Inorg. Chem. **1996,** *35,* 504−509

Synthesis of Lower Valent Molybdenum Oxides by an Ambient Temperature Reduction of Aqueous K_2MoO_4 by KBH_4

C. Tsang, A. Dananjay, J. Kim, and A. Manthiram*

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

Received July 28, 1995[⊗]

Reduction of aqueous K_2MoO_4 with aqueous KBH_4 at ambient temperatures has been investigated systematically to obtain lower valent molybdenum oxides. Several lower valent oxides such as MoO_2, Mo_4O_{11}, $K_{0.26}MoO_3$ (red bronze), $K_{0.30}MoO_3$ (blue bronze), and $K_{0.85}Mo_6O_{17}$ are formed during the reduction process; however, only MoO_2 has been obtained as single-phase product. The nature of the product formed is strongly influenced by the reducing power of KBH_4. The reducing power increases with decreasing pH or increasing concentration and volume of KBH_4. The as-prepared samples are amorphous as revealed by X-ray diffraction and transmission electron microscopy. They crystallize sharply at around 350−500 °C as revealed by differential scanning calorimetry. Since the products formed are amorphous in nature, they may become particularly attractive for battery electrodes and catalysis.

Introduction

Complex inorganic solids are generally synthesized by repeated grinding and firing at elevated temperatures of the reactants. The higher firing temperature is essential in order to overcome the larger diffusion distance associated with the micrometer size particles of the reactants. The high-temperature procedure leads sometimes not only to larger particle size and inhomogeneity but also to an inaccessibility of metastable phases that may have unusual valence states or atomic arrangements. These difficulties have prompted solid state chemists in recent years to develop new synthetic routes that can bring down the reaction temperatures.[1]

A sol-gel approach has been investigated[2] extensively to obtain simple as well as complex metal oxides at lower temperatures. The sol-gel process is based on hydroxylation and condensation of molecular precursors. The aqueous chemistry of the process is, however, quite complex due to the numerous molecular species that can exist depending on the oxidation state, pH, and concentration. While metal ions with charge $<4+$ tend to exist as aquo ions in aqueous solutions, those with charge $>4+$ tend to exist as oxo ions. For example, ions like Al^{3+} and Fe^{3+} form $[M(H_2O)_6]^{3+}$ in aqueous solutions. On the other hand, group V, VI, and VII metals readily form metalates $(MO_4)^{n-}$ such as $(VO_4)^{3-}$, $(CrO_4)^{2-}$, $(MoO_4)^{2-}$ and $(MnO_4)^{-}$ in aqueous solutions. The difference arises to maintain a lower net charge on the ions. The aquo ions condense progressively with increasing pH to give polycations first and then the neutral oxide. For example, the condensation process in the case of Al is given as

$$[Al(H_2O)_6]^{3+} \rightarrow [Al(H_2O)_5(OH)]^{2+} \rightarrow [Al_{13}O_4(OH)_{24}]^{7+} \rightarrow Al_2O_3 \tag{1}$$

On the other hand, the oxo ions condense progressively with decreasing pH to give polyanions first and then the neutral oxide.[3] For example, the condensation process in the case of W is given as

$$[WO_4]^{2-} \rightarrow [WO_3(OH)]^{-} \rightarrow [W_{12}O_{41}]^{10-} \rightarrow WO_3 \tag{2}$$

The above type of condensation reactions have been utilized to obtain a number of simple metal oxides such as V_2O_5, Nb_2O_5, Ta_2O_5, MoO_3, WO_3, ZrO_2, Fe_3O_3, Al_2O_3, etc., as well as mixed-metal oxides. Although the higher valent oxides could be readily obtained by these sol-gel methods, little was known about obtaining lower valent oxides of transition metals in aqueous solutions. We identified recently that alkali metal borohydrides such as $NaBH_4$ and KBH_4 can be used as effective reducing agents in aqueous solutions to obtain reduced transition metal oxides such as MoO_2, VO_2, Na_xWO_3, etc.[4,5] The borohydride ion hydrolyzes in aqueous solutions to give hydrogen[6] as

