 are given, respectively, in Tables 1 and 2. The as-prepared samples were found to be amorphous from X-ray diffraction (Figure 1). Therefore, some samples in Table 1 were subjected to DSC and TGA in order to understand the evolution of crystalline phases upon heating. The DSC and TGA plots of sample 5 in Table 1 are given, respectively, in Figures 2 and 3. DSC shows a broad endotherm around 200 °C and two relatively sharp exothermic peaks around 460 and 560 °C. TGA shows a weight loss of ~5% below 250 °C, and there is no further weight loss above 300 °C. A very small weight increase observed above 450 °C could be due to the oxidation caused by residual oxygen present in the nitrogen cylinder and/or an inefficient purging. Comparison of the DSC and TGA data suggests that the broad endotherm around 200 °C could be due to the loss of water as the samples were prepared in aqueous solutions. The persistence of weight loss up to ~250 °C also suggests that some water (or hydroxide group) is bound to the lattice. The X-ray powder diffraction patterns recorded before and after the first exotherm and after the second exotherm are all compared with that of the as-prepared sample in Figure 1. The sample heated to 400 °C is still amorphous. The sample heated to 490 °C shows two or three reflections, which could not be readily assigned to any known phases in the Na−W−O or W−O systems. Although the reflections in Figure 1c seem to show some resemblance to some strong reflections of the ReO_3 structure,[8] the structure could not be identified unambiguously as the X-ray pattern is not well-defined; prolonged annealing around 460 °C did not help much to improve the pattern. On the other hand, the sample heated up to 600 °C shows several sharp reflections, which could all be indexed on the basis of the tetragonal tungsten bronze structure reported for $Na_{0.28}WO_3$.[9] These results suggest that the first exotherm at 460 °C may correspond to a crystallization of the product to give a metastable phase and the second exotherm at 560 °C to a transformation of the metastable phase to the thermodynamically more stable tetragonal tungsten bronze. We believe the metastable phase obtained after the first exotherm has a perovskite-related ReO_3 structure. From these product identification, we can also now write the chemical reaction for the reduction process as

$$Na_2WO_4 + NaBH_4 + (3 - x)H_2O \rightarrow NaBO_2 + Na_xWO_3 + (2 - x)NaOH + (4 - 0.5x)H_2 \quad (2)$$

Knowing from the above information that well-crystallized samples are obtained above 560 °C, all the samples in Table 1 and 2 were heated in an evacuated sealed silica tube at 600 °C for 24 h and analyzed by X-ray diffraction. The results obtained on the phase identification are given in Tables 1 and 2 for

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(8) JCPDS Card No. 05-0361, Joint Committee on Powder Diffraction Standards, Swarthmore, PA.

(9) JCPDS Card No. 24-1009, Joint Committee on Powder Diffraction Standards, Swarthmore, PA.

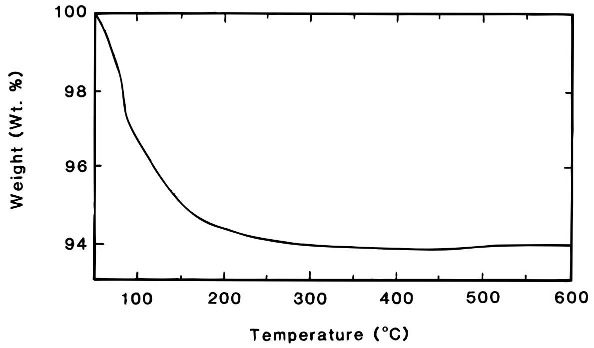

Figure 3. TGA plot recorded in N_2 atmosphere with a heating rate of 10 °C/min for the as-prepared sample 5 in Table 1.

