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Cobalt powder from $Co(OH)_2$ by hydrogen reduction

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Abstract

A study was performed to prepare spherical cobalt powder of about 400 nm from aqueous cobaltous hydroxide slurry under hydrogen reduction conditions using palladium chloride as a catalyst. The reduction kinetics showed good agreement with a surface reaction core model equation, and the activation energy of 35.6 kJ/mol was obtained from the Arrhenius plot at the temperature range of 145–195°C. Additionally, a relationship between the half-life of the reduction, the induction period, and the hydrogen gas pressure was found to be as $t_{1/2} - t_i = aP_{H_2}^{1-n}$.

Keywords: A. Metals; A. Interfaces; B. Chemical synthesis

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1. Introduction

Fine metallic materials with high purity offer new physical and mechanical properties. Considerable efforts have been put into the chemical preparation of these powders from aqueous phases. Among various wet chemical methods, the precipitation of metals from metallic salt solutions by hydrogen reduction at elevated pressure and temperature has been widely used as a convenient technique to prepare fine metallic powders [1,2]. On the other hand, studies on metal powder preparation from aqueous metallic salt slurry systems have been rare even though the heterogeneous method is favorable for maintaining equilibrium conditions in controlling the particle size and shape [3]. Their complex heterogeneous reactions are very complicated,

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because of difficulties in controlling the system's pH values and in transferring hydrogen from gas to liquid phases [4,5].

Some studies on the hydrothermal reduction of nickel hydroxide slurry suggest that the slurry first dissolves under hydrothermal conditions, and then the nickel ions are reduced to metallic nickel particles by hydrogen [6,7]. The reduction kinetics of their experiments was in good agreement with a core model equation of solid–gas surface reaction, and the rate determination step differs in low and high temperatures [8].

The domain of thermodynamic stability of cobalt has a small area in common with that of water [9]. In this respect, it is very similar to nickel. Like nickel, cobalt metal ions in a cobaltous 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 generates H^+ ions lowering the pH of the system resulting in the cessation of the reduction if no neutralizing agent is present.

A prerequisite for cobalt powder production is to initially form fine particles in the nucleation stage. Different cobalt metal powders can be produced by varying the composition of the feed solution and by adding inorganic salts or organic compounds which catalyze or modify the reduction mechanisms. Known cobalt-reduction catalysts such as ferrous sulphate or palladium chloride behave similarly in increasing the number of active sites on the basic cobalt slurry system.

The present work investigates the reduction kinetics of $Co(OH)_2$ using palladium chloride as a catalyst under hydrothermal conditions to produce fine cobalt powder. The effects of various parameters on the reduction conditions in the formation of sub-micron sized cobalt powders were studied. The parameters were pH of slurry, hydrogen pressure, temperature and the use of a catalyst.

2. Experiment

The hydrogen reduction experiments were carried out in an autoclave equipped with a 2 l glass lined reactor (10 cm × 25 cm H) and an agitator having a 5.8 cm diameter six-blade marine type impeller rotated at 800 rpm. The reactor is charged with 500 ml $Co(OH)_2$ slurry prepared by mixing solutions of $CoSO_4$ and NaOH stoichiometrically, and then a small amount of $PdCl_2$ was added as an activator and acetic acid as a buffer solution. Table 1 summarizes the standard hydrogen reduction conditions adapted in the present work. The chemicals used were reagent grade in purity. Sodium hydroxide was also used as a neutralizing agent.

Once the reaction temperature reached a predetermined level, hydrogen gas was introduced into the reactor after flushing a few times. The change of hydrogen pressure with reaction time was recorded to check the reduction fraction. After completion of the reaction, the cobalt powder was filtered, washed 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 while the residual cobalt ion concentration in the filtrate was measured

Table 1
Experimental conditions for hydrogen reduction

Factor	Conditions
Temperature	145–195°C
$PdCl_2$	2–12 mg/l
P_{H_2}	1–4 MPa
pH of the end solution	3.3–9.8
Co^{2+} concentration	20–60 g/l
NaOH (stoichiometrically)	110%
Acetic acid	0.8 v/o

