Preparation of Fine Co Powder from $Co(OH)_2$ Slurry by Hydrothermal Reduction with Hydrogen

Kening Yu*, Dong J. Kim and Hun S. Chung

*Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing 100080 China

Korea Institute of Geology, Mining and Materials, Taejeon, 305-350, Korea

Abstract

The fine Co powder with an average particle size of less than 1㎛ was prepared by hydrothermal reduction with hydrogen from $Co(OH)_2$ slurry obtained by mixing the solutions of $CoSO_4 \cdot 7H_2O$ and NaOH. A method to control pH of the end solution around neutrality was proposed. The reduction rate was found to be a function of pH, temperature, hydrogen pressure and the amount of catalyst.

1. Introduction

Cobalt and nickel, in form of metal powders, can be prepared by reduction of aqueous solutions(1,2) or slurries(3~7) with hydrogen under pressure, and their production has been successfully introduced a commercial process for a long time(8). Among the literatures of the reduction of aqueous slurries, more attention was paid to nickel metal and the system with pH of the end solution lower than 8. In brief, the rise of pH of the end solution and the decline of metal recovery were very sharply occurred when the amount of alkali was near the stoichiometry, no matter what a precipitator, alkali or alkaline oxides, was used. An amount of 98% theoretical alkali was hoped to be used. Less amount gave a pH lower than 4 with a metal recovery of 90 to 95%, while larger amount gave too high a pH value for reduction to take place. But it was practically difficult to control pH so exactly in previous works.

In the present paper, the hydrogen reduction of $Co(OH)_2$ slurry obtained by mixing the solutions of $CoSO_4 \cdot 7H_2O$ and NaOH was studied. A simple and effective method of controlling pH of the end solution between 5 and 8 was pursued. The influences of pH, temperature, pressure and catalyst etc. on the reduction were investigated.

2. Experimental Method

The hydrogen reduction experiments were carried out in a 2 liter stainless steel autoclave equipped with a glass liner of the same volume and an agitator having one 5.8 ㎝-diameter 6-blade marine type impeller.

The autoclave was charged with 500㎖ of a slurry obtained by mixing the solutions of $CoSO_4 \cdot 7H_2O$ and NaOH, and, meanwhile small amounts of $PdCl_2$ as a catalyst and acetic acid as a buffer were added into the slurry. After sealing, the autoclave was purged with hydrogen for two or three times and heated up to a presetted temperature. Once the reaction temperature was reached, hydrogen gas was introduced into the autoclave. The reduction rate was determined from the rate of pressure decrease. After the completion of the reaction, cobalt powder was filtered, washed and dried under nitrogen gas. The chemicals used for the study were reagent-graded in purity. In most of the tests, a rotation speed of 800rpm was used to obtain a good gas/liquid transfer.

3. Result and Discussion

Fig. 1 shows that pH of the end solution has obvious effects on the reduction rate and Co metal recovery. The reduction can be finished in 15min. with the Co metal recovery of 90 to 95% at pH of the end solution lower than 3.5, and contrarily it needs 1 hour and more at pH higher than 8 although 100% of Co is possible to be reduced to metal. So it is desirable to meet the pH of the end solution between 5 and 8 considering both the two sides. It is practically impossible to do so precisely without buffer agent. Therefore acetic acid was chosen to form a buffer system of pH 5~8 together with a small excess amount of NaOH. In case of adding several ㎖ of CH_3COOH into 500㎖ of $Co(OH)_2$ slurry, it was not necessary to control precisely the addition of alkali, thus simplifying actual operation.

The effects of temperature, hydrogen pressure and the amount of $PdCl_2$ (as the catalyst) on the reduction rate are separately shown in Fig. 2, 3 and 4. It can be seen that the reduction rate is mainly a function of temperature and the amount of $PdCl_2$. It shows about twice when temperature increases from 145℃ to 180℃ or the addition of $PdCl_2$ varies from 2㎎/ℓ to 4㎎/ℓ. Short induction periods always occur and mainly depend on hydrogen pressure, which may influence the appearance of the first cobalt nuclei.