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2 \tag{3}$$

and the hydrolysis reaction is facilitated by acidic conditions. While the borohydrides ABH_4 (A = Na or K) reduce the aquo ions $[M(H_2O)_6]^{n+}$ (M = Fe, Co, Ni, or Cu) to metallic M or the corresponding borides,[6−8] they reduce the oxo ions $(MO_4)^{n-}$ (M = V, Mo, W) to MO_2 or the ternary oxide $A_xM_yO_z$ (A = Na or K).[4,5] We found that the nature of the products obtained in the reduction of oxo ions depends strongly on the reaction conditions such as reaction pH and concentration and amount of the reactants. We present in this paper a systematic study

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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of the influence of the reaction conditions on the products obtained in the reduction of aqueous K_2MoO_4 by KBH_4.

Experimental Section

KBH_4 solutions with two different concentrations (0.25 and 2.5 M) were prepared by dissolving required quantities of KBH_4 in dilute KOH solution having a pH of 11−12. The higher pH of 11−12 was necessary to suppress the hydrolysis of borohydride (reaction 3) and prevent a rapid loss of hydrogen and of the reducing power of borohydride. K_2MoO_4 solution with a concentration of 0.25 M was prepared by dissolving the required quantity of K_2MoO_4 in deionized water. Reduction reactions were carried out at various pH values with 50 mL of 0.25 M K_2MoO_4 and varying amounts of both 0.25 and 2.5 M KBH_4 solutions. An experiment at a given pH was carried out by adding a fixed quantity of the borohydride solution from a buret to the molybdate solution that was kept at the predetermined pH under constant stirring on a magnetic stirrer. Since the pH tends to increase due to the formation of the metaborate ion BO_2^- as the borohydride solution is added, concentrated HCl was added carefully to keep the pH constant. For reductions at pH > 10, the borohydride solution was added directly to the molybdate solution since the change in pH is negligible and the reaction is slow.

Addition of borohydride to the molybdate solution results in a formation of a colored precipitate. The color change indicates the reduction of Mo^{6+}. After the complete addition of a specific amount of borohydride, the precipitate formed was filtered or centrifuged. In the case of reactions at pH ≥ 10, the reduction was so slow that the reaction mixture was left for 3−10 days to obtain precipitates. Centrifuging was preferred in cases where the solid formed was so fine that it might pass through the ceramic filter funnel. The precipitate was washed several times with water to remove other reaction products such as KCl or boric acid. The solid was then dried either in vacuum or in an air oven at 100 °C before characterization. X-ray powder diffraction patterns were recorded with a Philips diffractometer. Differential scanning calorimetric (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.

Results and Discussion

X-ray powder diffraction shows that the as-prepared samples obtained by reducing K_2MoO_4 with KBH_4 are all amorphous as indicated by the absence of any discernible reflections (Figure 1). Therefore, the as-prepared samples were all heated in a N_2 atmosphere in DSC or in evacuated sealed silica tubes in order to crystallize them; the crystallized products were characterized by X-ray diffraction. DSC plots generally show a sharp exothermic peak corresponding to crystallization in the temperature range 350−500 °C (Figure 2), confirming the amorphous nature of the as-prepared samples; the products obtained after the crystallization peak in DSC showed sharp X-ray diffraction peaks. Even though the crystallized product is found to contain more than one phase in many cases (see later), only a single exotherm was observed in DSC. This is because a strong exothermic process associated with the crystallization releases locally an enormous amount of heat, which leads to a crystallization of the entire sample at approximately the same temperature once the crystallization process is initiated. The amorphous nature of the as-prepared samples was also confirmed by the absence of diffraction spots or ring patterns in a transmission electron microscopy (TEM) study. The TEM photograph revealing the morphology of an as-prepared sample that was obtained by reducing 50 mL of 0.25 M K_2MoO_4 with 250 mL of 2.5 M KBH_4 is shown in Figure 3. This sample was found to be MoO_2 after crystallization (see later).