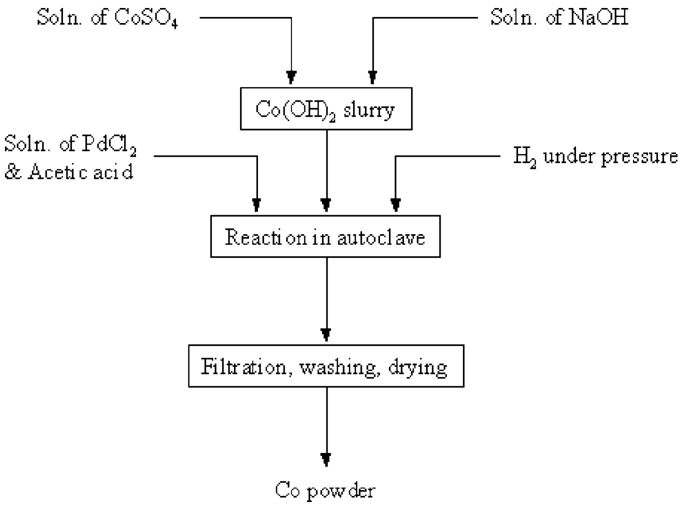

Fig. 1. Experimental procedure.

colorimetrically. Fig. 1 shows a brief overview of the experimental procedure for the present work.

3. Results and discussion

3.1. Effect of catalyst

In the cobaltous hydroxide slurry system, a catalyst is required to initiate the hydrogen reduction of cobalt ions at an appreciable rate. Palladium chloride was used and its effects on the reduction rate were studied. The concentration of palladium chloride varied in a range of 2–12 mg/l, and its effect on the reduction fraction with time is shown in Fig. 2. The reduction fraction herein essentially indicates the mol ratio of precipitated Co metal to starting Co ions. It is seen that the increase 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

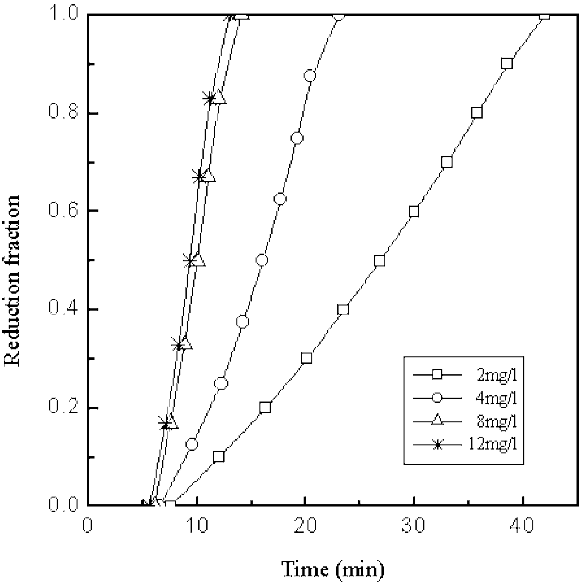

Fig. 2. Reduction fraction at various amount of $PdCl_2$ ($Co^{2+} = 30$ g/l, pH = 6, $T = 180°C$, $P_{H_2} = 3$ MPa).

the reduction reaction. An induction period of about 5–8 min is needed under the present operating conditions. Fig. 3 shows the reduction rate of Co ions with the increase in the concentration of palladium chloride. The rate increases linearly up to <8 mg/l, and becomes constant at palladium chloride concentrations above it. In other

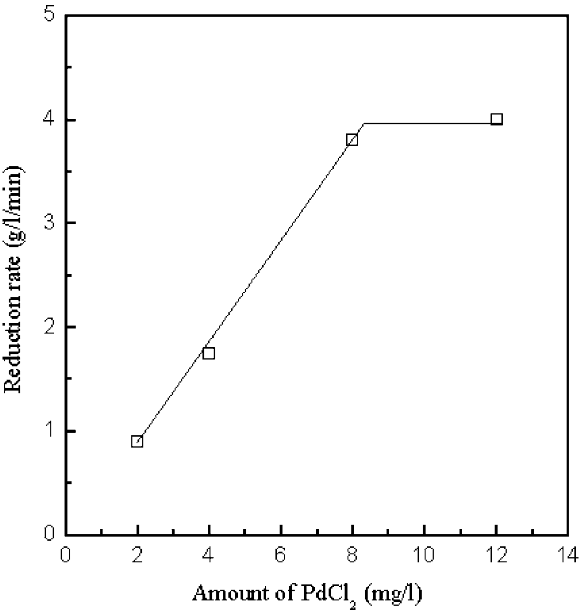

Fig. 3. Reduction rate as a function of $PdCl_2$ ($Co^{2+} = 30$ g/l, pH = 6, $T = 180°C$, $P_{H_2} = 3$ MPa).

