Synthesis of lower-valent molybdenum oxides in aqueous solutions by reducing Na_2MoO_4 with $NaBH_4$

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Reduction of Na_2MoO_4 with $NaBH_4$ in aqueous solutions at ambient temperatures has been investigated systematically by varying the concentration and volume of $NaBH_4$ as well as the reaction pH. The reduction products have been characterized by X-ray diffraction and differential scanning calorimetry (DSC). The reduction yields metastable, amorphous oxides of lower-valent molybdenum, which crystallize around 350 °C to give the binary oxide MoO_2 and the sodium molybdenum bronze $Na_{0.88}Mo_6O_{17}$. The relative amounts of MoO_2 and $Na_{0.88}Mo_6O_{17}$ formed are correlated to the overall reducing power that can be achieved. The concentration and volume of $NaBH_4$, the reaction pH and the changes in the degree of condensation of the molybdate ions are all found to influence the overall reducing power.

Complex metal oxides are traditionally made by firing the reactants at elevated temperatures with intermediate grindings in order to overcome the diffusional limitations. Such a high-temperature approach generally gives the thermodynamically stable phases and often leads to an instability of metastable phases that may have unusual valence states or structural arrangements. In addition, the high-temperature approach results in samples with larger particle size and lower surface area, which are undesirable for some applications such as catalysis as well as for ceramic processing to achieve higher densities. There has been considerable interest in recent years to develop low-temperature methods to synthesize complex inorganic solids.[1–3] While there are several low-temperature techniques such as sol–gel processing to obtain higher-valent metal oxides, methods to synthesize lower-valent transition-metal oxides, particularly in aqueous solutions, are limited or not known. For example, higher-valent binary oxides such as Al_2O_3, Fe_2O_3, Nb_2O_5 and WO_3, and ternary oxides such as $SrMoO_4$, $SrTiO_3$ and $LaNbO_4$ can be made by sol–gel processing, control of pH, or precipitation reactions in aqueous solutions. In contrast, lower-valent binary oxides such as VO_2, MoO_2, and WO_2 or ternary oxides such as $SrMoO_3$, Na_xWO_3, $LaTiO_3$ are difficult to make in aqueous solutions.

We demonstrated[4,5] recently that oxo-ions $(MO_4)^{n-}$ (M = V, Mo or W) can be readily reduced with alkali-metal tetrahydroborates ABH_4 (A = Na or K) in aqueous solutions to give the binary oxides or the ternary oxides A_xMO_3. The method gives amorphous or nanocrystalline products which are attractive as electrode materials for rechargeable lithium batteries.[6,7] We then studied systematically the reduction of K_2MoO_4 with KBH_4 and identified the conditions that influence the reaction products.[8] The concentration and amount of tetrahydroborate and the reaction pH were all found to influence the reduction products. We present in this paper a systematic investigation of the reduction of Na_2MoO_4 with $NaBH_4$. This reduction can yield at ambient temperatures ternary oxides such as the bronzes $Na_xMo_yO_z$, which are otherwise generally made by either controlled electrolytic reduction or high-pressure methods.[9–11] The structural and physical properties of the molybdenum bronzes have drawn considerable interest in recent years as they exhibit interesting electronic properties with quasi-low-dimensional characteristics.

Experimental

Reduction reactions were carried out at various pH values with a fixed volume (25 ml) of 0.25 M Na_2MoO_4 and varying amounts of 0.25 and 2.5 M $NaBH_4$. In order to understand the influence of pH, reactions were also carried out with fixed amounts of Na_2MoO_4 (25 ml) and $NaBH_4$ (50 ml) at different pH values. The 0.25 M Na_2MoO_4 solution was prepared by dissolving 1.3 g of Na_2MoO_4 in 25 ml of deionized water. Both the 0.25 and 2.5 M $NaBH_4$ solutions were prepared by dissolving required quantities of $NaBH_4$ in dilute NaOH solution having a pH of 11–12. The initial pH of the tetrahydroborate solution was maintained high at 11–12 in order to suppress the hydrolysis of tetrahydroborate [reaction (1)] and prevent a rapid loss of hydrogen as the hydrolysis is facilitated by acidic conditions.[12]

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

Experiments were carried out by keeping the molybdate solution under constant stirring on a magnetic stirrer at a predetermined pH value and adding the tetrahydroborate solution from a burette. The pH tends to increase as the tetrahydroborate solution is added due to the formation of the basic $NaBO_2$ and NaOH [see reactions (2) and (3), later] and so concentrated HCl was added carefully to maintain the pH constant.