Influence of pH on the Reduction Products. First, a series of experiments were carried out at various pH values by reducing 50 mL of 0.25 M K2MoO4 with a constant amount (150 mL) of 0.25 M KBH_4. The results of the products obtained after crystallization in DSC are given in Table 1 and Figure 4. As we see, the major product is MoO_2 at 1 ≤ pH ≤ 8, and no precipitate is formed at pH = 11. Although MoO_2 is the major product, the secondary product varies depending on the pH. At pH ≤ 4, the blue molybdenum bronze[9,10] $K_{0.3}MoO_3$ is formed as the secondary product. As the pH increases above 4, the unreduced phase $K_2Mo_3O_{10}$ begins to form as the secondary product, and the blue bronze is completely suppressed at pH ≥ 6. Also, the relative amount of the major product MoO_2 decreases with increasing pH.

The above results can be understood by considering the variation of the reducing power of borohydride with pH. It is known[6] that the extent of hydrolysis of borohydride to give hydrogen (eq 3) decreases with increasing pH. Therefore, the amount of MoO_2 decreases with increasing pH, and no reduction product is formed at a high enough pH of 11. The decreasing reducing power with increasing pH is also reflected in the

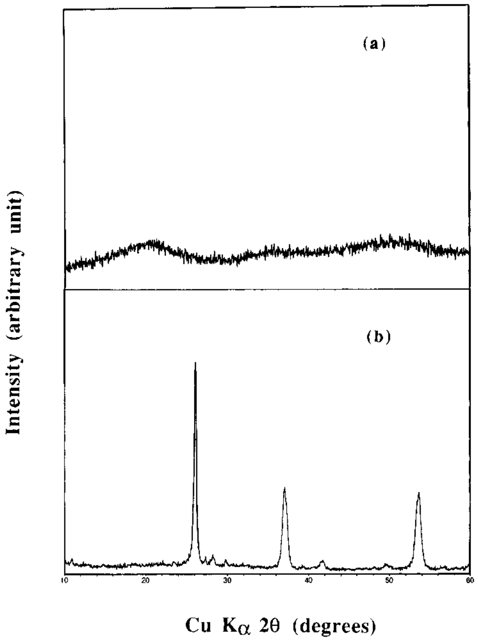

Figure 1. X-ray powder diffraction patterns of the product obtained by reducing 50 mL of 0.25 M K_2MoO_4 with 30 mL of 2.5 M KBH_4: (a) as-prepared sample and (b) after crystallization in DSC. The peaks in (b) refer to crystalline MoO_2.

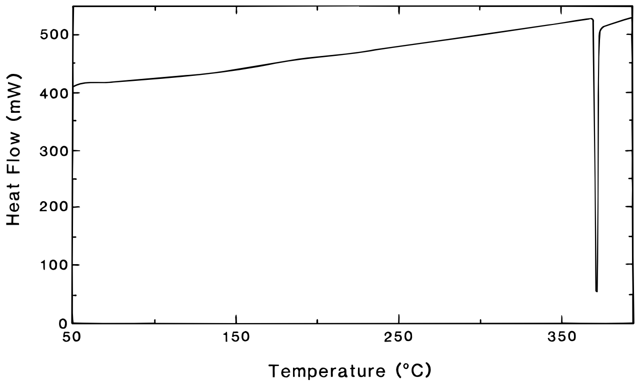

Figure 2. DSC plot recorded in a N_2 atmosphere with a heating rate of 10 °C/min for the as-prepared sample in Figure 1.

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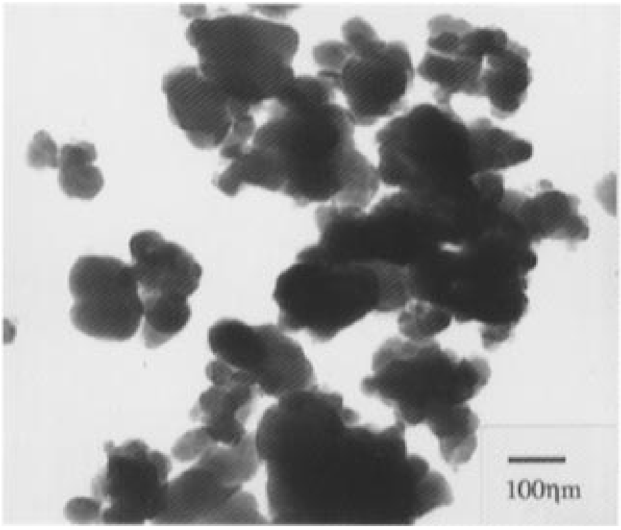

Figure 3. Transmission electron micrograph of the as-prepared sample obtained by reducing 50 mL of 0.25 M K_2MoO_4 with 250 mL of 2.5 M KBH_4 at pH = 4 (see Table 3).

