

## New Route to Reduced Transition-Metal Oxides

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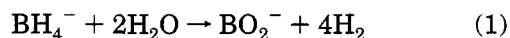
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Conventional solid-state syntheses involve reaction between the components at elevated temperatures with repeated grindings in order to overcome the diffusional limitations. Such a "brute force" approach not only results in larger particle size but also leads to an inaccessibility of metastable phases and unusual valence states. This recognition has created enormous interest among the solid-state community to design and develop synthetic routes that can bring down the reaction temperatures.<sup>1</sup> Low-temperature preparative techniques such as sol-gel processing,<sup>2</sup> design of molecular precursors,<sup>3</sup> coprecipitation,<sup>4</sup> chemical and electrochemical lithium insertion/extraction,<sup>5</sup> electrochemical oxygen insertion,<sup>6</sup> molten flux reactions,<sup>7</sup> and ion-exchange reactions<sup>8</sup> have attracted much attention in the synthesis of simple and complex inorganic materials. An intimate or atomic scale mixing of the components or the availability of the structural framework in these techniques lowers the processing temperatures and provides kinetic accessibility to metastable phases and unusual valence states. We present here a novel approach to obtain reduced transition-metal oxides in aqueous solutions using borohydrides as reducing agents.

Alkali-metal borohydrides such as NaBH<sub>4</sub> were recognized as effective reducing agents in aqueous solutions first by Brown's group.<sup>9</sup> The borohydride ion hydrolyzes in aqueous solution as



to give hydrogen, which is facilitated by acidic condition and by transition-metal ions such as Co<sup>2+</sup>, Fe<sup>2+</sup>, or Ni<sup>2+</sup>. The reaction of these metal ions with aqueous borohydride gives finely divided black precipitates of metals or metal borides, which seem to catalyze the hydrolysis reaction. Borohydrides have since then been used extensively for the generation of metallic catalysts in organic syntheses.<sup>10</sup> They have also gained enhanced interest recently to generate amorphous or ultrafine,

nanophase magnetic particles of Fe, Co, or Ni.<sup>11</sup> The chemistry of borohydride reduction, however, seems to be quite complex and the nature of the products depends sensitively on the reaction conditions. Recent careful investigations<sup>12</sup> show that a rapid mixing of the reagents yields metallic particles under aerobic conditions and metal borides under anaerobic conditions. The results obtained in aqueous<sup>13</sup> and nonaqueous<sup>14</sup> solutions have also helped to understand the reaction steps and the factors that influence the process.

Quite recently, Murphy et al.<sup>15</sup> have utilized borohydrides for the synthesis of metal hydrides. We have been utilizing borohydrides during the past year to obtain reduced transition-metal oxides.<sup>16</sup> We showed that borohydrides can be used to obtain tungsten oxide bronzes in aqueous solutions. We show in this communication that borohydrides are much more versatile and can be used to obtain binary reduced oxides of vanadium, molybdenum or tungsten as well as the ternary bronzes.

Vanadates, molybdates and tungstates form tetrahedral oxoions (MO<sub>4</sub>)<sup>n-</sup> (M = V, Mo, or W) in aqueous solutions. These oxoions condense progressively with decreasing pH to give complex polyions, and the final product of condensation at lower pH is the binary oxides WO<sub>3</sub>, MoO<sub>3</sub>, or V<sub>2</sub>O<sub>5</sub>.<sup>17</sup> Interestingly, addition of aqueous alkali-metal borohydrides to aqueous solutions of alkali metal vanadates, molybdates, or tungstates in air results in an instantaneous color change due to the reduction of the transition-metal ions. Continued addition of borohydrides from a burette while maintaining the pH constant at a given value by adding dilute HCl or NaOH results in the formation of deeply colored sols or precipitates. Whether or not a precipitate (or gel) is obtained at the end of borohydride addition depends on the reaction pH as well as the concentration and amount of the reagents. Through a series of experiments we have identified the conditions to obtain the binary oxides and the bronzes. The concentrations and amounts of the metalate (vanadate, molybdate, and tungstate) and borohydride solutions and the pH to obtain different products are summarized in Table 1.

