Formation of Cobalt Nitrate Hydrate, Cobalt Oxide, and Cobalt Nanoparticles Using Laser Vaporization Controlled Condensation

Garry P. Glaspell,[†] Paul W. Jagodzinski,[‡] and A. Manivannan*,[§]

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506, Department of Chemistry & Geochemistry, Colorado School of Mines, Golden, Colorado 80401, and Department of Physics, West Virginia University, Morgantown, West Virginia 26506

In this paper, we report for the first time the synthesis of cobalt nitrate hexahydrate, cobalt oxide, and cobalt particles formed from a high purity cobalt metal by a novel laser vaporization controlled condensation (LVCC) method under controlled pressures of N_2 and O_2. The metal vapor produced from a cobalt target in the presence of 50% N_2 and 50% O_2 results in the formation of cobalt nitrate. We also explored the possibilities of forming cobalt oxide and cobalt nanoparticles by altering the ratio of N_2 and O_2 present. For example, the synthesis of pure cobalt oxide (CoO) nanoparticles is of importance and challenging since a simple chemical route is complex. We believe that this work will be of significant importance since the present method is promising for the synthesis of metal mono oxides.

Introduction

Recently, synthesis of various semiconductor and intermetallic nanoparticles via LVCC has been of particular interest.[1−12] This method utilizes well defined conditions to produce nanoparticles of controlled size and composition without the need for chemical precursors or heat treatments. Specifically, a laser is used to produce a supersaturated metal vapor from a target inside a chamber. Convection currents, resulting from the top plate of the chamber being cooled and the bottom plate heated, affect the rate of nucleating metal vapor. Particles generated by this procedure are predominately spherical and have significantly less fluctuation in size compared to most reduction procedures. This can be achieved by the choice of laser power, chamber pressure, and temperature gradient. El-Shall and co-workers have explored the synthesis of a variety of metal oxide nanoparticles using LVCC by adding oxygen to the reaction chamber.[13,14] This method provides insight into the physical chemistry of the formation of these materials. In this regard, we attempted to synthesize metal nitrates from a metal target in the presence of N_2 and O_2 at controlled pressures. For the first time, we have successfully synthesized cobalt nitrate hexahydrate. We have also explored how the ratio of N_2 and O_2 controls the physical chemistry of the various types of cobalt compounds produced. Surprisingly, we could also synthesize cobalt oxide (CoO) nanoparticles. It is important to mention that pure CoO cannot be synthesized easily by a simple chemical route since this approach typically produces a mixture of Co_3O_4 with small amounts of CoO. Therefore, our objective is to optimize the conditions to synthesize pure CoO nanoparticles and other related cobalt compounds.

In this report, we describe the LVCC method for the synthesis of cobalt nitrate hydrate, cobalt oxide, and cobalt nanoparticles produced using high purity cobalt metal target at various N_2 and O_2 pressures.

Experimental Section

The cobalt target (99.9%) was purchased from Alpha Aesar (Ward Hill, MA). The N_2 (99%) and O_2 (99%) were obtained from Air Gas (Westover, WV) and used without any further purification. The LVCC chamber was home-built and consists of two metal plates modified to provide uniform heating and cooling. To provide convection, the top plate was cooled with liquid nitrogen and the bottom plate was heated with circulating water. A Laserphotonics Nd:YAG laser (Orlando, Florida) was used to ablate the metal target. Altering the laser power, chamber pressure, and temperature gradient between the two plates results in the formation of particles of various sizes. The size and shape of the particles were confirmed using a JEOL 1220 transmission electrom microscopy (TEM) operating at 80 KeV. X-ray diffraction (XRD) patterns of the powder sample were measured at room temperature with a Rigaku Diffractometer (DMAX-B) and Cu Kα radiation ($\lambda = 1.5418$ Å). The samples were mounted on a silicon plate for X-ray measurements. IR spectra were obtained using a MIDAC M2000 series FT-IR (Costa Mesa, CA).

Results and Discussion

We have carried out numerous experiments by varying the O_2 and N_2 pressures in the chamber in order to obtain various compounds of Co. As a technique, LVCC has been used to make nanoparticles of various semiconductors and metal oxides. In our experiment, it has been demonstrated how various compounds of Co are formed by simply varying the O_2 and N_2 ratios during synthesis. Moreover, the physical chemistry of the formation of cobalt nitrate is intriguing. The cobalt metal vapor formed via the laser simply reacts with the N_2 and O_2 to produce cobalt nitrate. The details of the formation of various Co compounds are described below.