Table 1. Reduction of 50 mL of 0.25 M K_2MoO_4 (12.5 mmol of K_2MoO_4) with 150 mL of 0.25 M KBH_4 (37.5 mmol of KBH_4) at Various pH Values

	% products formed[a]		
pH	$K_2Mo_3O_{10}$ (Mo^{6+})	$K_{0.3}MoO_3$ ($Mo^{5.7+}$)	MoO_2 (Mo^{4+})
1		13	87
4		17	83
6	17		83
8	20		80
11		no precipitate	

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

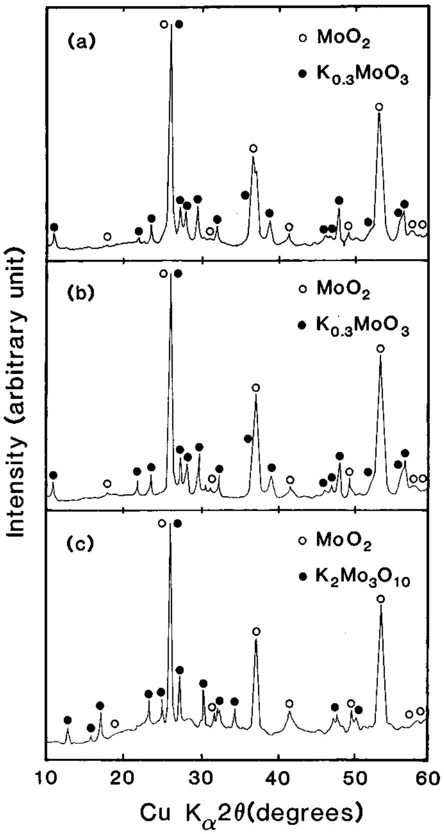

Figure 4. X-ray powder diffraction patterns recorded after crystallization in DSC of the products obtained with 50 mL of 0.25 M K_2MoO_4 and 150 mL of 0.25 M KBH_4 at various pH values: (a) pH = 1, (b) pH = 4, and (c) pH = 8.

Table 2. Reduction of 50 mL of 0.25 M K_2MoO_4 (12.5 mmol of K_2MoO_4) with 50 mL of 2.5 M KBH_4 (125 mmol of KBH_4) at Various pH Values

	% products formed[a]		
pH	$K_2Mo_3O_{10}$ (Mo^{6+})	$K_2Mo_2O_7$ (Mo^{6+})	MoO_2 (Mo^{4+})
1			100
4			100
7	7		93
11		9	91

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

suppression of the secondary reduction product $K_{0.3}MoO_3$ and an appearance of the unreduced phase $K_2Mo_3O_{10}$.

Influence of KBH_4 Concentration on the Reduction Products. In order to understand the influence of the concentration of borohydride, reduction experiments were also carried out at various pH values with a constant amount (50 mL) of a higher concentration (2.5 M) KBH_4. The results of the products obtained after crystallization in DSC are given in Table 2 and Figure 5. A higher reducing power arising from a 10-fold increase in the concentration of KBH_4 leads exclusively to the formation of the more reduced phase MoO_2 at pH $\leq$ 4 and eliminates completely the less reduced phase $K_{0.3}MoO_3$ compared to the results of Table 1 and Figure 4. The appearance of trace amounts of the unreduced phases $K_2Mo_3O_{10}$ and $K_2Mo_2O_7$ at pH $\geq$ 7 is a result of a decreasing reducing power with increasing pH. As the pH increases from 7, the unreduced phase changes from $K_2Mo_3O_{10}$ having a condensation of three MoO_4 units to $K_2Mo_2O_7$ having a condensation of two MoO_4 units. This is due to a progressively increasing condensation of MoO_4 units with decreasing pH.[3]

Influence of KBH_4 Amount on the Reduction Products. In order to understand the influence of the amount of KBH_4 on the products, reduction experiments were carried out at a constant pH with varying quantities of KBH_4 solution. The results obtained at pH = 4 with varying amounts of 0.25 M KBH_4 are given in Table 3. The product identification was carried out after crystallization in DSC as in the previous experiments. No precipitate is formed up to an addition of about 5 mL of KBH_4. At 5.3 mL of KBH_4, only the unreduced phase $K_2Mo_3O_{10}$ is formed in small quantity. As the amount of KBH_4 increases to about 15 mL, the reduced phases begin to form due to an increase in the reducing power. The amount of unreduced phase $K_2Mo_3O_{10}$ decreases with increasing KBH_4, and it vanishes completely at around 50 mL of KBH_4.