The reduction product formed after the addition of a specific amount of tetrahydroborate was filtered, washed several times with water and dried in an air-oven at 100 °C. The products were then characterized by X-ray powder diffraction and differential scanning calorimetry (DSC). The DSC plots were recorded with a Perkin-Elmer Series 7 thermal analysis system in a flowing N_2 atmosphere at a heating rate of 10 °C min^{-1}. As the as-prepared samples were found to be amorphous, the reduction products were heated in an evacuated sealed silica tube at 400 °C for one day to obtain crystalline products.

Results and Discussion

Influence of the amount of $NaBH_4$

In order to understand the influence of the amount of tetrahydroborate on the reduction products, experiments were first carried out at pH = 4 and 7 with varying volumes of 0.25 M $NaBH_4$. The as-prepared samples were found to be amorphous as indicated by the absence of any discernible peaks in the X-ray diffraction pattern (Fig. 1). The samples were found to crystallize around 350 °C as indicated by exothermic peaks in DSC plots. The DSC plot for a representative sample is, for example, shown in Fig. 2. The room-temperature X-ray patterns recorded after the DSC peaks showed sharp reflections indicating that the exothermic peaks correspond to crystalliz-

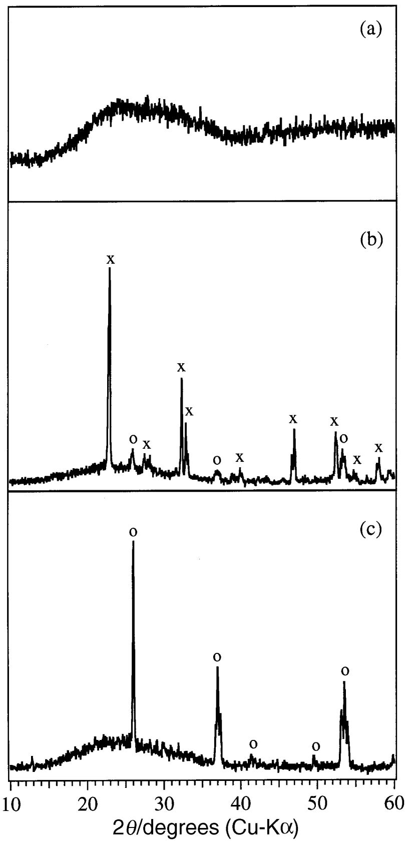

Fig. 1 X-Ray powder diffraction patterns of the product obtained by reducing 25 ml of 0.25 M Na_2MoO_4 with 10 ml of 0.25 M $NaBH_4$ (sample 2 in Table 1): (a) as-prepared sample, (b) after heating in an evacuated sealed silica tube at 400 °C (X, $Na_{0.88}Mo_6O_{17}$ and O, MoO_2), and (c) after heating in an evacuated sealed silica tube at 550 °C (O, MoO_2)

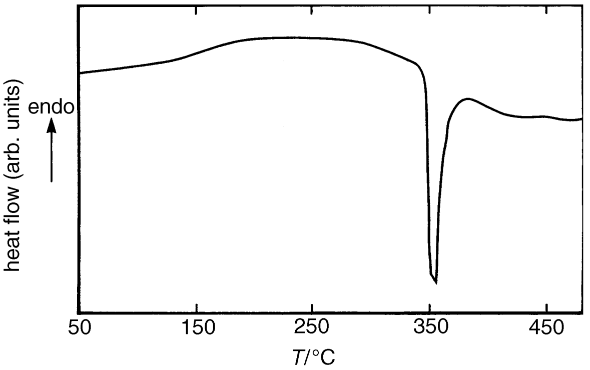

Fig. 2 DSC plot recorded with sample 9 in Table 1 with a heating rate of 10 °C min^{-1}

Table 1 Reduction of 25 ml of 0.25 M Na_2MoO_4 (6.25 mmol of Na_2MoO_4) with varying amounts of 0.25 M $NaBH_4$ at pH = 4

sample no.	amount of $NaBH_4$ ml	mmol	% products formed $Na_2Mo_2O_7$	$Na_{0.88}Mo_6O_{17}$	MoO_2
1	5	1.25	no solid is formed		
2	10	2.5	—	93	7
3	15	3.75	—	89	11
4	30	7.5	—	87	13
5	50	12.5	6	44	50
6	80	20	5	6	89
7	100	25	<5	10	88
8	150	37.5	<5	4	90
9	200	50	<5	7	89

