

# Hydrothermal Reduction of $\text{Co}(\text{OH})_2$ to Cobalt Powder Preparation

Dong-Jin Kim, Hun-Saeng Chung and Yu Kening\*

Korea Institute of Geology, Mining and Materials (KIGAM), Dae Jeon, 305-350, KOREA

\*Institute of Chemical Metallurgy, CAS, Beijing, 100080, CHINA

## Co(OH)<sub>2</sub>로부터 수열법에 의한 코발트 분말제조

김동진 · 정헌생 · Yu Kening\*

한국자원연구소

\*화공야금연구소, 중국과학원, 북경, 100080

(1998년 10월 30일 받음, 1999년 5월 21일 최종수정본 받음)

**초 록** PdCl<sub>2</sub>를 촉매제로 사용한 수소환원분위기에서 Co(OH)<sub>2</sub>로부터 약 400nm 크기인 구형의 코발트분말 제조에 관한 연구를 수행하였다. 본 실험에서 코발트의 환원반응속도는 표면반응 코어모델식에 잘 일치하였으며 이때 활성화 에너지는 145~195 °C에서 약 55.6KJ/mol 이었다. 또한 코발트의 환원속도는 초기 수소분압의 0.63승에 비례하는 가스화착흡착반응식으로 표시할 수 있다.

**Abstract** An investigation was performed to prepare spherical cobalt powder with about particle size of 400nm from aqueous cobalt hydroxide slurry under hydrothermal reduction conditions using palladium chloride as a catalyst. The reduction kinetics was in good agreement with a surface reaction core model equation, and the activation energy obtained from Arrhenius plots was 55.6 KJ/mol at the temperature range of 145~195°C. Additionally, the study showed that the cobalt reduction rate is proportional to the initial hydrogen pressure with a reaction order of  $n=0.63$ , which corresponds to the gas chemisorption reaction type.

## 1. Introduction

High purity fine materials offer new physical and mechanical properties. Therefore, a considerable effort has been put into the chemical preparation of these powders from aqueous phases. Among various wet chemical methods, the precipitation technique of metals from metallic salt solutions by hydrogen reduction at elevated pressure and temperature has been widely used to prepare fine metallic powders.<sup>1-3)</sup>

However, studies on metal powder preparation from aqueous metallic salt slurry systems have been little available. Their complex heterogeneous reactions are highly complicated compared to the homogeneous one, because of difficulties in controlling the system's pH values and in transferring hydrogen from gas to liquid phases.<sup>4,5)</sup> Studies on the hydrothermal reduction of nickel hydroxide slurry suggest that the slurry first dissolves under hydrothermal conditions, and then the nickel ion is reduced to metallic nickel particles by hydrogen.<sup>6,7)</sup> The reduction kinetics of their experiments was in good agreement with a core model equation, and the rate determining step was different.<sup>8)</sup>

The present work investigates the reduction of Co(OH)<sub>2</sub> using palladium chloride as catalyst under hydrothermal conditions to produce fine cobalt powder. The reduction conditions were examined for various parameters, such as pH of slurry, hydrogen pressure, temperature and catalyst.

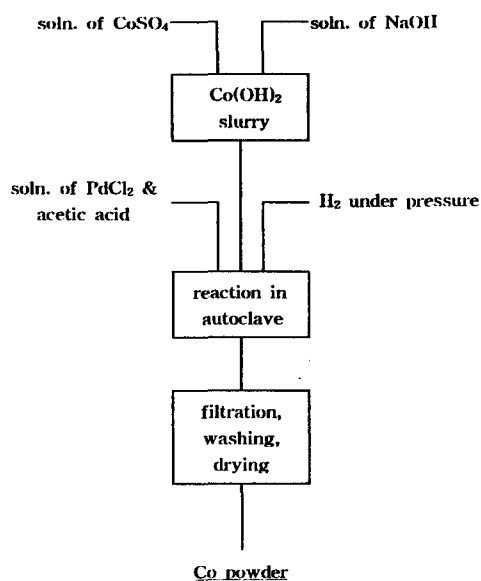
## 2. Experiment

The hydrogen reduction experiments were carried out in an autoclave equipped with a 2 liter glass lined reactor (10cm  $\phi$  x 25cm H) and an agitator having a 5.8 cm diameter 6-blade marine type impeller rotated at 800rpm. The reactor is charged with 500ml Co(OH)<sub>2</sub> slurry prepared by mixing solutions of CoSO<sub>4</sub> and NaOH stoichiometrically, then a small amount of PdCl<sub>2</sub> were added as a catalyst and acetic acid as a buffer solution. Table 1 gives the standard hydrogen reduction conditions. The chemicals used in present study were reagent grade in purity.

