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Sodium Borohydride Reduction of Cobalt Ions in Nonaqueous Media. Formation of Ultrafine Particles (Nanoscale) of Cobalt Metal

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The reduction of $CoBr_2$ with $NaBH_4$ in diglyme solution has been studied as a method of preparing ultrafine Co particles. The primary proucts are Co, H_2, and B_2H_6. However, in the presence of the catalytic cobalt particles, B_2H_6 is decomposed to boron and H_2. These results are quite different from aqueous reductions of CoX_2 with $NaBH_4$, where Co_2B is the primary product (in the form of ultrafine particles).

Introduction

The reduction of transition metal ions by BH_4^- is a ubiquitous reaction that is useful for the production of ultrafine particles of metals and metal borides.[2-4] Unfortunately the chemical details of this process are not well understood. Change in reaction conditions or mixing procedures can lead to different products, variable yields, and many complications that are not understood.

As the need to find reproducible ways to produce ultrafine materials increases (for use in magnets, electronics, catalysts, etc.), it becomes necessary to gain a better understanding of this unique reduction chemistry.

In recent reports[5,6] we have described the chemical reactions and steps occurring during the BH_4^- reduction of Co^{2+} in aqueous solution. A reaction scheme was presented detailing the key role played by water in the formation of the two primary products, ultrafine particles of Co_2B or $Co(BO_2)_2$. It was determined that Co metal particles were only formed by sacrificial oxidation of the primary product Co_2B and thus is a secondary product.

In our continuing effort to understand the chemistry and mechanisms of reduction processes leading to ultrafine magnetic particles, we undertook an examination of the reduction of Co^{2+} in nonaqueous solution. As expected, the results showed that the chemistry is very different from that in aqueous media, and the primary product is Co metal when the reduction is carried out in diglyme $[CH_3O(CH_2CH_2O)_2CH_3]$.

Experimental Section

General Procedures. Reactions were carried out in a 1-L 3-necked round-bottom flask attached to a vacuum line of known volume and equipped with a mercury manometer (unless otherwise described). The flask had two side arms arranged so that liquid could be added to the vessel in vacuo. Products were isolated and dried using standard inert-atmosphere and Schlenk techniques[7] unless otherwise stated. Diglyme $[CH_3O(CH_2CH_2O)_2CH_3]$ was distilled under argon from sodium metal. Distilled water and acetone were purged with argon for several hours prior to use. Total amounts of gas evolved during a reaction were determined by pressure changes in a known volume. The % H_2 in the gas was determined by GC using a powdered molecular sieve column at ambient temperature. Heat treatment of samples was carried out in a quartz tube (wrapped with heating tape) under argon. Generally, samples were brought to the desired temperature within 2–5 min, held there for 2 h, and cooled to room temperature in 5–10 min.

X-ray powder diffraction data were collected on a SCINTAG 2000 machine with Kα Ni filtered radiation. Pyrophoric samples were protected with mineral oil (Nujol) prior to powder diffraction studies. Mass spectroscopic measurements were carried out on a Finnigan 4021C quadrupole instrument.

Reaction of $CoBr_2$ and $NaBH_4$ in Diglyme. One Schlenk tube was charged with anhydrous $CoBr_2$ (0.42 g, 1.9 mmol), and another with $NaBH_4$ (0.15 g, 4.0 mmol). Each tube was then charged with 50 mL of purified diglyme and magnetically stirred to dissolve the solid reagents. A round-bottom flask (1 L) equipped as described under General Procedures was connected to the vacuum line and evacuated to 10^{-3} Torr. The flask was isolated from the pump, and then two 60-mL syringes were used to simultaneously transfer the diglyme solutions to the flask over a 45-s period at room temperature with stirring. The initially blue $CoBr_2$–diglyme solution reacted instantaneously with the colorless $NaBH_4$–diglyme solution to yield a pink liquid and white precipitate. A black solid then began to precipitate slowly with steady gas evolution over 15 min. Gas evolution ceased after 60 min, and the resulting black suspension was filtered through a fine glass frit under argon and then washed with three 20-mL portions of deoxygenated water (to remove NaBr and boron in the form of $B(OH)_3$) followed by two 20-mL portions of deoxygenated acetone. The residue was dried in vacuo. The filter frit with its filter cake was transferred into an inert-atmosphere box where 0.11 g of black pyrophoric Co powder (97% yield) was obtained. The total amount of gas evolved was 9.4 mmol with H_2 making up 8.0 mmol of this total (the remainder of the gas was B_2H_6 and diglyme vapor as determined by mass spectrometric studies). The water/acetone washings were dried, and the white solid obtained was shown to be NaBr mixed with small amounts of $B(OH)_3$ by X-ray powder diffraction.