The nanoparticles generated in pure nitrogen are primarily cobalt and are also the primary product at low concentrations

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* To whom correspondence should be addressed. E-mail: amanivan@wvu.edu.
† Department of Chemistry, West Virginia University.
‡ Colorado School of Mines.
§ Department of Physics, West Virginia University.

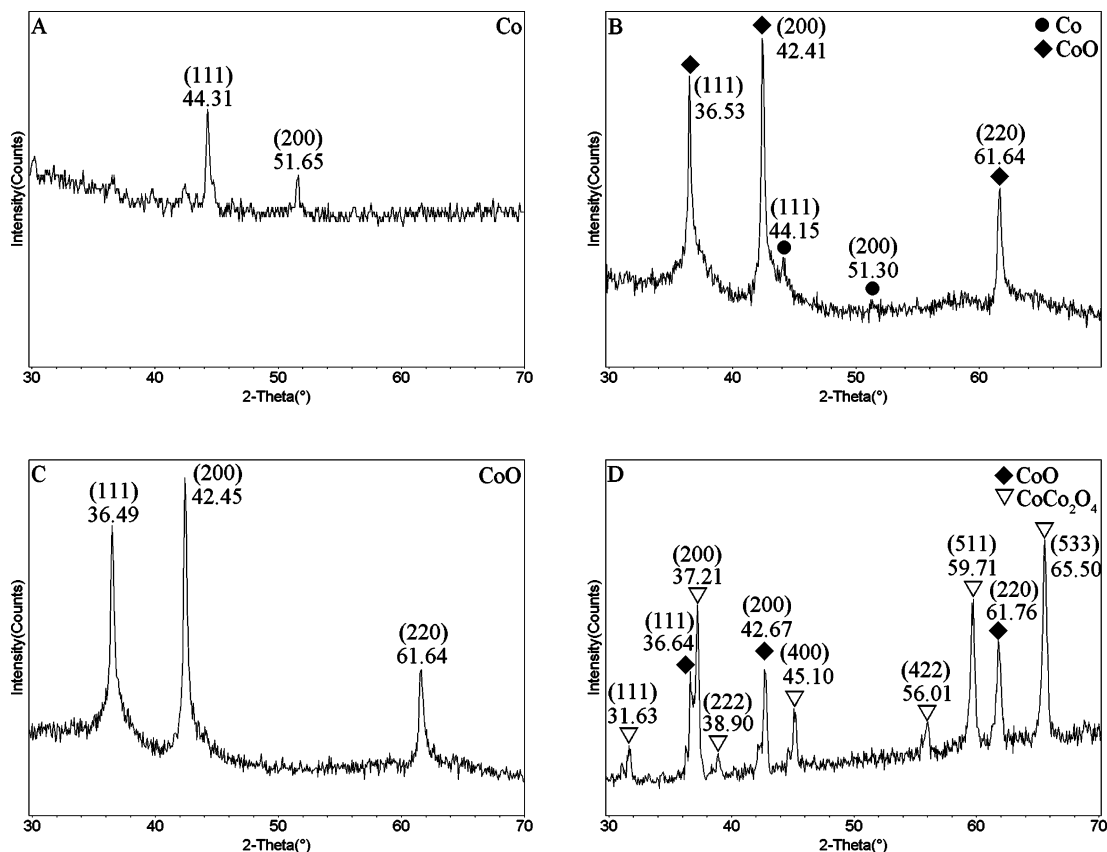Formation of Cobalt Compounds

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Figure 1. XRD showing (A) cobalt (PDF 15−0806) as the primary product formed when the ratio of O_2 to N_2 is 0.3%; (B) the decline of cobalt (PDF 15−0806) and the emergence of cobalt oxide (PDF 43−1004) when the ratio of O_2 to N_2 is 2.3%; (C) cobalt oxide (PDF 43−1004) as the primary product formed when the ratio of O_2 to N_2 is 3%; (D) Alfa Aesar 95% CoO having mixed oxide phases matching with $CoCo_2O_4$ (PDF 01−1152) and CoO (PDF 43−1004).