Although MoO_2 is the major reduction product as found in the data of Table 1, the secondary reduction products do reveal the effect of the KBH_4 amount. At lower amounts (30−125 mL) of KBH_4, the less reduced red bronze[10,11] $K_{0.26}MoO_3$ is formed along with MoO_2. In this volume range, the relative amount of the red bronze increases initially with increasing amount of KBH_4, reaches a maximum at about 50 mL, and then decreases. At about 150 mL of KBH_4, the red bronze vanishes completely and the slightly more reduced blue bronze $K_{0.30}MoO_3$ begins to form. The blue bronze prevails as a secondary phase throughout the volume range 150−750 mL. In this volume range, the relative amount of blue bronze increases initially with increasing amount of KBH_4, reaches a maximum at around 250 mL, and then decreases. When the amount of blue bronze

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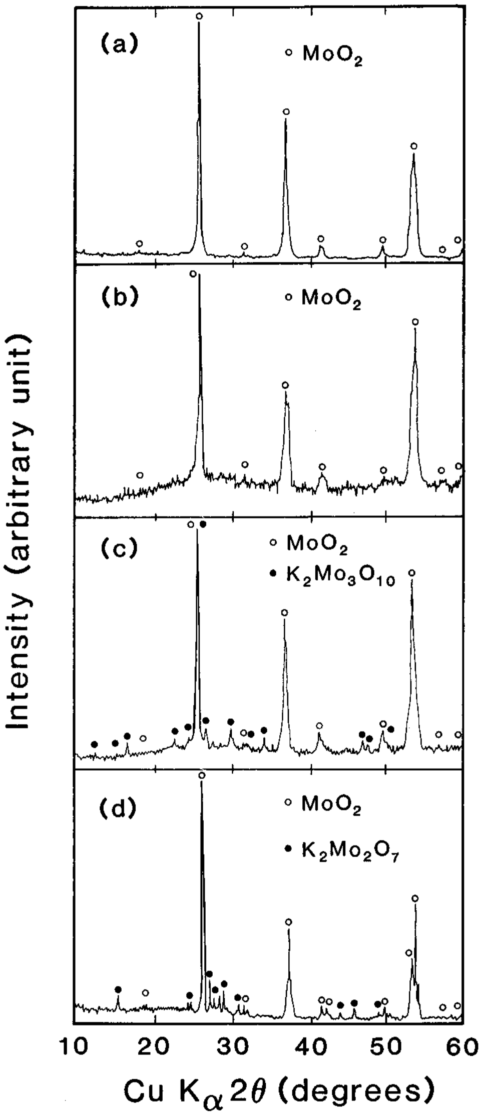

Figure 5. X-ray powder diffraction patterns recorded after crystallization in DSC of the products obtained with 50 mL of 0.25 M K_2MoO_4 and 50 mL of 2.5 M KBH_4 at various pH values: (a) pH = 1, (b) pH = 4, (c) pH = 7, and (d) pH = 11.

begins to decrease at around 300 mL, another relatively more reduced bronze[10,12] $K_{0.85}Mo_6O_{17}$ begins to form. $K_{0.85}Mo_6O_{17}$ is formed only for a narrow range (300 mL) of KBH_4 volume. Even at 300 mL of KBH_4, the relative amount of $K_{0.85}Mo_6O_{17}$ varies sensitively from one experiment to another. As the KBH_4 amount increases to 750 mL, the binary oxide Mo_4O_{11} is formed as the major reduction product with some MoO_2 and traces of the blue bronze as the secondary products. As the volume of KBH_4 increases further to 1000 mL, the more reduced binary oxide MoO_2 is formed exclusively as single-phase product.