If the product from the above reaction was filtered out, washed, and dried under ambient conditions, a green-black powder (0.18 g, air stable) was obtained.

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Table I. Behavior of the $(Diglyme)_nCo(BH_4)_2$ Intermediate in the Presence of H_2O

vol of H_2O, mL	$NaBH_4/CoBr_2$ ratio[a]	gas evolved, mmol[b]	H_2 evolved, mmol[c]
0	8	4.4	4.0 (16)
1	2	13	12 (8)
10	8	54	54 (32)
100	8	60	62 (32)

[a] Total mmol of $NaBH_4$:total mmol of $CoBr_2$: No H_2O, 8:1; 1 mL of H_2O, 4:2; 10 mL of H_2O, 16:2; 100 mL of H_2O, 16:2. [b] Mass spectroscopy studies on gases obtained from all samples indicated the presence of B_2H_6 and diglyme. [c] Numbers in parentheses indicate amount of H_2 expected if each BH_4^- was used specifically for Co^{2+} reduction and yielded 2 mol of H_2.

Table II. Behavior of $CoBr_2$ and $NaBH_4$ Reaction in the Presence of H_2O[a]

H_2O added, mmol[b]	H_2O/Co^{2+} ratio	gas evolved, mmol	weight of product, mg
0	0	9.6	108
2	1	9.9	109
8	4	11.0	119
64	32	13.5	111
2048	1024	15.5	114
6111	3056		115
3333[c]	1667	15.8	102
6666[d]	3333	15.3	
11111[e]	5556	14.8	119

[a] 2.0 total mmol of $CoBr_2$ in diglyme reacted with 4.0 total mmol of $NaBH_4$ in diglyme. [b] Appropriate volume of H_2O added to the 50-mL diglyme solution of $CoBr_2$. [c] A 50-mL H_2O solution of $CoBr_2$ was allowed to react with a 50-mL diglyme solution of $NaBH_4$. [d] A $CoBr_2$ solution containing 100 mL of H_2O and 12 mL of diglyme was treated with the 25-mL diglyme solution of $NaBH_4$. [e] Reaction carried out in H_2O.

Generation of $(Diglyme)_nCo(BH_4)_2$ at Low Temperature Followed by Reaction with Water. Diglyme solutions of $CoBr_2$ (0.40 g, 1.8 mmol) and $NaBH_4$ (0.15 g, 4.0 mmol) were prepared as described above. The 1-L flask described above was charged with a magnetic stirring bar, evacuated, and cooled to −78 °C with a dry ice–acetone bath. The diglyme solutions were syringed in simultaneously with rapid stirring. The resulting pink solution was allowed to slowly warm while gas evolution and temperature were monitored. After being warmed over a period of 80 min to −20 °C, the solution was still pink with a white precipitate. At this point 1.0 mL of water (55.6 mmol) was syringed in. Immediately a black precipitate began to form and steady gas evolution commenced. Within 2–3 min a black suspension was obtained. The black solid was isolated as described above yielding Co (0.08 g, 74%), and the gas analyzed as described above (13 mmol total, 12 mmol H_2). The above reaction was repeated using a BH_4^-/Co^{2+} ratio of 8 with 0, 10, and 100 mL of H_2O (see Table I).

Reaction of $CoBr_2$ and $NaBH_4$ in Diglyme in the Presence of Water. A series of reactions were carried out as described above using a BH_4^-/Co^{2+} ratio of 2 with the exception that the diglyme solution of $CoBr_2$ (0.43 g, 2.0 mmol) was treated with an appropriate amount of H_2O to give a desired H_2O/Co^{2+} ratio (see Table II) prior to mixing with the $NaBH_4$–diglyme solution.