Table 2 Reduction of 25 ml of 0.25 M Na_2MO_4 (6.25 mmol of Na_2MoO_4) with varying amounts of 0.25 M $NaBH_4$ at pH = 7

amount of $NaBH_4$ ml	mmol	% products formed $Na_2Mo_2O_7$	$Na_{0.88}Mo_6O_{17}$	MoO_2
15	3.75	17	5	78
30	7.5	12	8	80
40	10	13	6	81
50	12.5	5	63	32
100	25	6	70	24
130	32.5	7	—	93
150	37.5	—	—	100

ation. Knowing this information, the as-prepared samples were heated in evacuated sealed silica tubes at 400 °C for one day to obtain crystalline products. The products identified after the heat treatment at 400 °C are given in Tables 1 and 2, respectively, for pH = 4 and 7. The percentages of the phases were calculated from the observed peak intensities in the X-ray diffraction patterns. Fig. 1 shows the X-ray diffraction pattern recorded after annealing at 400 °C for one of the samples.

At pH = 4, no solid product is formed at 5 ml of $NaBH_4$. At 10 ml of $NaBH_4$, the sodium molybdenum bronze $Na_{0.88}Mo_6O_{17}$[13] is formed along with traces of MoO_2.[14] As the volume of $NaBH_4$ is increased, the amount of MoO_2 increases and the amount of $Na_{0.88}Mo_6O_{17}$ decreases. For example, the sample obtained with 200 ml of $NaBH_4$ has only a small amount of $Na_{0.88}Mo_6O_{17}$. Also, at higher volumes (⩾50 ml) of tetrahydroborate, traces of the unreduced phase $Na_2Mo_2O_7$ are formed. The increase in the amount of MoO_2 formed with increasing volume of tetrahydroborate can be understood to be due to an improved reducing power arising from an increasing amount of tetrahydroborate. This observation is similar to that we found with the reduction of K_2MoO_4 with KBH_4.[8]

A question arises why the more reduced MoO_2 is formed at all volumes of $NaBH_4$. This could be due to either of the following reasons. (i) The experiments are carried out with slow addition of the tetrahydroborate from a burette over several minutes and concentrated hydrochloric acid is added in order to maintain the pH at a given value. It is possible that the addition of tetrahydroborate causes an instantaneous local reduction of some molybdate units to give MoO_2. (ii) It is also possible that the reduction products are formed as a metastable, single-phase amorphous $Na_xMo_yO_z$, which upon heating undergoes crystallization and disproportionation to give the thermodynamically more stable line phases $Na_{0.88}Mo_6O_{17}$ and MoO_2. Crystalline sodium molybdenum bronzes are known to form only for specific compositions and unique structures, unlike the analogous sodium tungsten bronzes Na_xWO_3 that are formed over a wide range of x.[9–11,15,16] In fact, $Na_{0.88}Mo_6O_{17}$ is the only known phase in the Na–Mo–O system with an average oxidation state of Mo in between 4+ and 6+. It is thus possible that a metastable $Na_xMo_yO_z$ compound with x, y and z values varying with the volume of tetrahydroborate is formed and that it disproportionates upon heating to give different proportions of the crystalline phases $Na_{0.88}Mo_6O_{17}$ and MoO_2.

From the identification of the reduction products, we can now write chemical reactions for the formation of MoO_2 or the bronze $Na_xMo_yO_z$ (which can also be represented for simplicity as $Na_\eta MoO_{3-\delta}$) as follows [eqn. (2) and (3)].

$$Na_2MoO_4 + NaBH_4 + 2H_2O \rightarrow NaBO_2 + MoO_2 + 2NaOH + 3\ H_2 \quad (2)$$

$$Na_2MoO_4 + NaBH_4 + (3-\eta-\delta)H_2O \rightarrow NaBO_2 + Na_\eta MoO_{3-\delta} + (2-\eta)NaOH + (4-0.5\eta-\delta)H_2 \quad (3)$$

We would like to point out that the stability of the crystalline bronze decreases as the temperature exceeds *ca.* 500 °C. For example, the X-ray pattern recorded after heating sample 2 in Table 1 at 550 °C is compared with that of the sample heated at 400 °C (Fig. 1). The reflections corresponding to the bronze disappear and only reflections corresponding to MoO_2 are found after heating at 550 °C. The observed instability clarifies why special procedures such as controlled electrolytic reduction had to be generally used to synthesize molybdenum bronzes.