The data of Table 3 clearly reveal that the reducing power increases with increasing amount of KBH_4, as indicated by a decreasing oxidation state of molybdenum in the secondary phase. However, a question arises as to why the more reduced MoO_2 is formed as a major phase at almost all volumes of KBH_4 in Table 3. We believe that it is partly because of the way in which the reductions are carried out. The addition of KBH_4 causes an instantaneous local reduction of some of the molybdate units to MoO_2. Furthermore, the filtrates obtained after filtering the precipitate were tested in all the experiments of Table 3 for unreduced molybdate ions by adding barium chloride solution; the unreduced molybdate ions are expected to combine with Ba^{2+} to give a white precipitate of $BaMoO_4$. It was found that no molybdate ions exist in the filtrate in all cases excepting the first experiment with 5.3 mL of KBH_4 in Table 3. This suggests that for KBH_4 volumes ≥ 15 mL, all the molybdenum is present in the precipitate either as all reduced phases or as a mixture of reduced and unreduced phases. Since the experiments are carried out by a slow addition of KBH_4 from a buret over several minutes, these results also suggest that the solid phases formed initially undergo changes in composition with increasing amount of KBH_4. That is, beyond about 15 mL of KBH_4, further reduction with increasing KBH_4 occurs mainly in the solid phase, but with a participation of K^+ ions in solution.

Experiments were also carried out with varying amounts of 2.5 M KBH_4 at pH = 4, and the results obtained after crystallization of the products in DSC are given in Table 4. Although MoO_2 is the major phase at all volumes, the secondary phases do again follow a systematic trend. The oxidation state of Mo in the secondary phase decreases with increasing reducing power resulting from an increasing borohydride amount. A 10-fold increase in KBH_4 concentration compared to that in Table 3 results in the exclusive formation of MoO_2 at a much lower volume (50 mL) of KBH_4.

Reduction reactions were carried out with varying amounts of both 0.25 and 2.5 M KBH_4 at pH = 1 also. The results obtained after crystallization in DSC are given in Tables 5 and 6. The data obtained with 0.25 M KBH_4 in Table 5 indicate that the amount of the secondary reduced phase $K_{0.3}MoO_3$ decreases and the amount of MoO_2 increases with increasing KBH_4 volume in the range 50−250 mL due to an increasing reducing power. However, comparison of the data with that obtained at pH = 4 in Table 3 reveals that for the same volume of KBH_4, the secondary phases are more reduced at pH = 1 than at pH = 4. For example, at 50 mL of KBH_4, the secondary reduced phase is the relatively more reduced $K_{0.3}MoO_3$ at pH = 1 and the relatively less reduced $K_{0.26}MoO_3$ at pH = 4. This difference is due to an increasing reducing power of KBH_4 with decreasing pH.

The data obtained with 2.5 M KBH_4 at pH = 1 in Table 6 reveal that the secondary reduced phase Mo_4O_{11} decreases with increasing KBH_4 and vanishes completely at 30 mL of KBH_4 due to an increasing reducing power. Also, no ternary phases containing potassium are formed at pH = 1 with 2.5 M KBH_4 compared to that at pH = 4 in Table 4; only binary oxides are formed at pH = 1. The differences between the data obtained at pH = 1 (Table 6) and pH = 4 (Table 4) can be understood by considering the nature of $(Mo_xO_y)^{n-}$ species existing at different pH values. It is known[3] that the MoO_4^{2-} units condense progressively with decreasing pH to give polyanions first and finally the neutral oxide MoO_3 (eq 2). For example, the polyanion paramolybdate $(Mo_7O_{24})^{6-}$ exists around pH = 4, and neutral MoO_3 begins to form close to pH = 1. Reduction of the polymolybdate $K_6Mo_7O_{24}$ in solution at pH = 4 facilitates the formation of the potassium molybdenum bronzes $K_{0.26}MoO_3$ or $K_{0.3}MoO_3$, while the reduction of the more condensed species containing little or no K at pH = 1 leads to an exclusive formation of the binary oxides without any potassium.

Influence of Methods of Mixing on the Reduction Products. Since MoO_2 is formed easily compared to other reduced products in all the experiments, changes in the method of mixing of K_2MoO_4 and KBH_4 were pursued. Two experiments were first carried out with 50 mL each of 0.25 M KBH_4 and 0.25 M K_2MoO_4. In both the experiments, the initial pH values of K_2MoO_4 and KBH_4 were maintained, respectively, at 4 and 11.