words, the catalytic reaction with an excessive addition of the activator does not show any significant contribution to the increase in the reduction rate or the decrease in the induction period.

A serious problem in the hydrogen reduction of solutions is the tendency for the precipitated metal to plate out on the surfaces of the reactor and to form agglomerates. A considerable amount of cobalt metal was often observed to deposit on the wall of the reactor at palladium chloride concentrations under 2 mg/l. This may be because the reduction in the heterogeneous process is too slow to form cobalt metal precipitates in solution due to the insufficient addition of the catalyst; instead, the internal surfaces of the reactor act as a catalyst. On the other hand, virtually no deposition on the wall were found at palladium chloride concentrations above 8 mg/l, but some cobalt particle agglomerates existed in solution, which likely resulted from the rapid nucleation and growth of the cobalt precipitates by the excess addition of palladium chloride.

3.2. Effect of temperature

The experiments were carried out in the temperature range of 145–195°C and the kinetic values are plotted in Fig. 4. The initial reduction rates against time at different temperatures are in good agreement with the rate equation of the shrinking core model dominated by chemical reaction control for small spherical particles [10]:

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

where x is the reduction fraction, k the rate constant, and t_i is the induction period.

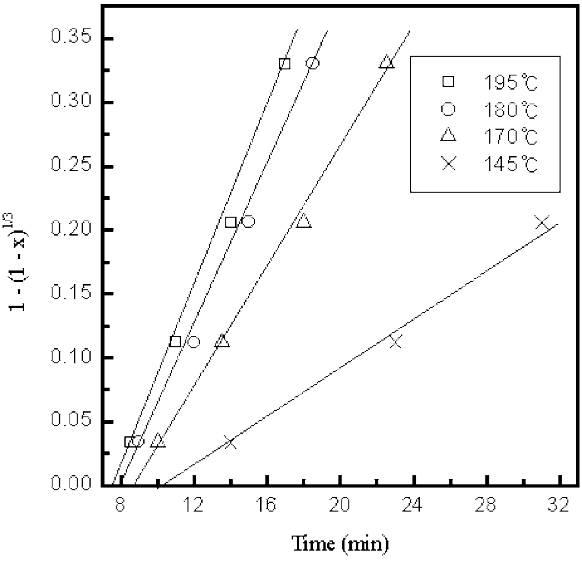

Fig. 4. $1 - (1 - x)^{1/3}$ as a function of reduction time ($Co^{2+} = 30$ g/l, pH = 6, $P_{H_2} = 3$ MPa, $PdCl_2 = 4$ mg/l).

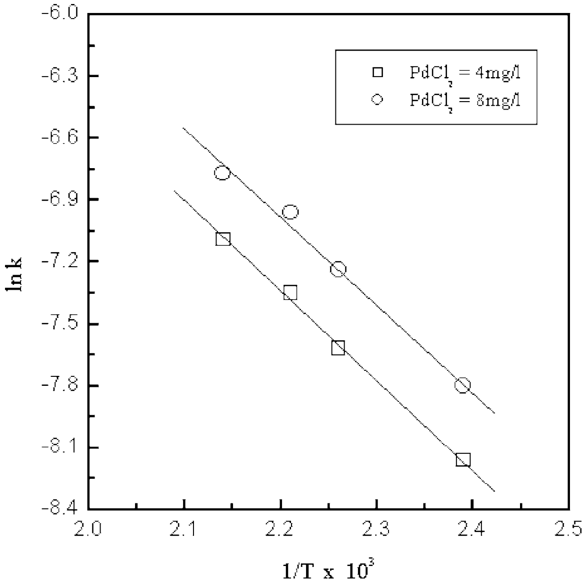

Fig. 5. Arrhenius plot of reduction rate ($Co^{2+} = 40$ g/l, pH = 6, $P_{H_2} = 3$ MPa).