The dark precipitates (or gel) formed at the end of borohydride addition were allowed to settle for a few hours, filtered or centrifuged, washed with distilled water, and dried. These as prepared products are amorphous as indicated by the absence of any peaks in the X-ray diffraction patterns. For example, the X-ray diffraction pattern of the as prepared sample of MoO<sub>2</sub>

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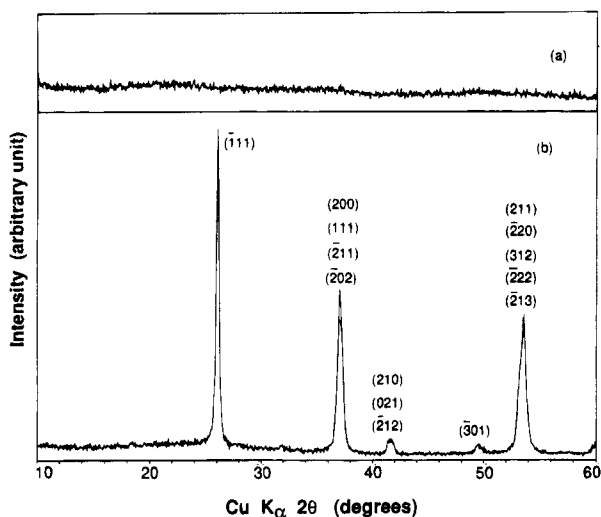
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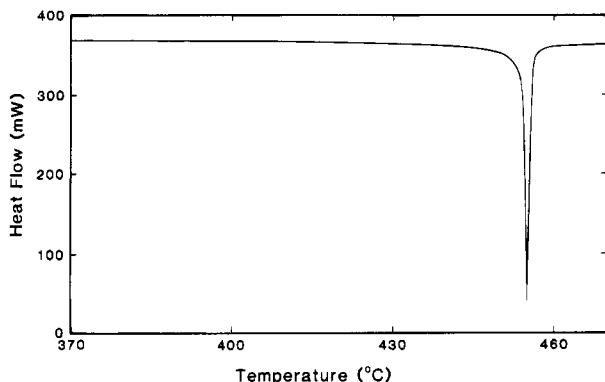
**Table 1. Reduced Transition Metal Oxides Obtained by Borohydride Reduction**

metalate <sup>a</sup>		borohydride		pH	cryst temp (°C) <sup>b</sup>	phase identification
concn	vol (mL)	concn	vol (mL)			
0.25 M Na <sub>2</sub> MoO <sub>4</sub>	50	2.6 M NaBH <sub>4</sub>	50	1	375	MoO <sub>2</sub>
0.25 M Na <sub>2</sub> MoO <sub>4</sub>	100	0.25 M NaBH <sub>4</sub>	15	4	340	Na <sub>0.88</sub> Mo <sub>6</sub> O <sub>17</sub> (with traces of MoO <sub>2</sub> )
0.25 M Na <sub>2</sub> WO <sub>4</sub>	50	2.6 M NaBH <sub>4</sub>	50	1	450	WO <sub>2</sub> (with about 20% W <sub>18</sub> O <sub>49</sub> )
0.25 M Na <sub>2</sub> WO <sub>4</sub>	200	0.25 M NaBH <sub>4</sub>	200	6.5	440	Na <sub>0.55</sub> WO <sub>3</sub>
0.25 M K <sub>3</sub> VO <sub>4</sub> <sup>c</sup>	50	2.2 M KBH <sub>4</sub>	50	2.5	400	VO <sub>2</sub> (with traces of unknown impurity)

<sup>a</sup> Refers to vanadate, molybdate, and tungstate. <sup>b</sup> Obtained from DSC plot. <sup>c</sup> Prepared by dissolving required amount of V<sub>2</sub>O<sub>5</sub> in aqueous KOH solution.



**Figure 1.** X-ray powder diffraction patterns of MoO<sub>2</sub>: (a) as-prepared amorphous sample; (b) after heating the as-prepared sample in N<sub>2</sub> atm in DSC up to 470 °C at a heating rate of 10 °C/min.