Based on the results, the hydrogen reduction of $Co(OH)_2$ slurry could be completed in 20~30 min under following conditions : a small excess amount of NaOH to ensure the total conversion of cobalt from $CoSO_4$ into $Co(OH)_2$, a small amount of CH_3COOH as the buffer to keep pH of the end solution between 5 and 8, 180℃ of reduction temperature,

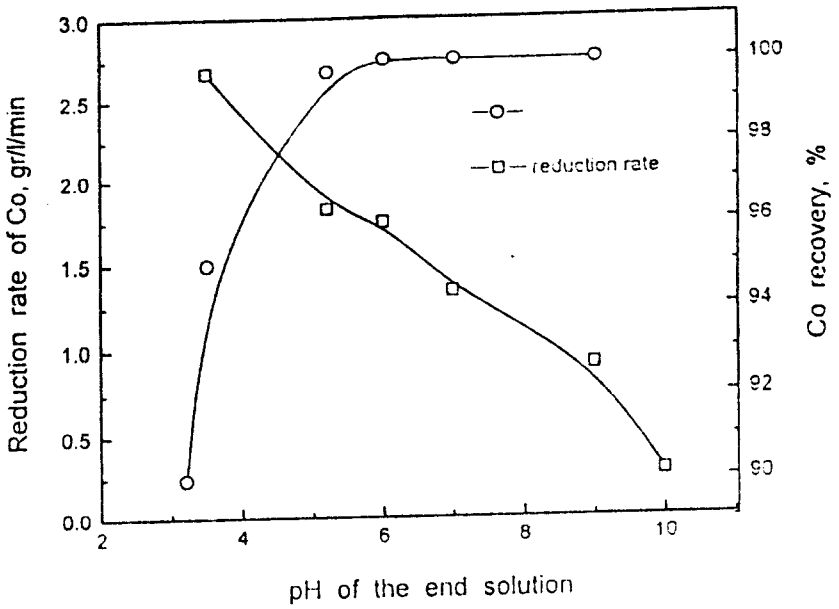

Fig. 1. Co recovery % and reduction rate at different pH of the end solution.

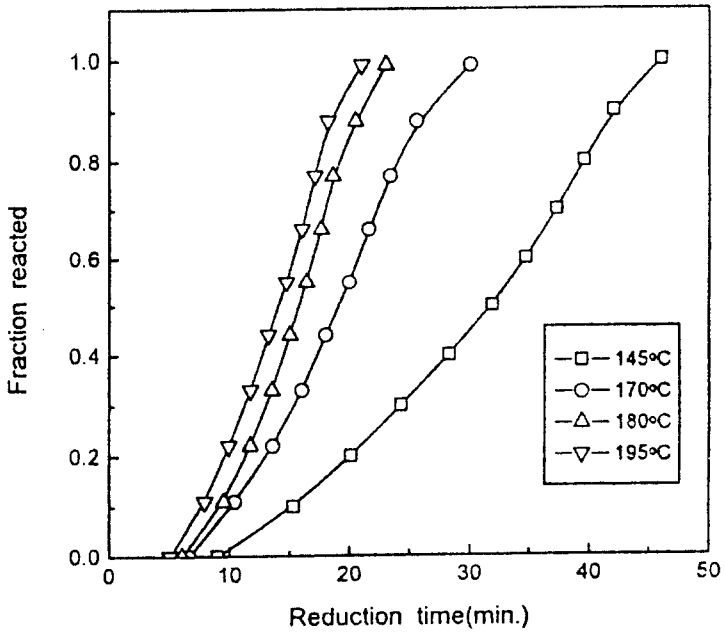

Fig. 2. Fraction reacted at different temperature.