The Arrhenius plots of the reduction rate in the temperature range of 145–195°C are given in Fig. 5. The apparent activation energies at two different concentrations, 4 and 8 mg/l, of $PdCl_2$ are 35.6 kJ/mol, and it can be concluded that the reaction rate is chemically controlled.

Therefore, it is certain from the results of both Figs. 4 and 5 that the chemical reaction is the dominant factor in determining the hydrogen reduction rate in the cobaltous hydroxide slurry system to produce metallic cobalt powder in the temperature of 145–195°C.

3.3. Effect of hydrogen pressure

The partial pressure of hydrogen gas in the reactor is directly involved in the reduction reaction and will affect the rate. The tests were performed with an initial hydrogen pressure in the range of 1–4 MPa, and with different temperatures, amount of catalysts, and cobaltous ions concentrations. Fig. 6 shows the experimental values of $t_{1/2} - t_i$ as a function of the initial hydrogen pressure, P_{H_2}, where $t_{1/2}$ is the half decay period resulting in half of the initial cobalt concentration and t_i is the induction period in which the initial concentration stays the same. Based on the $\log(t_{1/2} - t_i)$ versus $\log P_{H_2}$ plots which give straight lines, the following relation was found to be obeyed:

$$\log(t_{1/2} - t_i) = (1 - n)\log P_{H_2} + \log a \tag{2}$$

or

$$t_{1/2} - t_i = aP_{H_2}^{1-n} \tag{3}$$

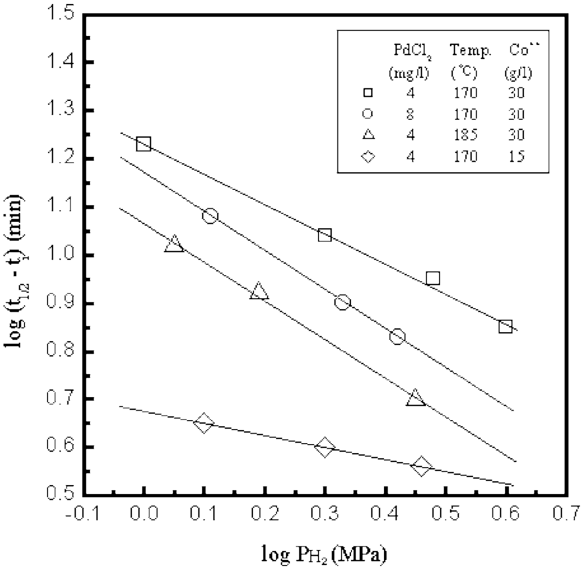

Fig. 6. Reduction time as a function of hydrogen pressure at pH = 6.

where P_{H_2} is the initial hydrogen partial pressure and n and a are constants. The value of n, the slope of a line, varies between 1.6 and 1.8 at 30 g/l of cobaltous ion concentration regardless of changes in catalyst concentration and reaction temperature, but it decreases down to about 1.3 at 15 g/l.

For irreversible reactions in a constant-volume batch reactor, it is known that the half-life of the reaction, $t_{1/2}$, as the time needed for the concentration of reactants to drop one-half the original value can be written as [11]:

$$t_{1/2} = bC_0^{1-n} \tag{4}$$

where C_0 is the initial concentration and b is a constant. Therefore, one can notice that the experimental Eq. (3) expressing the half reduction period as a term of the initial partial pressure of hydrogen gas is analogous to Eq. (4) in which a plot of log $t_{1/2}$ versus log C_0 gives a straight line of slope $1 - n$.