Once the reaction temperature reached at predetermined value, hydrogen gas was introduced into the reactor after flushing a few times. After the completion of the reaction, the cobalt powder was filtered, washed

Table 1. The hydrogen reduction<sup>a</sup> experiment conditions.

Factor	Conditions
Temperature	145~195°C
PdCl <sub>2</sub>	2~12mg/ℓ
PH <sub>2</sub>	1~4MPa
pH of end solution	3.3~9.8
Co <sup>++</sup> conc.	20~60g/ℓ
NaOH amounts(stoich.)	110%
Acetic acid	0.8v/o

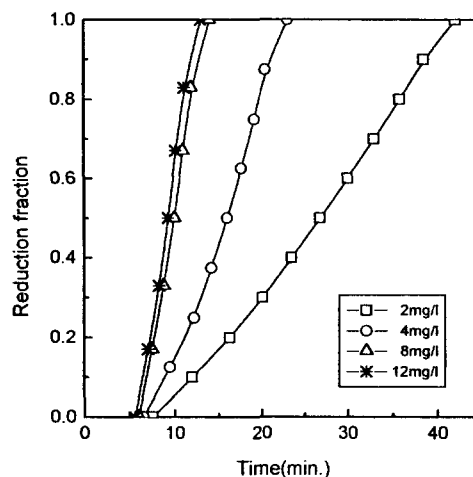
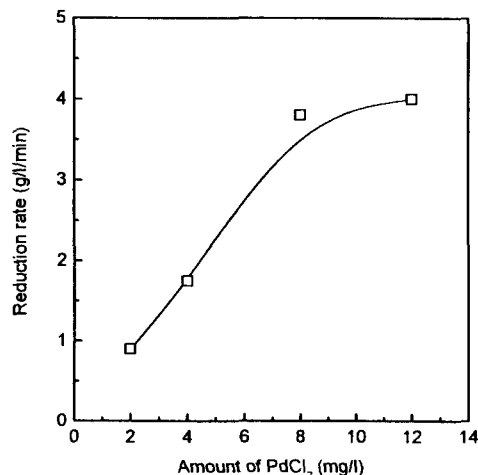
Fig. 1. Experimental procedure for the preparation of Co powder from Co(OH)<sub>2</sub> slurry.

and dried under nitrogen gas atmosphere to prevent the oxidation of cobalt metal. The collected powder was characterized in chemical composition, particle size, and morphology. The residual cobalt ion concentration in the filtrate was measured colorimetrically. Figure 1 shows the brief experimental procedure.

### 3. Result and Discussion

Cobalt metal ions in cobalt hydroxide slurry system can be reduced by hydrogen gas only when the pH is higher than a certain value, which depends on the specific conditions in the reactor, i.e. temperature, pressure and ion concentrations. The reduction reaction creates H<sup>+</sup> ions and if no neutralizing agent is present, this ion will lower the pH of the system so that the reduction ceases. The most frequently used neutralizing agent is ammonia but sodium hydroxide was used in this experiment.

A prerequisite in cobalt powder production is initially to form fine particles in the nucleation stage. By varying the composition of the feed solution and by adding

Fig. 2. Reduction fraction at various amounts of PdCl<sub>2</sub>. (Co<sup>++</sup> : 30gr/l, pH : 6, 180°C, PH<sub>2</sub> : 3MPa)Fig. 3. Reduction rate vs PdCl<sub>2</sub>. (Co<sup>++</sup> : 30g/l, pH : 6, 180°C, PH<sub>2</sub> : 3MPa)

inorganic salts or organic compounds which catalyze or modify the reduction mechanisms, different metal powders can be produced. Known cobalt-reduction catalysts, such as ferrous sulphate, palladium chloride behaves similarly. These additives increased the number of active sites on the basic cobalt slurry system, but it is difficult to determine accurately the necessary amount of catalyst to be added.