Results and Discussion

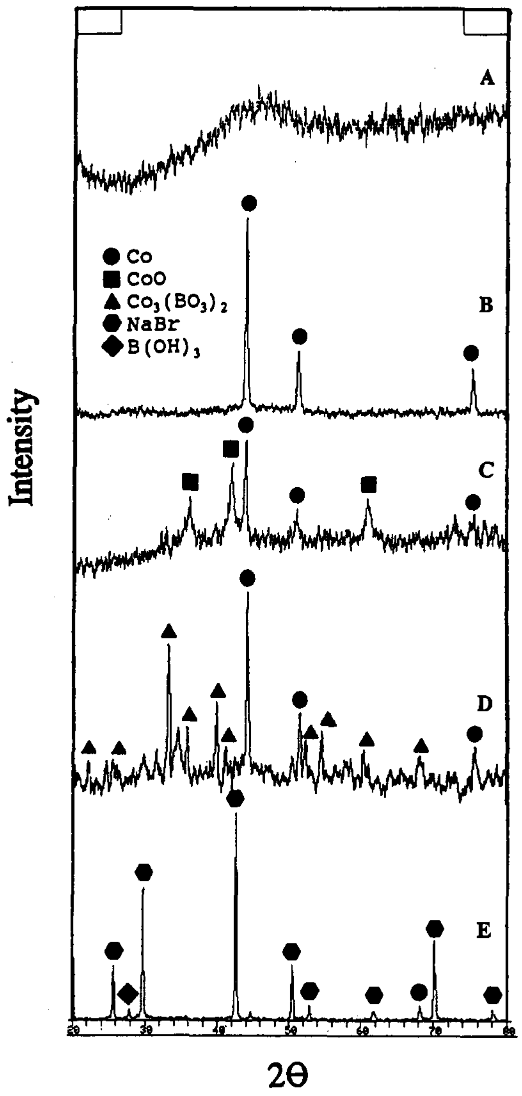

Figure 1. Powder X-ray diffraction of (A) fresh Co sample protected with Nujol, (B) sample heat processed at 500 °C, (C) exposed Co sample heat processed at 500 °C, (D) reduction product isolated under ambient condition and heat processed at 500 °C, and (E) powder obtained on air drying the H_2O/acetone washing.

The difference between nonaqueous and aqueous reduction of Co^{2+} is remarkable. In aqueous solution the primary product is Co_2B.[5,6] In nonaqueous media the primary product is Co, and eq 1 describes what was found when $CoBr_2$ and $NaBH_4$ were allowed to react in diglyme solvent. The species **1** is only stable at low temperatures and upon warming decomposes yielding

$$CoBr_2 + 2NaBH_4 \xrightarrow[\text{solvent}]{\text{L = diglyme}} \underset{\mathbf{1}}{(L)_nCo(BH_4)_2} + 2NaBr \qquad (1)$$

$$\mathbf{1} \xrightarrow{-nL} Co(s) + H_2 + B_2H_6 \qquad (2)$$

$$B_2H_6 \xrightarrow[\text{Co cat.}]{\text{diglyme}} B(s) + 3H_2 \qquad (3)$$

Co(s) ultrafine powder. The catalytic decomposition of B_2H_6 to boron and hydrogen was confirmed in reactions in which BH_3·THF solutions were decomposed in the presence of the suspension generated from the $CoBr_2$ and $NaBH_4$ reaction, as well as a diglyme suspension of isolated fine Co powder. The latter was a more effective catalyst although neither catalyst was as effective as the Co particles generated in eqs 1 and 2. After washing with water (which caused the original fine powder to fluff up as a result of the reaction shown in eq 4) and acetone

$$B + 3H_2O \rightarrow B(OH)_3 + {}^3/_2H_2 \qquad (4)$$

to remove NaBr, this powder exhibited a broad X-ray diffraction pattern (Figure 1A), which upon heat treatment under argon yielded larger crystallites of pure Co(s) (Figure 1B). However, exposure of the fine Co powder (after washing) to air followed by heat treatment under argon yielded crystallites of Co and CoO (Figure 1C) (eq 5). If the water and acetone washing was

$$3Co(s) + O_2 \rightarrow \xrightarrow[\text{Ar}]{\text{heat}} Co + 2CoO \qquad (5)$$

omitted in the isolation procedure, the fine powder obtained yielded $Co_3(BO_3)_2$ and Co on exposure to air followed by heat treatment.