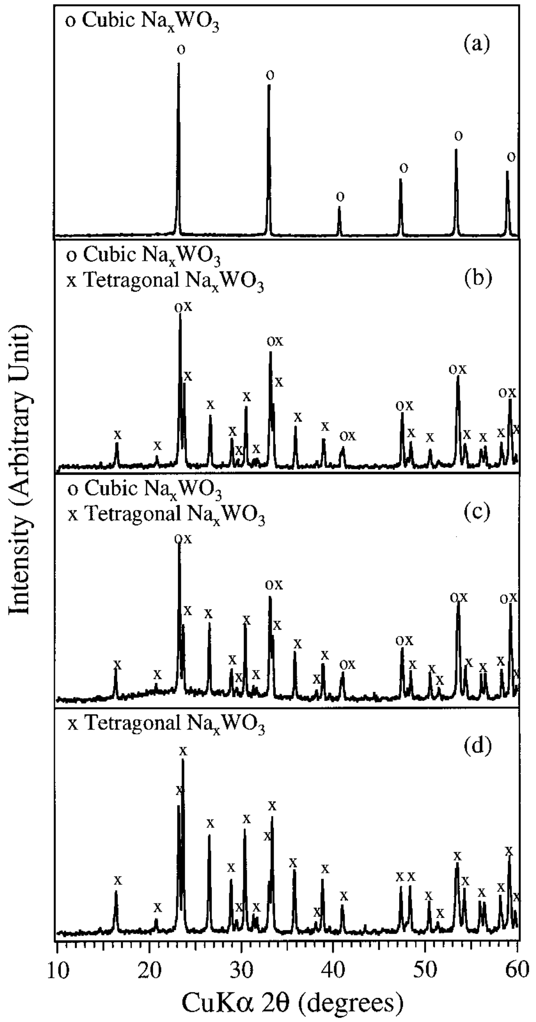

Figure 4. X-ray powder diffraction patterns recorded after heating the reduction products in an evacuated sealed silica tube at 600 °C for 1 day: (a) sample 1 in Table 1 (cubic Na_xWO_3), (b) sample 3 in Table 1 (mixture of cubic and tetragonal Na_xWO_3), (c) sample 4 in Table 1 (mixture of cubic and tetragonal Na_xWO_3), and (d) sample 5 in Table 1 (tetragonal Na_xWO_3).

various volumes of $NaBH_4$. The percents of the phases listed in the tables were calculated from the observed intensities of the peaks in the X-ray diffraction patterns. The corresponding X-ray diffraction results for samples in Table 1 are given in Figure 4. Sample 1 obtained with 50 mL of $NaBH_4$ gives cubic sodium tungsten bronze Na_xWO_3 with $x = 0.62$. As the samples are not readily soluble in acidic conditions, the Na content could not be estimated by atomic absorption spectroscopy or inductively coupled plasma analysis. However, the Na content x in the cubic Na_xWO_3 could be calculated from the experimentally observed lattice parameter a_o using the literature relationship[10-12]

$$a_o = (3.7845 + 0.0820x)\ \text{Å} \qquad (3)$$

Also, the crystalline bronzes Na_xWO_3 were found to exhibit interesting colors ranging from deep blue to violet to red as the value of x increases, which is in accordance with the absorption spectra reported in the literature.[10,12]

As the amount of $NaBH_4$ increases in Table 1, the value of x in Na_xWO_3 decreases, which results in a transition from pure cubic tungsten bronze (up to 150 mL of $NaBH_4$) to pure tetragonal tungsten bronze (at 400 mL of $NaBH_4$) with an intermediate regime (300−350 mL) giving the two phases. These results are consistent with the reported phase diagram for the Na_xWO_3 system.[12,13] According to the phase diagram, tetragonal phases are formed below $x \approx 0.38$ and cubic phases are formed above $x \approx 0.43$ if the temperature is below ~500 °C; for $0.38 < x < 0.43$, both the tetragonal and cubic phases coexist, giving a two-phase region. The reported temperature−composition diagram[12,13] also indicates that the cubic phase region is stabilized to lower x values as the temperature increases from about 500−1000 °C. For example, the cubic phase is formed above $x \approx 0.34$ and the tetragonal phase below $x \approx 0.31$ at around 900 °C with a narrower two-phase region. In order to see whether the temperature of synthesis also influences the crystal chemistry in our study, samples 3−5 in Table 1 were heated in an evacuated sealed silica tube at 850 °C. X-ray diffraction results show that samples 3−5 have the cubic tungsten bronze structure (single phase) after heating at 850 °C. For example, the X-ray pattern for sample 5 after heating at 850 °C is shown in Figure 1e. These results suggest that samples 3−5 have x values around 0.4 and, as the temperature increases, the cubic phase becomes stable as expected from the phase diagram for this composition.

