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Borohydride Reductions of Metal Ions. A New Understanding of the Chemistry Leading to Nanoscale Particles of Metals, Borides, and Metal Borates

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The reduction of $CoCl_2$(aq) with $NaBH_4$ yields ultrafine particles of Co_2B as the primary product if the two reagents are rapidly mixed and the product is handled under argon. However, the Co_2B is converted to Co(s) particles plus boron oxides if exposed to oxygen (sacrificial reaction where boron is oxidized while cobalt is reduced). Still a third product, $Co(BO_2)_2$, can be formed if time is allowed for the Co^{2+}/Co_2B catalysis of the aqueous $BH_4^- \rightarrow BO_2^-$(aq) oxidation to occur before the major part of the $CoCl_2$(aq) is added. The $Co(BO_2)_2$ is converted to $Co_3(BO_3)_2$ and small amounts of Co on heat processing at 500 °C.

During the years of the Manhattan project it was discovered that sodium borohydride was an effective reducing agent for metal ions, yielding either particles of metal borides or zero-valent metals. Schlesinger, Brown, and co-workers,[1] reporting on this work in the 1950s, observed the formation of Co_2B from the reaction of $NaBH_4$ and $CoCl_2$ in aqueous solution, utilizing anaerobic conditions for product workup.[1] In later years, Brown and co-workers pointed out that such chemistry is quite complex, partly due to the fact that metal ions (or the product metal/metal boride particles) serve as catalysts for BH_4^- oxidation by water[2]

$$BH_4^- + 2H_2O \xrightarrow{\text{cat.}} BO_2^- + 4H_2 \qquad (1)$$

Over the last 30 years, BH_4^- reduction of metal ions has been used extensively for the formation of metallic particles and is perhaps the most widely used of the four general methods of producing such ultrafine materials.[3-6] In recent years it has taken on additional importance due to enhanced interest in nanoscale magnetic particles.[7-9]

The recipes used for aqueous BH_4^- reductions of metal ions are so varied that it is startling. Almost any change in procedure can make a difference. Concentrations, BH_4^-/M ion ratio, pH, method of mixing, and rate of mixing can determine particle size and reactivity and can even change the product identity. It becomes clear that better understanding is needed of this important chemistry.

We have studied in some detail the reduction of Co^{2+} by aqueous BH_4^- and have learned that simply through mixing procedures and product handling we can control whether the final product is Co, Co_2B, or $Co(BO_2)_2$.

The primary product of rapidly adding and mixing (~45 s) 0.01 M $CoCl_2$(aq) with solid $NaBH_4$ ($Co^{2+}:BH_4^-$ = 1:2) is a precipitate of ultrafine, almost amorphous Co_2B. The approximate stoichiometry is shown in reaction 2[10-12] and

$$2CoCl_2 + 4NaBH_4 + 9H_2O \xrightarrow{H_2O} Co_2B + 4NaCl + 12.5H_2 + 3B(OH)_3 \qquad (2)$$

the powder X-ray diffraction pattern is shown in Figure 1. It is important to point out that the isolation of Co_2B and subsequent heat treatments must be carried out under anaerobic conditions.[11] Indeed, the only method of obtaining pure Co_2B particles regardless of the starting ratio of $Co^{2+}:BH_4^-$, is by the rapid mixing/anaerobic handling procedure.

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(1) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E.; Gilbreath, J. R.; Hockstrue, H. R.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 215.

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(6) Metal vapor methods: Klabunde, K. J.; Murdock, T. O. *J. Org. Chem.* **1979**, *44*, 3901. Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic Press: New York, 1980. Davis, S. C.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153. Kernizan, C.; Klabunde, K. J.; Sorensen, C. M.; Hadjapanayis, G. *Chem. Mater.* **1990**, *2*, 70.

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(9) Corrias, A.; Ennas, G.; Licheri, G.; Marongiu, G.; Paschina, *Chem. Mater.* **1990**, *2*, 363.