The concentration of palladium chloride varies in a range of 2 to 12 mg/ℓ, and its effect on the reduction fraction with time is shown in Figure 2. The reduction fraction herein indicates the mol ratio of precipitated Co metal to starting Co ions. It is seen that the increases in palladium chloride highly accelerates the reduction of Co ions after an induction period which is a time lag between the injection of hydrogen gas and the initiation of the reduction reaction. An induction period of about 5~8 minutes is needed under the present operation

conditions. Figure 3 shows the reduction rate of Co ions with the increase in the concentration of palladium chloride. The rate increases linearly up to  $\sim 4\text{g}/\ell/\text{min}$ , and becomes constant at a palladium chloride concentration of above  $8\text{mg}/\ell$ . In other words, the catalytic reaction with an excessive addition of activator does not show any significant contribution to increase the reduction rate or decrease the induction period.

But a lot of cobalt metal was plated on the walls of the reactor at a palladium chloride concentration under  $2\text{mg}/\ell$ . At a palladium chloride concentration above  $12\text{mg}/\ell$ , plating is virtually absent, but some cobalt particles result in agglomeration. A serious problem in the hydrogen reduction of solutions is the tendency for the precipitated metal to form agglomerates and to plate out on the surfaces of the reactor. If precipitation by gas reduction is not properly nucleated or incomplete, reduction may be too slow and a lot of metal will plate on the walls of the reactor. In general, a faster reduction rate results in less plating. Plating is virtually absent when a large surface area of seed is available.

The experiments were carried out in the temperature range of  $145^\circ\text{C}$  to  $195^\circ\text{C}$  and the kinetic values are plotted in Figure 4. The initial reduction rates against the time at the different temperatures are in good agreement with the rate equation of the shrinking core model dominated by chemical reaction control for small sphere particles<sup>9)</sup>:

$$1 - (1 - x)^{1/3} = k t \quad (1)$$

where  $x$  is the reduction fraction and  $k$  is the rate constant.

The Arrhenius plot of the reduction rate in the temperature range of  $145^\circ\text{C}$  to  $195^\circ\text{C}$  was given in Figure 5. It appears that the apparent activation energy in the temperature range of  $145^\circ\text{C}$  to  $195^\circ\text{C}$  is  $55.6\text{KJ/mol}$ , and it can be said that the reaction rate is chemically controlled.

Assume that the electrons generated from dissolving the hydrogen in water will be chemisorbed onto the metal hydroxide surface. Let the reduction rate be proportional to the  $n$ -th order of the gas pressure, analogous to the solid-gas chemisorbed reaction system,<sup>10)</sup> i.e.

$$-dw/dt = C P_o^n \quad (2)$$

where  $w$  is the concentration of metallic ions,  $P_o$  is the initial hydrogen pressure,  $C$  and  $n$  are constants. By the integration from  $t_i$  to  $t_{1/2}$ , Eq. (2) becomes

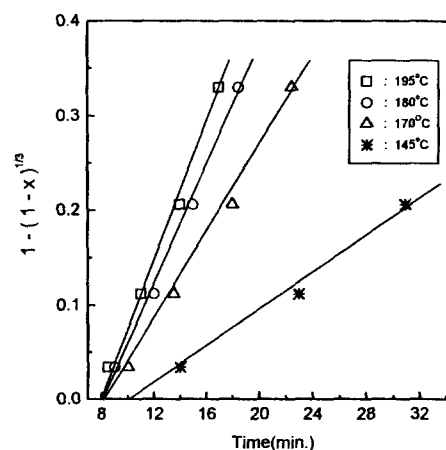


Fig. 4.  $1 - (1 - x)^{1/3}$  vs reduction time. ( $\text{Co}^{++}$ :  $40\text{g}/\ell$ ,  $\text{pH}$ : 6,  $\text{PH}_2$ :  $3\text{MPa}$ ,  $\text{PdCl}_2$ :  $4\text{mg}/\ell$ )