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Table 3. Reduction of 50 mL of 0.25 M K_2MoO_4 (12.5 mmol of K_2MoO_4) with Varying Amounts of 0.25 M KBH_4 at pH = 4

amount of KBH_4		% products formed[a]					
mL	mmol	$K_2Mo_3O_{10}$ (Mo^{6+})	$K_{0.26}MoO_3$ ($Mo^{5.74+}$)	$K_{0.3}MoO_3$ ($Mo^{5.7+}$)	$K_{0.85}Mo_6O_{17}$ ($Mo^{5.53+}$)	Mo_4O_{11} ($Mo^{5.5+}$)	MoO_2 (Mo^{4+})
5.3	1.33	100					
15	3.75	46					54
30	7.50	15	20				65
45	11.3	10	30				60
50	12.5		43				57
75	18.8		35				65
125	31.3		28				72
150	37.5			7			93
200	50.0			23			77
250	62.5			29			71
300	75.0			10	15		75
300	75.0			4	47		49
400	100			10			90
450	113			7			93
600	150			7			93
700	175			11			89
750	188			12		56	32
800	200		5				95
1000	250						100

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

Table 4. Reduction of 50 mL of 0.25 M K_2MoO_4 (12.5 mmol of K_2MoO_4) with Varying Amounts of 2.5 M KBH_4 at pH = 4

amount of KBH_4		% products formed[a]		
mL	mmol	$K_{0.26}MoO_3$ ($Mo^{5.74+}$)	$K_{0.3}MoO_3$ ($Mo^{5.7+}$)	MoO_2 (Mo^{4+})
10	25	26		74
20	50	34	22	44
30	75		35	65
50	125			100

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

Table 5. Reduction of 50 mL of 0.25 M K_2MoO_4 (12.5 mmol of K_2MoO_4) with Varying Amounts of 0.25 M KBH_4 at pH = 1

amount of KBH_4		% products formed[a]	
mL	mmol	$K_{0.3}MoO_3$ ($Mo^{5.7+}$)	MoO_2 (Mo^{4+})
50	12.5	26	74
100	25.0	16	84
150	37.5	13	87
250	62.5	9	91

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

Table 6. Reduction of 50 mL of 0.25 M K_2MoO_4 (12.5 mmol of K_2MoO_4) with Varying Amounts of 2.5 M KBH_4 at pH = 1

amount of KBH_4		% products formed[a]	
mL	mmol	Mo_4O_{11} ($Mo^{5.5+}$)	MoO_2 (Mo^{4+})
10	25.0	23	77
20	50.0	7	93
30	75.0		100
50	125		100

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

Table 7. Reduction of 50 mL of 0.25 M K_2MoO_4 (12.5 mmol of K_2MoO_4) by Adding at Once Varying Amounts of 0.25 M KBH_4

amount of KBH_4			% products formed[a]	
mL	mmol	final pH	$K_2Mo_3O_{10}$ (Mo^{6+})	MoO_2 (Mo^{4+})
10	2.5	6.0	40	60
20	5.0	7.9	23	77
50	12.5	8.5	17	83
100	25.0	8.5	23	77
200	50.0	8.5	13	87

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

Table 8. Reduction of 50 mL of 0.25 M K_2MoO_4 (12.5 mmol of K_2MoO_4) by Adding at Once Varying Amounts of 0.25 M KBH_4 Followed by Reducing the pH to 4

amount of KBH_4			% products formed[a]		
mL	mmol	final pH	$K_2Mo_3O_{10}$ (Mo^{6+})	$K_{0.26}MoO_3$ ($Mo^{5.74+}$)	MoO_2 (Mo^{4+})
75	18.8	4.0	22	24	54
150	37.5	4.0	21	28	51

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

In one experiment, the entire K_2MoO_4 solution was added at once to the KBH_4 solution and in the other experiment the K_2MoO_4 solution was added from a buret to the KBH_4 solution. In both experiments, the final pH was monitored to be 8.5. The filtrates in both cases contained unreduced molybdate ions, as indicated by the formation of white precipitate with barium chloride. This indicates an incomplete reduction of the molybdate ion due to a lower reducing power at a higher final pH of 8.5. The reaction product after crystallization in DSC was found to contain about 60% of the reduced phase MoO_2 and 40% of the unreduced phase $K_2Mo_3O_{10}$.