(10) Generation of Co_2B particles: In a typical reaction, a round-bottom flask (1000 mL) equipped with two side-arms (designed to allow solutions to be added to the vessel in vacuo) and a third outlet adapted for direct connection to a vacuum line was charged with $NaBH_4$ (0.15 g, 4.0 mmol) in an inert atmosphere box. The reaction vessel was then connected to a vacuum line equipped with a mercury manometer and evacuated to a constant pressure (~10^{-3} Torr). The outlet to the diffusion pump was then closed leaving the setup under static pressure. A 200-mL solution of $CoCl_2{\cdot}6H_2O$ (0.01 M, 2.0 mmol) prepared using distilled water purged with Ar was added to the reaction vessel via the side arms at ambient temperature over a period of 45 s. Rapid gas evolution which ceased within 2 min was apparent. The resulting black suspension was filtered and washed with prepurged H_2O and acetone using standard inert atmosphere and Schlenk techniques.[11] The filter frit was transferred into an inert atmosphere box where 0.12 g of the black, amorphous, pyrophoric powder was collected. Elemental analysis of the crude, dry powder yielded the following. Found: Co, 84.18; B, 7.92; Co/B ratio, 1.95. Calcd for Co_2B: Co, 91.6; B, 8.40. After heat treatment at 500 °C under argon. Found: Co, 94.25; B, 8.50; Co/B ratio = 2.03. Hydrogen evolved for reaction 2 was 14 mmol; expected = 12.5 mmol. Although, the analysis of the crude and heat processed powders show a Co/B ratio of 2, the sum of Co and B in the crude powder does not add up to 100%. It has been noted by Wang and Bartholomew[12] that metal boride prepared from $NaBH_4$ contains significant Na impurities.

(11) (a) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986. (b) Herzog, S.; Dehnert, J.; Luhder, K. *Technique of Inorganic Chemistry*; Johnassen, H. B., Ed.; Interscience: New York, 1969; Vol. VII.

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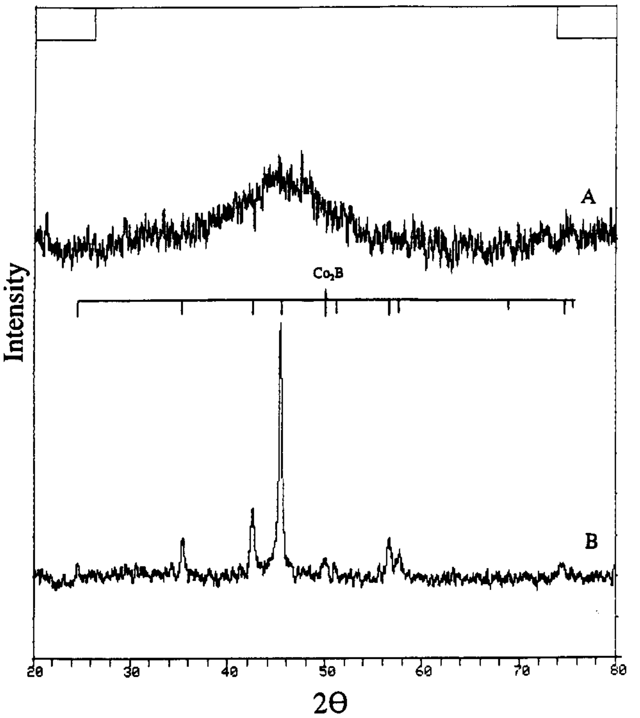


Figure 1. Powder X-ray diffraction pattern of Co_2B formed and precipitated by the reaction of 0.01 M $CoCl_2(aq)$ with solid $NaBH_4$ with rapid stirring. Addition time was 45 s. The product was handled under argon and protected with Nujol before XRD analysis: (a) as received; (b) after heat treatment at 500 °C for 120 min under argon.

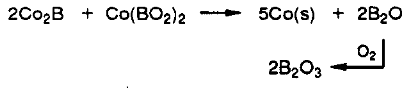
In contrast, Co metal is somewhat easier to obtain. The first way is by working up the product of the reaction discussed above under aerobic conditions. In this way a sacrificial reaction takes place where the initial product, fine Co_2B, is converted to cobalt metal (Figure 2) and boron oxides, probably as shown in eq 3

$$4Co_2B + 3O_2 \rightarrow 8Co(s) + 2B_2O_3 \qquad (3)$$

$$B_2O_3 + 3H_2O \rightarrow 2B(OH)_3$$

Water can be used to convert the B_2O_3 to boric acid, which can be separated by water washing.[13]

Interestingly, cobalt metal particles can also be obtained by adding about 10% of the $CoCl_2(aq)$ solution to the $NaBH_4$ and allowing about 8 min to elapse before adding the remainder of the solution.[14] In this way a small amount of Co_2B is formed that serves to catalyze eq 1 and form a significant amount of BO_2^-. This procedure yields a solid product that is a mixture of Co_2B and $Co(BO_2)_2$. Upon heating at 500 °C under Ar a solid–solid reaction occurs such as in eq 4, again yielding cobalt metal and