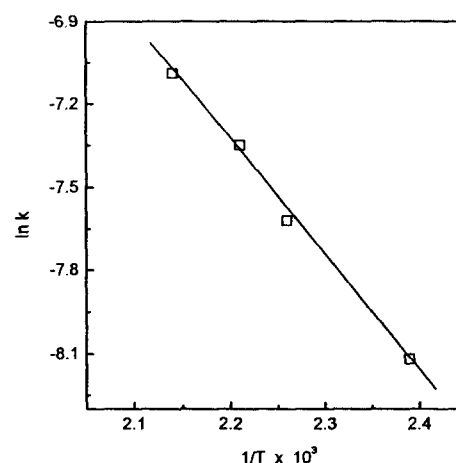


Fig. 5. Arrhenius plot of reduction rate. ( $\text{Co}^{++}$ :  $40\text{g}/\ell$ ,  $\text{pH}$ : 6,  $\text{PH}_2$ :  $3\text{MPa}$ ,  $\text{PdCl}_2$ :  $4\text{mg}/\ell$ )

$$t_{1/2} - t_i = C' P_o^{-n} \quad (3)$$

$$\text{or } t_{1/2} = C' P_o^{-n} + t_i \quad (4)$$

where  $t_{1/2}$  is the half decay period resulting in a half of the initial concentration,  $t_i$  is the induction period in which the initial concentration stays the same, and  $C'$  is constant.

The tests were performed in the initial hydrogen pressure in the range of  $1\text{MPa}$  to  $4\text{MPa}$ . Figure 6 shows the experimental values of  $t_{1/2} - t_i$  as a function of the hydrogen pressure. The plot is well agreed with Eq. (3) and the value of  $n$  from the slope is found to be  $0.63$ . It is also seen that the experimental values of  $t_{1/2}$  shows a good agreement with the Eq.(4) calculated based on  $n = 0.63$ . It is also shown that the induction period presented by the gap between  $t_{1/2}$  and  $t_{1/2} - t_i$  lines decreases with increasing the hydrogen pressure. In Figure 7, the reduction rates of cobalt ions in the slurry are plotted as a function of the initial hydrogen

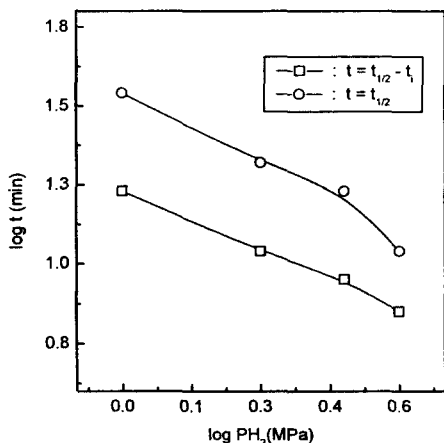


Fig. 6. Reduction time of Co<sup>++</sup> by hydrogen. (Co<sup>++</sup> : 30g/l, pH : 6, 170°C, PdCl<sub>2</sub> : 4mg/l)

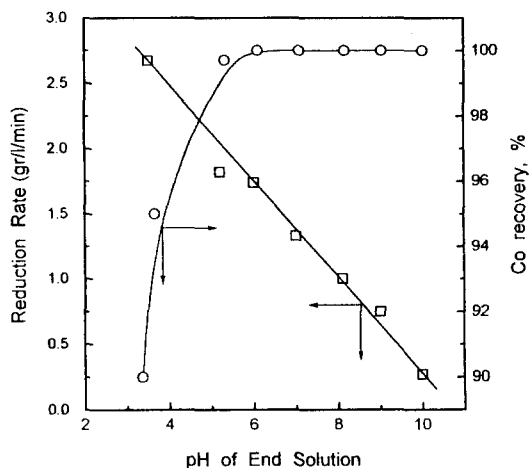


Fig. 8. Co recovery and reduction rate at different pH of end solution. (Co<sup>++</sup> : 40gr/l, PH<sub>2</sub> : 3MPa, 180°C, PdCl<sub>2</sub> : 4mg/l)

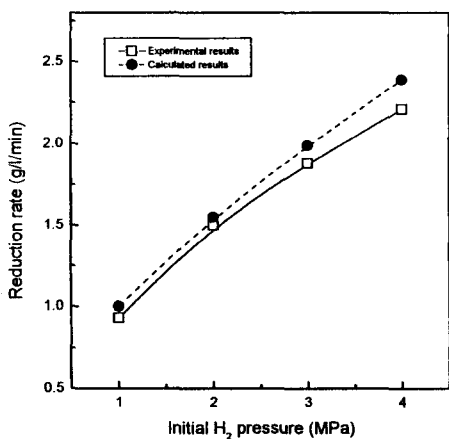


Fig. 7. Reduction rate of Co<sup>++</sup> by hydrogen. (Co<sup>++</sup> : 30g/l, pH : 6, 170°C, PdCl<sub>2</sub> : 4mg/l)