TABLE 1: Standard Crystallographic Peak Assignments for Cobalt Nitrate Hexahydrate Produced via LVCC

2-Theta LVCC	h	k	l	2-Theta LVCC	h	k	l
15.1	0	0	2	38.42	−2	1	5
15.84	−2	0	2	38.97	−4	2	2
16.28	0	1	1	40.46	−4	1	5
19.1	−2	1	1	40.95	−2	2	4
23	2	1	1	41.07	6	0	0
23.91	2	0	2	41.32	0	1	5
25.34	−4	0	2	42.76	0	2	4
26	−2	1	3	43.06	−2	0	6
27.06	0	1	3	43.93	−4	0	6
28.15	−2	0	4	46.66	0	0	6
29.09	0	2	0	48.4	2	1	5
30.54	0	0	4	48.73	2	2	4
31.51	1	2	1	49.67	6	0	2
32.1	−2	2	0	53.23	−4	1	7
32.84	0	2	2	58.37	−4	0	8
33.24	−2	2	2	63.65	0	0	8
34.26	4	1	1				

of O_2 below 0.3% (Figure 1A). It is evident from the XRD pattern of the Co nanoparticles that the diffraction peaks at scattering angles (2θ) of 44.31 and 51.65 are assigned to scattering from the 111 and 200 planes of the Co crystal lattice.[15] This would indicate that nanoparticles having the same crystal structure as bulk Co have been formed. When the percentage of O_2 is increased to 2.3%, we begin to observe the formation of cobalt oxide (CoO) together with trace amounts of cobalt as confirmed by XRD (Figure 1B). The CoO peaks are observed at scattering angles 36.53, 42.41, and 61.64 and are assigned to scattering from the 111, 200, and 220 planes of the CoO crystal lattice.[15] The trace amounts of cobalt disappear as the O_2 concentration is increased to 3% (Figure 1C). It is also observed

that the nanoparticles of CoO possess the same crystal structure as bulk CoO. The approximate crystallite size for the CoO was 4 nm determined via TEM (Figure 2). This is a significant result since the commercially available CoO (Alfa-Aesar) has mixed oxide phases as indicated by X-ray diffraction (Figure 1D). Strong peaks are observed at 2θ angles 31.63, 36.64, 38.90, 45.10, 56.01, 59.71, and 65.50 that can be assigned to scattering from the 111, 200, 222, 400, 422, 511, and 533 planes, respectively, of the $CoCo_2O_4$ crystal lattice.[15]

Formation of a mixture of cobalt nitrate tetrahydrate and cobalt oxide is observed when the percentage of O_2 is raised to 6.6% (Figure 3 A). The h, k, and l indicies are not reported for cobalt nitrate tetrahydrate as they are not available in the database (PDF 43−1004).[15] It is believed that hydrates are formed due to exposure of the nanoparticles to residual moisture that is present as they are collected. We cannot rule out surface moisture residing in the chamber even after the chamber was evacuated and purged repetitively with nitrogen.[16,17] Cobalt oxide peaks continue to diminish as the O_2 concentration is increased to the 33−50% range. The primary product is then cobalt nitrate hexahydrate as shown in Figure 3B with the major peaks labeled. The standard crystallographic peak assignments for the XRD pattern is given in Table 1 which indicates that cobalt nitrate hexahydrate produced via LVCC possesses the same crystal structure as its bulk counterpart.[15] The XRD pattern of cobalt nitrate hexahydrate, purchased from Aldrich, was recorded (Figure 3C) and compared to cobalt nitrate hexahydrate produced via LVCC. It is significant to note that the two spectra possess minor differences. Specifically, the XRD for cobalt nitrate produced via LVCC matches closely to the reference PDF. The absence of the peak at 2θ angle of 19
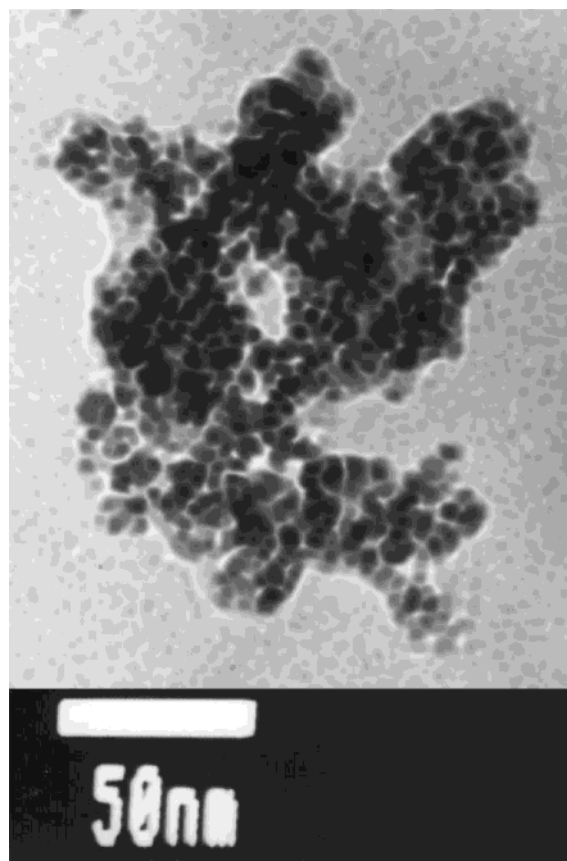
Figure 2. TEM of CoO nanoparticles. The average particle size was calculated to be ~4 nm.