It is clear from the X-ray data and lattice parameters that the value of x in Na_xWO_3 decreases slightly with increasing volume of borohydride. This implies that the average oxidation state of W increases slightly with increasing volume of borohydride. Although one would expect the increasing amount of borohydride to cause more reduction as we found before with molybdates,[6] the drastic changes in the contents of the reaction medium, particularly with a highly concentrated solution of $NaBH_4$, may play a role in controlling the degree of reduction. It is known[14] that the $(WO_4)^{2-}$ ions condense progressively as the pH decreases to give first polyanions such as $[HW_6O_{21}]^{5-}$ and $[H_2W_{12}O_{40}]^{6-}$ and finally the neutral binary oxide WO_3. In the present experiments, it is possible that the changes in the contents of the reaction medium with increasing amount of borohydride may increase the degree of condensation to give polyanions. The polyions are more difficult to reduce, as we have seen before,[6] and this can consequently cause a slight decrease in the degree of reduction. In addition, as the experiments are carried out by a slow and continuous addition of the borohydride while maintaining the pH constant, it is possible that the product formed initially may also have an

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Table 3. Reduction of 200 mL of 0.25 M Na_2WO_4 (50 mmol of Na_2WO_4) with Varying Amounts of 0.25 M $NaBH_4$ at pH = 6

amounts of $NaBH_4$		% products formed	
mL	mmol	tetragonal Na_xWO_3[a]	cubic Na_xWO_3[b]
10	2.5	no solid is formed	
34	8.5	no solid is formed	
50	12.5	5	95
100	25	2	98
150	37.5	15	85
200	50	17	83
300	75	35	65
400	100	30	70
500	125	63	37

[a] Tetragonal phase has $x < 0.38$. [b] Cubic phase has $x = 0.53 \pm 0.05$.

influence on the products formed with the continued addition of the borohydride.

The results obtained at pH = 4 with 2.5 M $NaBH_4$ are given in Table 2. The phases identified after heating at 600 °C in evacuated sealed silica tubes are listed. A two-phase mixture consisting of the cubic and tetragonal Na_xWO_3 are found for all volumes (15−600 mL) of borohydride. The relative amounts of the cubic and tetragonal phases do not vary significantly with the amount of borohydride. Also, the value of x in the cubic Na_xWO_3 that was obtained from the lattice parameter data was found to remain nearly constant at 0.50 ± 0.03. These observations suggest that the degree of reduction does not vary significantly with the volume of borohydride at pH = 4. This could be due to a balance between the increase in reducing power arising from the increasing volume of borohydride and a decrease in reducing power arising from an increasing condensation of the tungstate units, which may be due to the changes in the contents of the reaction medium as discussed in the previous paragraph. At pH = 6, however, the effect of increasing condensation seems to be predominant, resulting in a slight decrease in overall reducing power with increasing amount of borohydride.

Influence of $NaBH_4$ Concentration on the Reduction Products. In order to understand the influence of the concentration of borohydride, reduction experiments were also carried out at pH = 6 and 4 with a constant volume (200 mL) of 0.25 M Na_2WO_4 and varying volumes of a lower concentration (0.25 M) $NaBH_4$. The products identified after heating in an evacuated sealed silica tube at 600 °C are given in Table 3 for pH = 6. No solid reduction product could be isolated at least up to 200 mL of $NaBH_4$ and so no table is given for pH = 4. Compared to 2.5 M $NaBH_4$, a larger volume of 0.25 M $NaBH_4$ is required to obtain the solid reduction products. A lower reducing power associated with a lower concentration necessitates a larger volume of $NaBH_4$ to get the products. A two-phase mixture consisting of the cubic and tetragonal Na_xWO_3 is obtained at pH = 6 over a large volume interval (50−500 mL) of $NaBH_4$ (Table 3). The relative amount of the cubic phase decreases and that of the tetragonal phase increases slightly with increasing volume of borohydride. Also, the value of x in the cubic Na_xWO_3 decreases slightly with increasing volume of borohydride. These results suggest that the overall reducing power decreases slightly with the volume of borohydride, but the decrease is much less significant than that found with 2.5 M $NaBH_4$ at pH = 6 (Table 1). A lower concentration borohydride may alter the contents of the reaction medium and hence the degree of condensation only slightly compared to 2.5 M $NaBH_4$ and, thereby, causing only a slight change in the reducing power.