3.4. Effect of pH

Fig. 7 shows the reduction rate and the recovery ratio of cobalt metal plotted as a function of pH of the end solution after completing the $Co(OH)_2$ reduction. The reduction rate linearly decreases from 2.7 g/(l/min) at pH = 3.2 down to 0.27 g/(l/min) at pH = 10. On the other hand, as the pH increases, the recovery ratio rapidly increases up to nearly 100% at pH values of 6–7. Therefore, referring to the Pourbaix diagram [9], the following reduction processes can be contemplated depending on pH values.

$$\text{For pH} > 6-7, \quad Co(OH)_2 + 2H^+ + 2e^- \rightarrow Co + 2H_2O \tag{6}$$

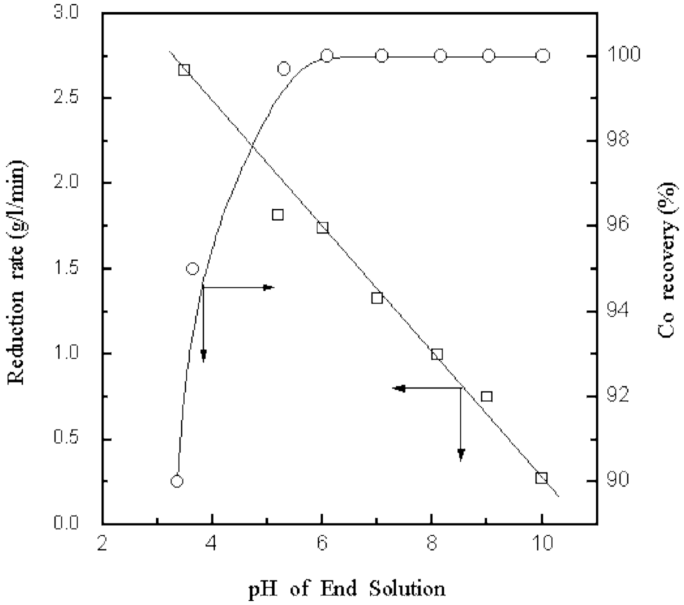

Fig. 7. Reduction rate and Co recovery at different pH of end solution (Co = 40 g/l, $P_{H_2} = 3$ MPa, $T = 180°C$, $PdCl_2 = 4$ mg/l).

and

$$\text{For pH} < 6\text{–}7, \quad Co(OH)_2 + 2H^+ \rightarrow Co^{2+} + 2H_2O, \qquad Co^{2+} + 2e^- \rightarrow Co \tag{7}$$

In the high pH range, the direct reduction from $Co(OH)_2$ 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 maximum recovery. On the other hand, Co ions which are

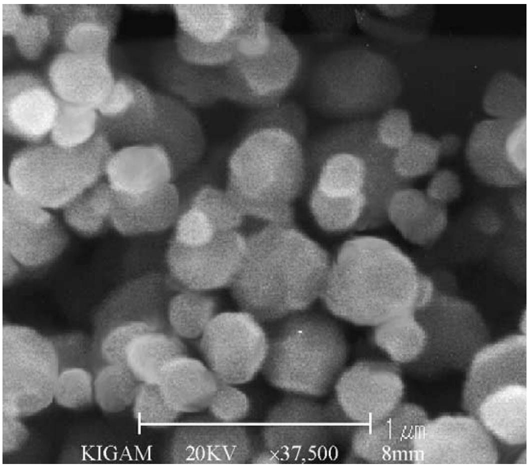

Fig. 8. SEM micrograph of Co powder.

dissolved in low pH is reduced with a high rate at first and then the lowered pH of the end solution limits the reduction resulting in low cobalt metal recovery.

A scanning electron microscopic photograph shown in Fig. 8 shows the cobalt powder produced from the cobaltous hydroxide particles generated from sulfate solution. As observed, the cobalt particles are spherical in shape with an average of 400 nm in size.

4. Conclusion

Hydrogen reduction was performed in the preparation of fine cobalt powder from cobaltous hydroxide slurry under hydrothermal conditions. It was found that the reduction rate was mainly affected by the amount of catalyst, hydrogen pressure, temperature, and the resulting pH. The cobalt powder obtained was spherical in shape with a particle size of about 400 nm.

The reduction kinetics in the temperature range of 145–195°C were well fitted to a core model equation, $1 - (1 - x)^{1/3} = k(t - t_{\mathrm{i}})$. The activation energy obtained from the Arrhenius plot was 35.6 kJ/mol at the temperature of 145–195°C. In addition, the half-life for the reduction started after the induction period was proportional to a fractional power of $1 - n$ of the initial hydrogen gas pressure.

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