The phases identified after heating the samples at 400 °C in evacuated sealed silica tubes are given in Table 2 for pH = 7. The bronze $Na_{0.88}Mo_6O_{17}$ and the unreduced phase $Na_2Mo_2O_7$ are formed along with MoO_2 up to about 130 ml of tetrahydroborate. The amount of the unreduced phase $Na_2Mo_2O_7$ decreases with increasing volume of tetrahydroborate and it is completely eliminated at 150 ml. The relative amount of $Na_{0.88}Mo_6O_{17}$ increases as the volume of tetrahydroborate increases from 15 to 100 ml and it vanishes completely at ⩾130 ml. At 150 ml of tetrahydroborate, only MoO_2 is formed. Unlike at pH = 4 (Table 1), the observed trend in the products at pH = 7 (Table 2) cannot simply be explained on the basis of improved reducing power with increasing volume of tetrahydroborate, particularly because the amount of bronze increases first and then decreases. As we have found before with the potassium molybdate[8] and sodium tungstate[16] systems, the degree of condensation of the molybdates may play a role in the overall degree of reduction that can be achieved. It is known[17] that the $(MoO_4)^{2-}$ ions condense progressively with decreasing pH to give first the polyanions such as $(Mo_7O_{24})^{6-}$ and finally the neutral oxide MoO_3. The ability to reduce the molybdate ions decreases as the degree of condensation increases. It is possible that the changes in the reaction medium with the addition of tetrahydroborate influence the degree of condensation and thereby the overall reducing power.

Influence of $NaBH_4$ concentration

Reduction experiments were also carried out at pH = 4 and 7 with varying volumes of $NaBH_4$ having a ten-fold increase in concentration (2.5 M) in order to understand the influence of concentration on the reduction products. The products identified after heating at 400 °C in evacuated sealed silica tubes are given in Tables 3 and 4.

At pH = 4, the amount of the bronze $Na_{0.88}Mo_6O_{17}$ decreases and that of MoO_2 increases with increasing volume of tetrahydroborate. For example, only MoO_2 is formed at 200 ml of $NaBH_4$. In addition, traces of the unreduced phase $Na_2Mo_2O_7$ is formed at lower volumes ⩽15 ml and small amount of the binary oxide Mo_4O_{11} is formed at 50 ml. The increase in MoO_2 with the volume of $NaBH_4$ is due to an increasing reducing power as we found with 0.25 M $NaBH_4$ (Table 1). As expected, a higher reducing power associated with the higher concentration (2.5 M) tetrahydroborate leads to single-phase MoO_2 at 200 ml of $NaBH_4$ while the 0.25 M $NaBH_4$ in Table 1 still gives traces of the bronze at 200 ml.

Table 3 Reduction of 25 ml of 0.25 M Na_2MO_4 (6.25 mmol of Na_2MoO_4) with varying amounts of 2.5 M $NaBH_4$ at pH = 4

amount of $NaBH_4$		% products formed			
ml	mmol	$Na_2Mo_2O_7$	$Na_{0.88}Mo_6O_{17}$	Mo_4O_{11}	MoO_2
5	12.5	<5	47	—	49
15	37.5	6	20	—	74
20	50	—	17	—	83
50	125	—	18	24	58
100	250	—	23	—	77
150	375	—	7	—	93
200	500	—	—	—	100

Table 4 Reduction of 25 ml of 0.25 M Na_2MO_4 (6.25 mmol of Na_2MoO_4) with varying amounts of 2.5 M $NaBH_4$ at pH = 7

amount of $NaBH_4$		% products formed		
ml	mmol	$Na_2Mo_2O_7$	$Na_{0.88}Mo_6O_{17}$	MoO_2
15	37.5	15	—	85
30	75	4	36	60
50	125	<5	—	95
100	250	<5	—	95
150	375	—	—	100

At pH = 7, only MoO_2 is formed as the reduction product at larger volumes (⩾50 ml) of $NaBH_4$. A small amount of the unreduced phase $Na_2Mo_2O_7$ is formed along with MoO_2 at ⩽100 ml of $NaBH_4$ and some amount of the bronze $Na_{0.88}Mo_6O_{17}$ is formed only at 30 ml of $NaBH_4$. The trend that the bronze is formed at intermediate volumes is similar to that observed with 0.25 M $NaBH_4$ at pH = 7. As discussed earlier, the changes in the degree of condensation of the molybdate ions with the changes in the reaction medium may play a role in controlling the products. More importantly, about the same volume (150 ml) of 0.25 M (Table 2) and 2.5 M (Table 4) $NaBH_4$ is required to give single-phase MoO_2; *i.e.* while about 37.5 mmol of 0.25 M $NaBH_4$ give single-phase MoO_2, about 375 mmol of 2.5 M $NaBH_4$ are needed to give single-phase MoO_2. This reveals that the reducing power is not simply proportional to the number of moles of $NaBH_4$, but rather the changes in the contents of the reaction medium also play an important role in influencing the reducing power and reduction products.