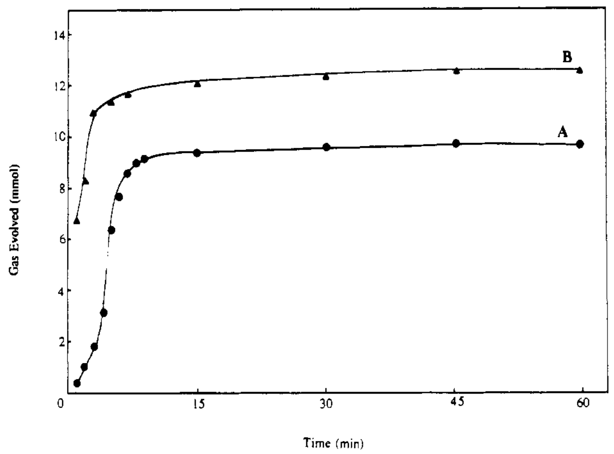

Figure 2. Gas evolution verses time for (A) $CoBr_2 + 2NaBH_4$ and (B) $CoCl_2{\cdot}6H_2O + 2NaBH_4$.

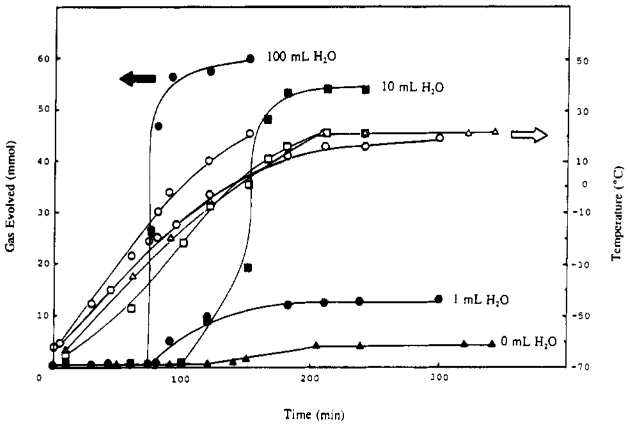

Figure 3. Reaction of $(diglyme)_nCo(BH_4)_2$ intermediate with H_2O. Gas evolution and temperature profile: ●, gas evolution; ○, temperature profile. Total mmol of $NaBH_4$:total mmol of $CoBr_2$: 0 mL of H_2O, 8:1; 1 mL of H_2O, 4:2, 10 mL of H_2O, 16:2; 100 mL of H_2O, 16:2. Different symbols are intended to guide the eye along the proper curve and to show which two curves belong to the same experiment.

Also, isolation of the black suspension produced in the reduction reaction under ambient conditions yielded an air-stable dark green powder which produced crystallites of $Co_3(BO_3)_2$ (Figure 1D) (eq 6) on heat processing under argon. These results indicate

$$Co/B \xrightarrow{O_2/H_2O} Co(BO_2)_2 \xrightarrow[Ar]{heat} Co_3(BO_2)_2 \tag{6}$$

that both cobalt and boron are present in the precipitate. These are not in the form of a boride but must instead be an intimate mixture of nanocrystalline cobalt plus boron. Starting with 2 mmol $CoBr_2$ and 4 mmol $NaBH_4$, the total amount of gas evolved was 9.4 mmol of which 8.0 mmol as H_2. (A profile of gas evolution over time is given in Figure 2A.) Part of this (2 mmol) was released directly whereas the rest (6 mmol) was generated as a result of catalytic decomposition of BH_3·diglyme by the fine Co particles (eq 3). Thus, eqs 1–3 predict the experimentally observed stoichiometry. Figure 2B shows the gas evolution over time in the equivalent reaction using 2 mmol of $CoCl_2{\cdot}6H_2O$.

The transient pink intermediate **1** can be prepared at low temperature and is indefinitely stable at –45 °C. Attempts to ligand stabilize and isolate this species have thus far been unsuccessful, and further spectroscopic and chemical studies are continuing. However, the behavior of **1** toward water is of interest in light of the significant changes water can cause in determining the primary product of the BH_4^- reduction of Co^{2+}. Therefore, a series of experiments were carried out where **1** was treated with varying amounts of H_2O. In all cases a black precipitate formed that was found to be metallic cobalt (eq 7). (See Table I and Figure 3.)