Further experiments were also carried out by adding at once 50 mL of 0.25 M K_2MoO_4 maintained at pH = 4 to varying amounts of 0.25 M KBH_4 maintained at pH = 12. The final reaction pH as well as the products obtained after crystallization in DSC is given in Table 7. The final pH increases from 6 to 8.5 on increasing the KBH_4 volume from 10 to 50 mL and remains constant at around 8.5 thereafter. The filtrates in all cases showed the presence of molybdate ions, indicating incomplete reduction. The reaction products were found to consist of both the reduced phase MoO_2 and the unreduced phase $K_2Mo_3O_{10}$ for all volumes of KBH_4. However, the amount of the unreduced phase decreases with increasing amount of KBH_4 due to an increasing reducing power.

Since the final pH rises invariably to about 8.5 in most of these experiments, a few further experiments were carried out in which the final pH after the addition of K_2MoO_4 was brought down to 4 by adding dilute HCl. The products obtained with 75 and 150 mL of KBH_4 after crystallization in DSC are given in Table 8. The results suggest that the lowering of pH leads to the formation of some red bronze $K_{0.26}MoO_3$ in addition to the already present MoO_2 and $K_2Mo_3O_{10}$.

Experiments were also carried out by adding at once 0.25 M KBH_4 solution maintained at pH = 12 to 0.25 M K_2MoO_4 solution maintained at pH = 4. With 150 mL of KBH_4 and 50 mL of K_2MoO_4, the final pH was found to be 8 and the filtrate consisted of unreduced molybdate. The reaction product after crystallization in DSC was found to consist of about 65% MoO_2 and 35% $K_2Mo_3O_{10}$. In an identical experiment, the final pH was lowered to 1 by adding dilute HCl. In this case, the product after heating in DSC to 500 °C was found to be single-phase MoO_2. This is due to an increasing reducing power with decreasing pH.

Conclusions

Reduction of aqueous K_2MoO_4 with aqueous KBH_4 has been investigated systematically at various pH values, concentrations, and amounts of the reactants. We arrive at the following conclusions:

1. The as-prepared samples are amorphous and crystallize at around 350−500 °C.

2. Lower valent molybdenum oxides such as MoO_2, Mo_4O_{11}, $K_{0.26}MoO_3$, $K_{0.3}MoO_3$, and $K_{0.85}Mo_6O_{17}$ are formed during the reduction process. $K_{0.26}MoO_3$ and $K_{0.3}MoO_3$ could previously be obtained only by electrochemical reduction under controlled conditions.

3. The nature of the products formed is strongly influenced by reaction pH, as well as the concentration and volume of KBH_4. For a given concentration and volume of KBH_4, the reducing power increases with decreasing pH. At a given pH, the reducing power increases with both increasing concentration and volume of KBH_4.

4. Only MoO_2 has been obtained as a single-phase product. All other reduced phases are formed as secondary phases with MoO_2 being present as the primary product. This difficulty seems to be due to an instantaneous local reduction of the molybdate ions to the more stable MoO_2. Also, the relative solubilities in aqueous solutions of other phases compared to MoO_2 may play a role. Our attempts of changing the method of additions or reaction conditions were unsuccessful in obtaining the other phases as single-phase products. Careful choice of other solvents instead of water might help in this respect, and such experiments are currently being pursued.

5. The technique offers amorphous products with high surface area, which are particularly attractive for catalysis and battery electrodes. For example, the amorphous MoO_2 obtained is currently being pursued as an anode material for lithium batteries.

6. Although borohydrides have been well exploited over the years by organic chemists, they remained to be explored for the synthesis of inorganic materials. This study demonstrates the potential use of borohydrides in inorganic materials synthesis. Similar synthesis approaches are currently in progress in our laboratory with other transition metals.

Acknowledgment. Financial support by the National Science Foundation Grant No. DMR-9401999 and the Welch Foundation Grant No. F-1254 is gratefully acknowledged.

IC950955W