Influence of pH

A series of experiments were also carried out at various pH values by reducing a constant volume (25 ml) of 0.25 M Na_2MoO_4 with a constant volume (50 ml) of both 0.25 and 2.5 M $NaBH_4$ in order to understand the role of pH on the reduction products. The phases identified after heating the reduction products at 400 °C in evacuated sealed silica tubes are given in Tables 5 and 6, respectively, for 0.25 and 2.5 M $NaBH_4$. With 0.25 M $NaBH_4$, no solid is formed at pH = 1. Both the bronze $Na_{0.88}Mo_6O_{17}$ and MoO_2 are formed at pH = 4 and 7 and only MoO_2 is formed at pH = 10. Traces of the unreduced phase $Na_2Mo_2O_7$ are also formed at pH = 4–10. On the other hand, with 2.5 M $NaBH_4$, only MoO_2 is formed as reduction product at pH = 1, 7 and 10 and the bronze $Na_{0.88}Mo_6O_{17}$, Mo_4O_{11} and MoO_2 are formed at pH = 4. As

Table 5 Reduction of 25 ml of 0.25 M Na_2MoO_4 (12.5 mmol of Na_2MoO_4) with 50 ml 0.25 M $NaBH_4$ (12.5 mmol of $NaBH_4$) at various pH

	% products formed		
pH	$Na_2Mo_2O_7$	$Na_{0.88}Mo_6O_{17}$	MoO_2
1		no solid is formed	
4	6	44	50
7	5	68	27
10	7	—	93

Table 6 Reduction of 25 ml of 0.25 M Na_2MoO_4 (12.5 mmol of Na_2MoO_4) with 50 ml 2.5 M $NaBH_4$ (125 mmol of $NaBH_4$) at various pH

	% products formed			
pH	$Na_2Mo_2O_7$	$Na_{0.88}Mo_6O_{17}$	Mo_4O_{11}	MoO_2
1	—	—	—	100
4	—	20	23	57
7	5	—	—	95
10	16	—	—	84

with 0.25 M $NaBH_4$, traces of the unreduced phase $Na_2Mo_2O_7$ are also formed at pH = 7 and 10.

While only the highly reduced reduction product MoO_2 is formed at low and high pH (1 and 10), moderately reduced $Na_{0.88}Mo_6O_{17}$ (and Mo_4O_{11} with 2.5 M $NaBH_4$) is formed along with MoO_2 at intermediate pH = 4–7. This suggests that the reducing power is high at low and high pH but is moderate at intermediate pH. This can be understood by considering the interplay between the following two opposing effects. The reducing power of the tetrahydroborate increases with decreasing pH as the hydrolysis reaction (1) is facilitated in acidic conditions. In contrast, the degree of condensation of the molybdate ions increases with decreasing pH, which will make the reduction difficult. An increasing ability of tetrahydroborate to give hydrogen at lower pH and an easier reducibility of the uncondensed, monomeric $(MoO_4)^{2-}$ ion at higher pH make the formation of MoO_2 easier at both lower and higher pH. Both a decreasing ability of tetrahydroborate to give hydrogen and a decreasing reducibility of condensed ions at intermediate pH make the overall reducing power moderate, which leads to the formation of some bronze and Mo_4O_{11}. In addition, a highly condensed ion with little or no Na at lower pH, *ca.* 1, can also facilitate the formation of the binary oxide MoO_2 and suppress the bronze $Na_{0.88}Mo_6O_{17}$.

Conclusions

Reduction of aqueous Na_2MoO_4 with aqueous $NaBH_4$ at ambient temperature has been investigated systematically in order to understand the factors that influence the reduction products. The concentration and volume of tetrahydroborate as well as the reaction pH are found to influence the reduction products. In addition, the changes in the contents of the reaction medium and the degree of condensation of the molybdates also influence the overall reducing power. Metastable amorphous products are formed during the reduction process, which crystallize around 350 °C to give the crystalline phases MoO_2 and the bronze $Na_{0.88}Mo_6O_{17}$. Although the crystallized samples generally consist of MoO_2 and $Na_{0.88}Mo_6O_{17}$, it is not clear whether the as-prepared, amorphous samples are single-phase $Na_xMo_yO_z$, which disproportionates during crystallization to give the line phases MoO_2 and $Na_{0.88}Mo_6O_{17}$ or the as-prepared samples also consist of both amorphous MoO_2 and $Na_{0.88}Mo_6O_{17}$. Future work with X-ray absorption spectroscopic techniques may clarify this. In addition, the bronze is found to be unstable above about 500 °C and disproportionates to give predominantly MoO_2 as the crystalline phase. This clarifies why the molybdenum bronzes have to be generally obtained by special procedures such as electrolytic reduction.

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