(4)

$$2Co_2B + Co(BO_2)_2 \longrightarrow 5Co(s) + 2B_2O_x \xrightarrow{O_2} 2B_2O_3 \qquad (4)$$

B_2O_3 (that can be separated with water washing). Indeed, the reaction of pure, ultrafine Co_2B and a pure sample of $NaBO_2$, at 500 °C, carried out as a control, yielded metallic cobalt

$$Co_2B + NaBO_2{\cdot}3H_2O \xrightarrow[2\,h]{500\,°C} 2Co(s) + B_2O_x \xrightarrow{O_2,\,H_2O} 2B(OH_3) + NaOH + xH_2O$$

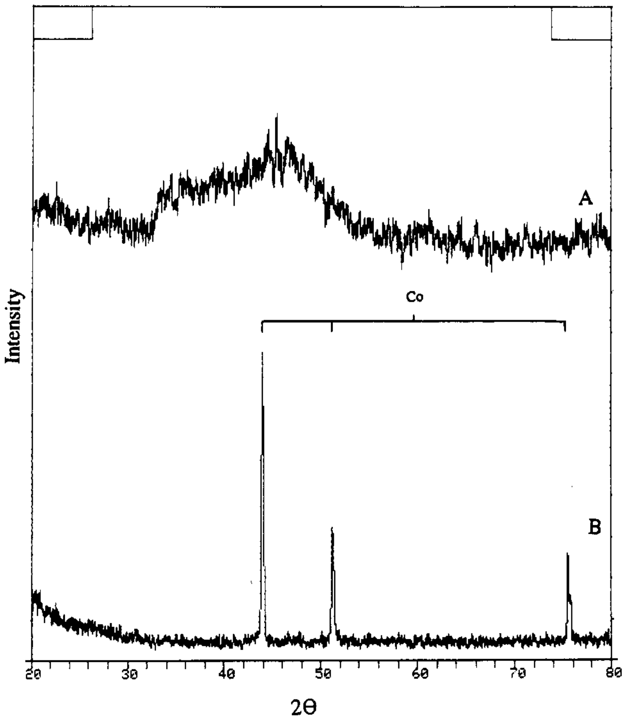
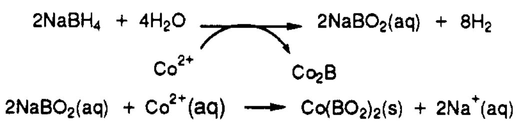


Figure 2. Powder X-ray diffraction pattern of Co metal particles formed by the controlled oxidation of ultrafine Co_2B followed by water wash: (a) as received; (b) after heat treatment at 500 °C for 120 min under argon.

Finally, a third product, $Co(BO_2)_2$, can be prepared by allowing a longer period (~15 min) of catalysis



$$2NaBH_4 + 4H_2O \xrightarrow[Co^{2+} \rightarrow Co_2B]{} 2NaBO_2(aq) + 8H_2$$

$$2NaBO_2(aq) + Co^{2+}(aq) \longrightarrow Co(BO_2)_2(s) + 2Na^+(aq)$$

Upon heat treatment of this precipitate, another solid state chemical reaction occurs, yielding $Co_3(BO_3)_2$ (eq 5 and Figure 3)

$$3Co(BO_2)_2 \rightarrow Co_3(BO_3)_2 + 2B_2O_3 \qquad (5)$$

Further information about these solid-state reactions has been gained through differential scanning calorimetry (Figure 4). For the sample that yielded Co_2B particles (eq 2), Figure 4A shows a single strong exotherm about 520 °C that can be assigned to Co_2B crystallization. We note that this could not correspond to a reaction of CoB with Co to yield Co_2B, since this should be an endothermic process.[15] In comparison, line B, which represents a sample from which metallic Co is obtained as a result of reaction between Co_2B and $Co(BO_2)_2{\cdot}xH_2O$, shows an endotherm at ~350 °C and two exotherms at ~490 and 550 °C. The endotherm corresponds to the loss of water of

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(13) Solubilities of products of reactions: $B(OH)_3$ (6.35 g/100 mL H_2O), B_2O_3 (slightly soluble), NaCl (35.7 g/100 mL H_2O), CoB (decomposes in H_2O) (*Handbook of Chemistry and Physics*, 66th ed.; CRD Press: Boca Raton, FL, 1985). $Co(BO_2)_2$ (0.02 g/100 mL H_2O), $Co_3(BO_3)_2$ (0.02 g/100 mL H_2O), Co_2B and Co fine powders are insoluble (based on work from our laboratory).