TABLE 2: Reaction Conditions Showing the Primary Products and How the Number of Water Molecules Coordinated to the Metal Nitrate Hydrate Change as the Ratio of Oxygen Changes

% O_2	products	no. of coordinated H_2O's
0.3	Co	
1.7	CoO/Co	
2.3	CoO/Co	
2.7	CoO	
3	CoO/CoNO$_3$OH	1
6.6	Co(NO$_3$)$_2$/CoO	4
20	Co(NO$_3$)$_2$/CoO	4
33	Co(NO$_3$)$_2$	6
50	Co(NO$_3$)$_2$	6

and the presence of peaks 24.48 and 41.78 2θ (indicated by *'s in the XRD spectrum) in the Aldrich sample may be due to impurities.

We have summarized all of the results in Table 2 indicating all of the reaction conditions responsible for the products that are produced at various concentrations of O_2 and N_2. It should be noted that the number of water molecules coordinated to the metal nitrate hydrate changes as the ratio of oxygen changes. This can be explained by the amount of oxygen available in the chamber. When oxygen is present in the 3−33% range, the amount of cobalt oxide surrounding the cobalt nitrate can vary significantly. In that range, the number of water molecules in contact with cobalt nitrate may be controlled by the amount of CoO which depends on the ratio of oxygen to nitrogen. Thus, oxygen plays a major role in this process of producing CoO, cobalt nitrate hydrate, as well as the number of water molecules bound to it. It is also important to note that the major product was cobalt nitrate hydrate with a maximum of six water molecules for the 33−50% oxygen range.
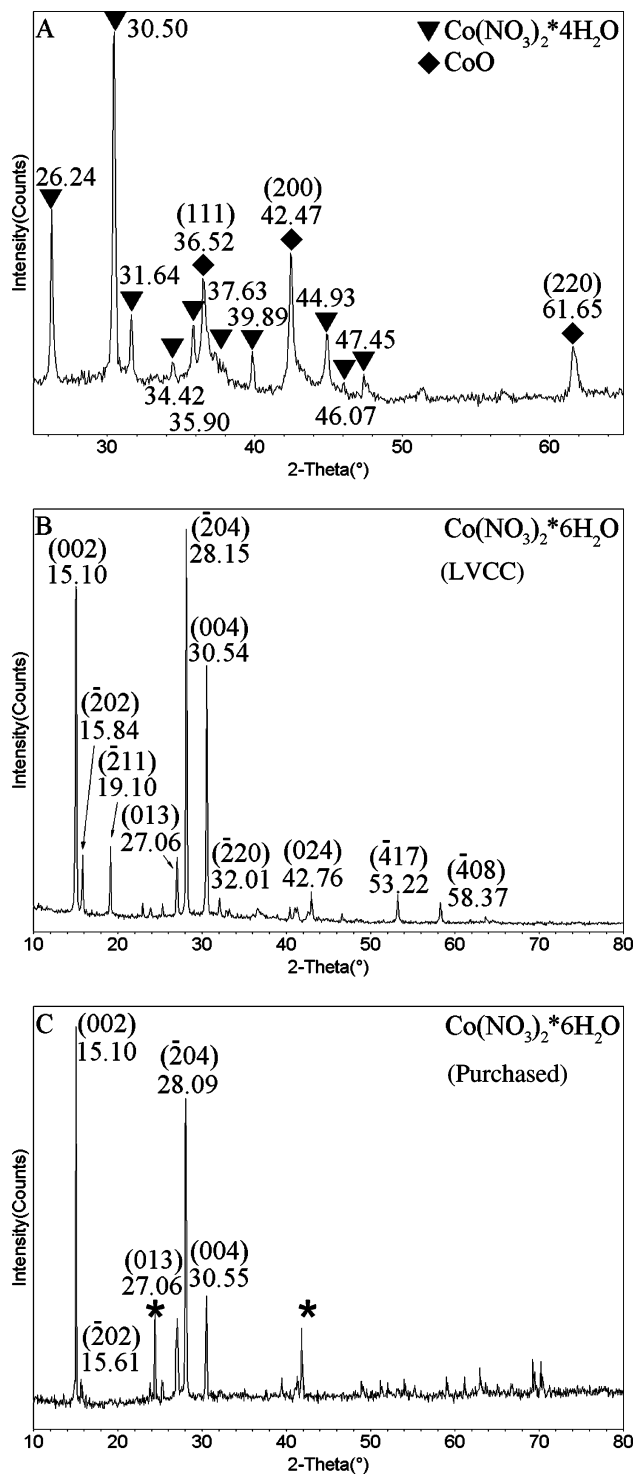