**Figure 2.** DSC curve of the amorphous MoO<sub>2</sub> recorded in N<sub>2</sub> atm with a heating rate of 10 °C/min and a sample weight of 15 mg.

is shown in Figure 1a. These amorphous products crystallize at around 300–500 °C in inert atmospheres to give crystalline products. The differential scanning calorimeter (DSC) plot recorded in N<sub>2</sub> atmosphere with a Perkin-Elmer Series 7 thermal analysis system is shown in Figure 2 for MoO<sub>2</sub>; the sharp exotherm observed at 455 °C corresponds to crystallization. The room-temperature X-ray diffraction pattern of the crystallized product is shown in Figure 1b. All the reflections correspond to MoO<sub>2</sub> indicating the single-phase nature of the product.

Unlike the tungsten oxide bronzes, Na<sub>x</sub>WO<sub>3</sub>, that are formed for a wide range of *x* with structures consisting of cornered shared WO<sub>6</sub> octahedra, the molybdenum oxide bronzes prepared at ambient pressures have complex structures, but with specific stoichiometry.<sup>18</sup> For example, Na<sub>0.88</sub>Mo<sub>6</sub>O<sub>17</sub> is the stable phase in the sodium molybdenum oxide bronze system under ambi-

ent-pressure conditions. Therefore, any precipitate (or gel) composition Na<sub>x</sub>Mo<sub>y</sub>O<sub>z</sub> obtained by borohydride reduction disproportionates to the stable bronze Na<sub>0.88</sub>Mo<sub>6</sub>O<sub>17</sub> and MoO<sub>2</sub> during crystallization. Nevertheless, we have optimized the experimental conditions to obtain nearly pure Na<sub>0.88</sub>Mo<sub>6</sub>O<sub>17</sub> as given in Table 1. At pH < 2, single-phase MoO<sub>2</sub> is readily obtained. At pH > 2, the bronze Na<sub>0.88</sub>Mo<sub>6</sub>O<sub>17</sub> begins to form. Nearly single-phase bronze Na<sub>0.88</sub>Mo<sub>6</sub>O<sub>17</sub> (with about 5% MoO<sub>2</sub> impurity phase) could be obtained only over a narrow range of conditions. Attempts to suppress MoO<sub>2</sub> impurity (i) by lowering the amount of borohydride results in an absence of gel or precipitate formation and (ii) by raising the pH results in the formation of Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> impurity.

Tungsten oxide bronzes, Na<sub>x</sub>WO<sub>3</sub>, are readily obtained as single-phase products at pH ≈ 6.5. Comparison of the lattice parameters with the literature data<sup>18</sup> yields an *x* = 0.55 for the bronze obtained at pH = 6.5. We believe Na<sub>x</sub>WO<sub>3</sub> can be obtained for a range of *x* values by altering the pH and the reagent concentrations and quantities. The formation of WO<sub>2</sub> seems to require stronger reducing conditions than that for MoO<sub>2</sub>. The product obtained at lower pH ≈ 1 after crystallization shows diffraction peaks corresponding to WO<sub>2</sub> with about 20% impurity peaks (Table 1). The impurity reflections appear to correspond to the less reduced phase W<sub>18</sub>O<sub>49</sub>. Further lowering of pH often results in the formation of WO<sub>3</sub> before the borohydride is added and so does not help to suppress the impurity phases.

Although vanadates are reduced readily by borohydrides, no precipitate (or gel) formation occurs at lower pH < 2.4. At pH > 3, the reducing power is low to obtain VO<sub>2</sub>. This makes the VO<sub>2</sub> formation to occur only over a narrow range of pH ≈ 2.5 (Table 1). Characterization of the products formed at pH > 3 is currently in progress.

In summary, we have shown that borohydrides can be used effectively to obtain a range of reduced transition metal oxides in aqueous solutions. The nature and composition of the products depend strongly on the pH and the concentration and quantity of the reactants. An exploration of this technique in the presence of other cations may lead to a formation of other ternary oxides in solution. The procedure generates amorphous products with high surface area, which may be of interest to catalysis, battery electrodes, and electrochromism. The technique also has a potential to generate metastable or new phases at low temperatures.

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