Influence of pH on the Reduction Products. In order to understand the influence of pH on the reduction products, a number of reduction experiments were also carried out at various pH values with a constant amount (50 mL) of 0.25 M Na_2WO_4 and with a constant amount (200 mL) of either 0.25 or 2.5 M $NaBH_4$. The products identified after heating at 600 °C are given in Table 4 for 2.5 M $NaBH_4$. At lower pH ≤ 2, a two-phase mixture of the binary oxides WO_2 and $W_{24}O_{68}$ is obtained (Figure 5). The relative amount of $W_{24}O_{68}$ decreases as the pH increases from 1 to 2. The chemical reaction for the formation of the binary oxides as reduction products can be given as

Table 4. Reduction of 50 mL of 0.25 M Na_2WO_4 (12.5 mmol of Na_2WO_4) with 200 mL of 2.5 M $NaBH_4$ (500 mmol of $NaBH_4$) at Various pH

	% products formed					
				Na_xWO_3		
pH	WO_2	$W_{18}O_{49}$	$W_{24}O_{68}$	tetragonal[a]	cubic[b]	$Na_2W_2O_7$
1	63		37			
2	91		9			
3				100		
4				91	9	
5				23	77	
6				9	91	
7					100	
10		35		5		60

[a] Tetragonal phase has $x < 0.38$. [b] Cubic phase has $x = 0.58 \pm 0.03$.

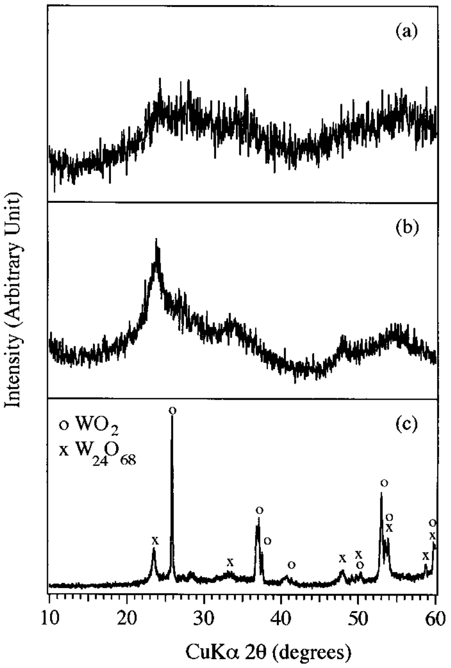

Figure 5. X-ray powder diffraction patterns of the reduction product obtained by reducing 50 mL of 0.25 M Na_2WO_4 with 200 mL of 2.5M $NaBH_4$ at pH = 2 (Table 4): (a) as-prepared sample (amorphous), (b) after heating in DSC to 460 °C (metastable $WO_{3-\delta}$ derived from possibly ReO_3-type structure), and (c) after heating in an evacuated sealed silica tube at 600 °C for 1 day (WO_2 with traces of $W_{24}O_{68}$).

$$Na_2WO_4 + NaBH_4 + (3 - \delta)H_2O \rightarrow NaBO_2 + WO_{3-\delta} + 2NaOH + (4 - \delta)H_2 \quad (4)$$

A $\delta = 1$ will correspond to the formation of WO_2 in eq 4. A $0 < \delta < 1$ will correspond to the formation of binary nonstoichiometric oxides $WO_{3-\delta}$ with average oxidation states in between W^{4+} and W^{6+}. We believe that, in our experiments in Table 4, a metastable $WO_{3-\delta}$ amorphous phase is formed during the reduction process and it disproportionates to WO_2 and $W_{24}O_{68}$ upon heating to 600 °C. This conclusion is supported by the observation of two DSC peaks, one around 450 °C and the other around 550 °C. X-ray diffraction shows after the first exotherm weak reflections reminescent of phases formed from ReO_3 structure[15] (for example, similar to the reflections of $W_{24}O_{68}$) and after the second exotherm reflections corresponding to WO_2 and $W_{24}O_{68}$.

At pH = 3, a single-phase tetragonal tungsten bronze Na_xWO_3 is obtained. As the pH increases above 3, a two-phase mixture consisting of the tetragonal and cubic tungsten bronzes Na_xWO_3 is obtained in the range $4 \leq pH \leq 6$ and a single phase cubic bronze at pH = 7. In the two-phase region, the relative amount of the cubic phase increases with increasing pH. At pH = 10, a three-phase mixture consisting of the binary oxide $W_{18}O_{49}$, the tetragonal bronze Na_xWO_3, and the unreduced $Na_2W_2O_7$ is obtained.