Figure 3. XRD showing (A) a mixture of cobalt oxide (PDF 43−1004) and cobalt nitrate tetrahydrate (PDF 18−0425) produced when the ratio of O_2 to N_2 is 6.6%, (B) cobalt nitrate hexahydrate (PDF 25−1219) as the primary product formed when the ratio of O_2 to N_2 is 50%, (C) cobalt nitrate hexahydrate (PDF 25−1219) purchased from Aldrich.

We have also carried out IR studies in order to investigate the cobalt nitrate compound. Figure 4 compares the IR spectra of cobalt nitrate hexahydrate formed by LVCC and cobalt nitrate hydrate purchased from Aldrich. The nitrate group has six normal vibarations that are IR active. These are the antisymmetric stretching ν_4 (A′), symmetric stretching ν_1 (A′), totally symmetric stretching ν_2 (A′), out of plane bending ν_6 (A″), antisymmetric in-plane bending ν_5 (A′), and the symmetric in-

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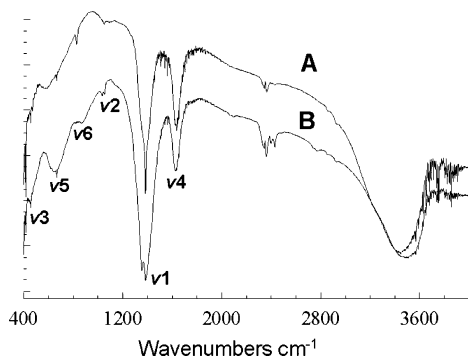

Figure 4. Comparison of IR spectra of cobalt nitrate hydrate purchased from Aldrich (A) and synthesized by LVCC (B), respectively. The nitrate normal vibrations are symmetric stretching v_1 (1388 cm^{-1}), totally symmetric stretching v_2 (1052 cm^{-1}), symmetric in-plane bending v_3 (664 cm^{-1}), antisymmetric stretching v_4 (1629 cm^{-1}), antisymmetric in-plane bending v_5 (729 cm^{-1}), and the out of plane bending v_6 (870 cm^{-1}).

plane bending v_3 (A′) observed at 1629, 1388, 1052, 870, 729, and 664 cm^{-1}, respectively.[18-20] The broad peak at 3500 cm^{-1} is indicative of moisture and the cluster of peaks at 2400 cm^{-1} can be assigned to CO_2. No significant differences were observed in the spectra which again confirm the formation of cobalt nitrate hexahydrate.

One possible explanation for the formation of the cobalt nitrate hexahydrate is the high temperature generated at the metal surface by the laser. This provides enough energy to form NO from N_2 and O_2. The NO then reacts with O_2 to form NO_2 (a brown gas which was observed in the chamber within minutes of turning on the laser). NO_2 in the presence of O_2 then reacts with the metal vapor to produce the resulting metal nitrate.[21] It is also important to indicate that the resulting product was Co_3O_4 when nitrogen was replaced by helium or argon. This is similar to chemical methods, where optimum conditions to produce CoO were not successful.

Conclusion

The results reported here clearly indicate that nanoparticles of cobalt, cobalt oxide, and cobalt nitrate hydrate were generated via LVCC by controlling the ratio of N_2 and O_2 present in the reaction chamber. Nanoparticles of cobalt can be synthesized in pure nitrogen and at low levels of O_2 since the metal vapor produced is cooled though collisions with N_2 before it can interact with O_2. As the concentration of O_2 increases (0.3%− 2%), the metal vapor is able to interact with oxygen before the

energy necessary for binding is quenched. The formation of only cobalt oxide (CoO) could be achieved by keeping the O_2 ratio at 3%. When the O_2 ratio was increased to the range 33−50%, the resulting product was found to be cobalt nitrate hydrate with six water molecules. Work is in progress to further understand such processes with other metals such as Ni, Fe, and Mn and to produce various particle sizes of these metal mono oxides by varying laser power, chamber pressure, temperature gradient, etc.

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