(14) The reaction vessel was charged with $NaBH_4$ (0.15 g, 4.0 mmol) as described in ref 10. The 200-mL $CoCl_2{\cdot}6H_2O$ (0.01 M, 2.0 mmol) solution was added in two portions of 20 and 180 mL with a time interval of 8 min. The suspension obtained was processed as described in footnote 10.

(15) Sato, S.; Kleppa, O. J. *Metall. Trans. B* **1982**, *13B*, 251.

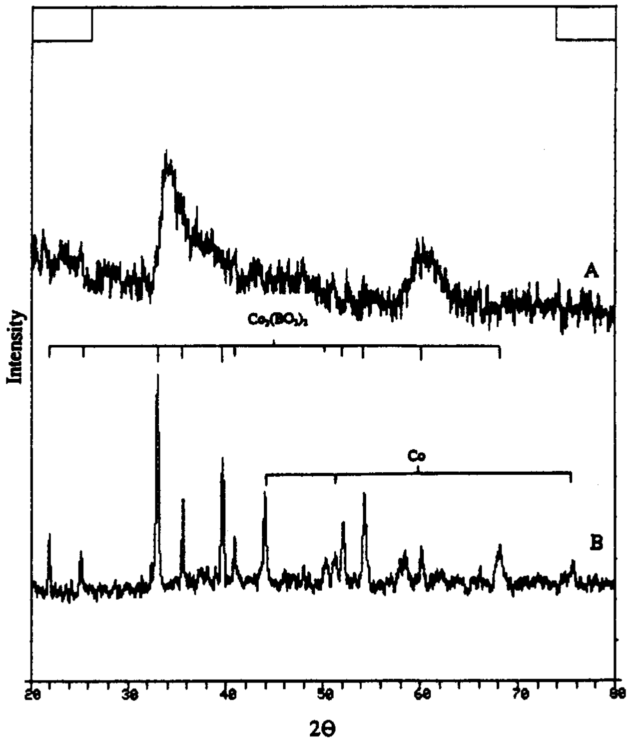

Figure 3. Powder X-ray diffraction pattern of $Co(BO_2)_2$ formed by the reaction of 0.01 M $CoCl_2$(aq) with solid $NaBH_4$ but with time allowed (15 min) for the $BH_4^- \rightarrow BO_2^-$ catalyzed oxidation to occur before addition of the major part of the $CoCl_2$ solution: (a) as received; (b) after heat treatment and conversion to $Co_3(BO_3)_2$.

crystallization from $Co(BO_2)_2 \cdot xH_2O$.[16] The two exotherms at 490 and 550 °C represent the heat of reaction and crystallization of metallic Co. A similar and more dominate endothermic transition is observed in line C, which was obtained on samples which were predominately $Co(BO_2)_2 \cdot xH_2O$. Line C corresponds to the $Co(BO_2)_2$ sample converting to $Co_3(BO_3)_2$ (eq 5) through a slow endothermic process.

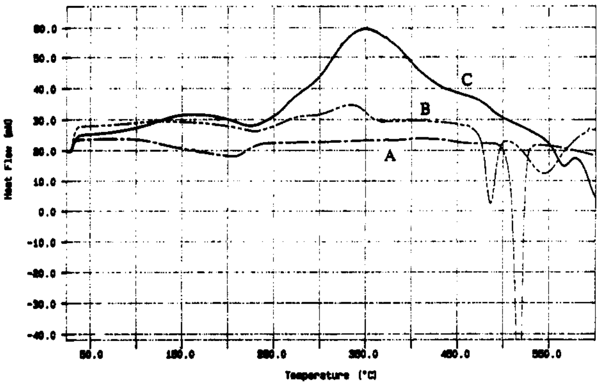

Figure 4. Differential scanning calorimetry of the Co_2B (A), Co (B), and $Co(BO_2)_2$ (C) fine powders.

To our knowledge, this is the first time that this complex redox chemistry has been manipulated and controlled in this manner. These results help clarify why borohydride reduction of metal ions is so sensitive to the exact experimental procedure used. Further details will be reported later.

Acknowledgment. The support of the National Science Foundation through the Materials Chemistry initiative is acknowledged with gratitude.

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[16] Kesans, A. *Synthesis of Borates in Aqueous Solution and Their Investigation*; Akad. Nauk Latv. SSR: Riga, 1955.