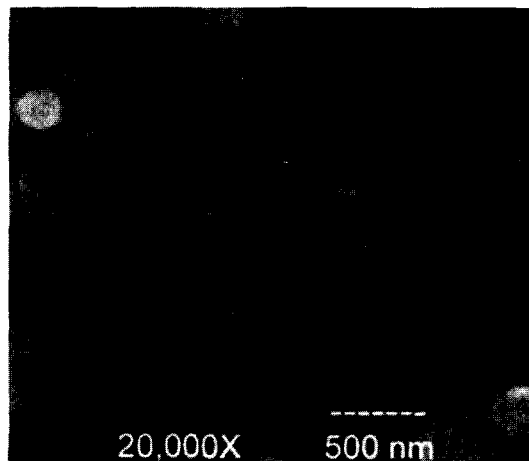


Fig. 9. SEM photograph of Co powders.

pressure. The experimental values of the reduction rate fit well to the calculated line from the rate expression of Eq. (2) using  $n = 0.63$ .

Figure 8 shows the reduction rate and the recovery ratio of cobalt metal plotted as a function of pH of the end solution after completing the Co(OH)<sub>2</sub> reduction. The reduction rate continuously decreases from 2.7g/ℓ/min at pH = 3.2 down to 0.27g/ℓ/min at pH = 10. On the other hand, as the pH decreases, the recovery ratio rapidly increases up to near 100% at pH value of 6~7. Therefore, referring to the Pourbaix diagram,<sup>11)</sup> the following reduction processes can be contemplated depending on pH values.

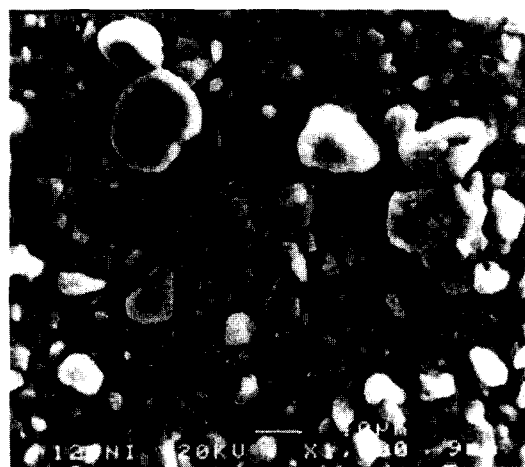
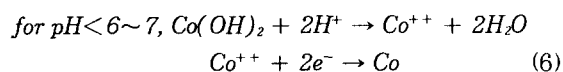
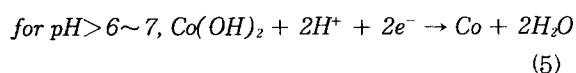


Fig. 10. SEM photograph of Co(OH)<sub>2</sub>.

In the high pH range, the direct reduction from Co(OH)<sub>2</sub> to Co proceeds at a slow rate, but the recovery becomes high. This is a necessary condition to slow

down the metal particle growth at the maximum recovery. On the other hand,  $\text{Co}^{++}$ , which is dissolved in the low pH, is reduced with the high rate at first and then the lowered pH of the end solution limits the reduction resulting in the low cobalt metal recovery.

Figure 9, 10 shows the cobalt product powder and  $\text{Co}(\text{OH})_2$  generated from sulfate solution. Cobalt powders are spherical in shape with about 400nm particle size.

#### 4. Conclusion

Hydrogen reduction performed in preparation of fine cobalt powder from cobalt hydroxide slurry under hydrothermal conditions. The reduction rate was mainly a function of the end pH, the amount of catalyst, hydrogen pressure, and temperature. The cobalt powder obtained was spherical in shape with a particle size of about 400nm at a pH value of 6~7 of end solution.

The reduction kinetics in the temperature range of 145°C to 195°C was well fitted to a core model equation,  $1 - (1 - x)^{1/3} = k t$ . The activation energy obtained from the Arrhenius plot was 55.6 KJ/mol at the temperature of 145~195°C. In addition, the cobalt ion reduction rate was closely related to the initial hydrogen pressure ( $P_0$ ). The rate could be expressed as  $-dw/dt = C P_0^n$ , analogous to a gas chemisorption reaction, where  $n = 0.63$ .

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