The observed variations in the nature of the products with pH can be understood as follows. At $pH \leq 2$, the degree of condensation is high and the neutral WO_3 forms in the absence of a reducing agent around pH = 1. Reduction of highly condensed ions with a much smaller Na/W ratio seems to result in the formation of reduced binary oxides such as WO_2 and $W_{24}O_{68}$ without any Na at $pH \leq 2$. At intermediate $3 \leq pH \leq 7$, the reduction of moderately condensed ions such as $[HW_6O_{21}]^{5-}$ and $[H_2W_{12}O_{40}]^{6-}$ with an increased Na/W ratio results in the formation of sodium tungsten bronzes Na_xWO_3. A decreasing degree of condensation with increasing pH seems to play a dominant role in the range $3 \leq pH \leq 7$ and cause an increase in the overall reducing power with increasing pH even though the decreasing hydrolysis of borohydride to give hydrogen (eq 1) is expected to decrease the reducing power. At pH = 10, the reducing power is weak due to a decreased hydrolysis of borohydride resulting in the formation of a major amount of the unreduced product $Na_2W_2O_7$ along with small quantities of $W_{18}O_{49}$ and Na_xWO_3.

The products identified after firing at 600 °C are given in Table 5 for 0.25 M $NaBH_4$. At $pH \leq 4$, the binary oxides WO_2 and $W_{24}O_{68}$ are obtained. At intermediate $5 \leq pH \leq 8$, the tetragonal and cubic bronzes are obtained with the amount of cubic bronze increasing with pH. These trends are similar to that found with 2.5 M $NaBH_4$ in Table 4. At pH = 10, the cubic bronze is formed predominantly, which is slightly different from that observed for 2.5 M $NaBH_4$ in Table 4. It appears that a higher concentration of borohydride changes the contents of the reaction medium and facilitates the formation of condensed ditungstate $Na_2W_2O_7$ predominantly.

Table 5. Reduction of 50 mL of 0.25 M Na_2WO_4 (12.5 mmol of Na_2WO_4) with 200 mL of 0.25 M $NaBH_4$ (50 mmol of $NaBH_4$) at Various pH

	% products formed			
			Na_xWO_3	
pH	WO_2	$W_{24}O_{68}$	tetragonal[a]	cubic[b]
1	83	17		
4		100		
5			100	
6			41	59 ($x = 0.53$)
8			4	96 ($x = 0.55$)
10			5	95 ($x = 0.62$)

[a] Tetragonal phase has $x < 0.38$.

Conclusions

Reduction of aqueous Na_2WO_4 with aqueous $NaBH_4$ at ambient temperatures has been investigated systematically as a function of pH and concentration and volume of $NaBH_4$. The results show that amorphous, binary and ternary oxides of lower valent tungsten are formed as the reduction products. These amorphous products crystallize around 450 °C to give the crystalline tungsten bronzes Na_xWO_3 or the binary oxides $WO_{3-\delta}$ and WO_2. The bronzes are generally obtained at $3 < pH < 8$ while the binary oxides are obtained at $pH < 3$. The tungsten bronzes undergo crystal-chemical changes as the as-prepared samples are annealed from 400 to 850 °C. The observed changes could be explained on the basis of the temperature−composition diagram reported in the literature.

The nature of the products formed at various reaction conditions could be explained by considering the increase in the reducing power of borohydride and the degree of condensation of the tungstate ions with decreasing pH. Although the reducing power of the borohydride increases with decreasing pH, a decreasing ability to reduce the tungstate ions with increasing degree of condensation tends to lower the degree of reduction in many instances. The effect of changes in the degree of condensation is seen on the reduction products to a greater extent in the tungstate system than in the molybdate system.[6] This could be due to the fact that the tungstate ions tend to condense easily compared to the molybdates and at a given pH the tungstate has a higher degree of condensation than the molybdate.[14]

While reductions of Na_2WO_4 with $NaBH_4$ and K_2WO_4 with KBH_4 are found to give, respectively, Na_xWO_3 and K_xWO_3, our preliminary experiments on the reduction of, for example, Na_2WO_4 with KBH_4 yields K_xWO_3 and not the mixed $(Na, K)_xWO_3$ as revealed by energy dispersive spectroscopic analysis. Further systematic and more elaborate experiments with mixed systems are currently in progress.

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