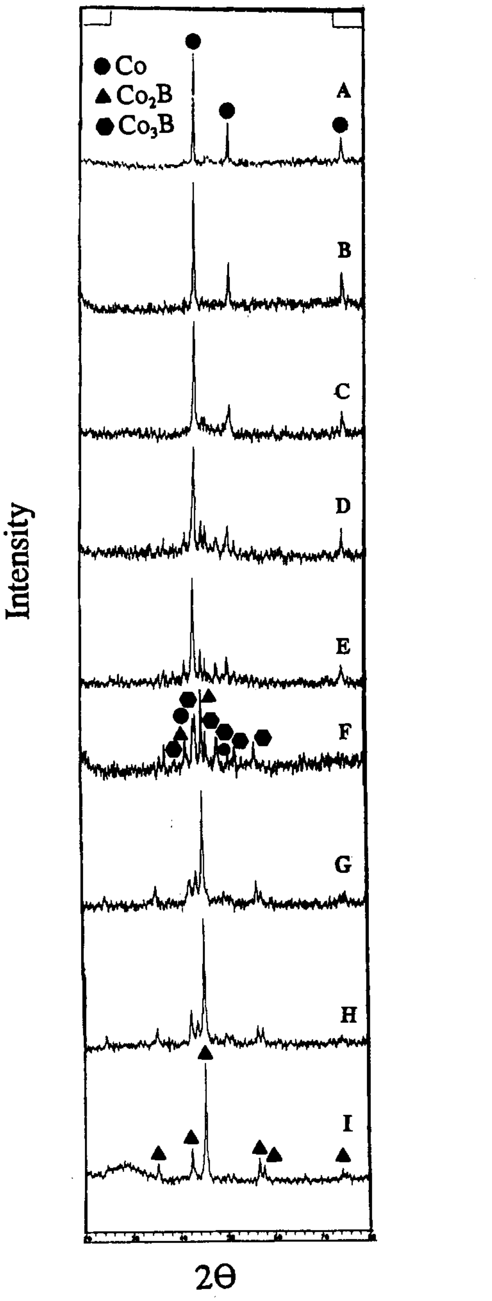

Figure 4. Powder X-ray diffraction of products from reactions in which different amounts of H_2O are added to diglyme solution of $CoBr_2$: (A) pure diglyme; (B) 2 mmol of H_2O; (C) 8 mmol of H_2O; (D) 64 mmol of H_2O; (E) 2048 mmol of H_2O; (F) 6100 mmol of H_2O; (G) a 50-mL H_2O solution of $CoBr_2$ reacted with 50 mL of diglyme solution of $NaBH_4$; (H) $CoBr_2$ solution in 100 mL of H_2O and 12 mL of diglyme reacted with a 25-mL diglyme solution of $NaBH_4$; (I) pure H_2O. Samples were heat processed at 500 °C.

$$1 + 6H_2O \xrightarrow{-nL} Co(s) + 7H_2 + 2B(OH)_3 \tag{7}$$

In contrast to what was observed in aqueous solution (Co_2B formation), these experiments yielded only metallic cobalt. And this result was not affected by overall BH_4^-/Co^{2+} ratio or the amount of added water.

These findings indicate that, after **1** forms in nonaqueous media, water no longer has a dominant role in determining the final cobalt-containing product. (Of course water does react with BH_3 released and leads to formation of $B(OH)_3$). Thus, **1** is kinetically stable and does not dissociate to form $Co(H_2O)_6^{2+}$.

By addition of water to the $CoBr_2$–diglyme solution prior to mixing with $NaBH_4$–diglyme, control over formation of Co(s) or Co_2B(s) can be achieved (Table II; Figure 3). As the amount of water added increased, the ratio of Co_2B(s)/Co(s) increased. These results underscore the importance of $Co(H_2O)_6^{2+}$ in the formation of Co_2B(s).[5,6]

Conclusions

Reduction of Co^{2+} by BH_4^- in nonaqueous media yields ultrafine metallic Co(s) as the primary product. A solvated species $(solv)_nCo(BH_4)_2$ appears to be an important intermediate in this process. These results are in contrast to aqueous-phase reduction, where ultrafine Co_2B(s) is the primary product and a $(H_2O)_5Co(OH)BH_2(HO)Co(H_2O)_5^{3+}$ species is believed to be an intermediate.[6]

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