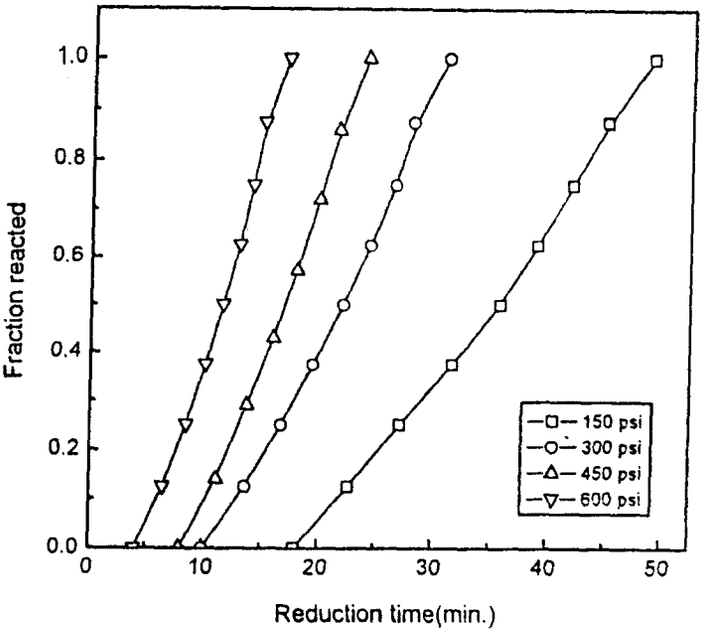

Fig. 3. Fraction reacted at different hydrogen pressure.

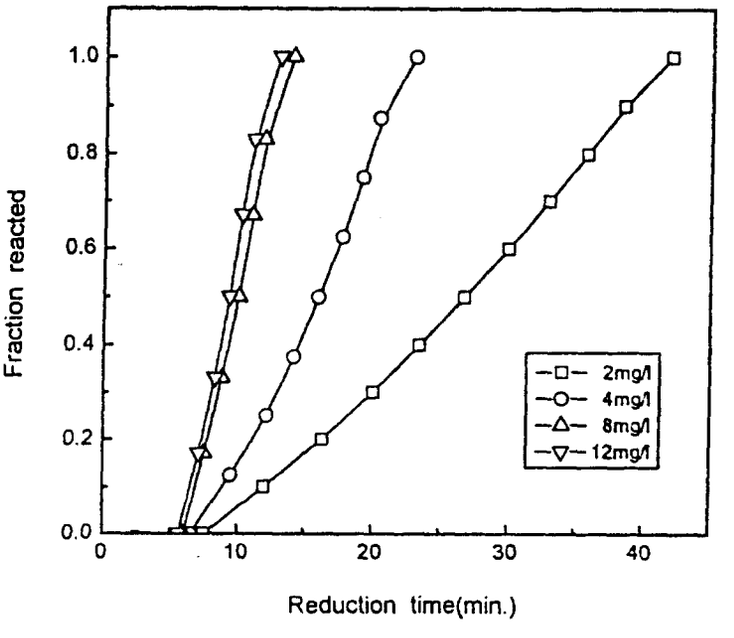

Fig. 4. Fraction reacted at various amounts of $PdCl_2$.

450psi of hydrogen pressure and 4~8㎎/ℓ of $PdCl_2$ as the catalyst.

4. Conclusion

The fine Co powder with an average particle size of less than 1㎛ was prepared by hydrothermal reduction with hydrogen under pressure from $Co(OH)_2$ slurry obtained by mixing the solutions of $CoSO_4 \cdot 7H_2O$ and NaOH.

The following results are summarized ;

1). The precise control of pH between 5 and 8 was achieved by adding a little acetic acid into the $Co(OH)_2$ slurry to form a buffer system together with a small excess amount of NaOH.

2) The reduction rate was mainly a function of pH of the end solution, the amount of $PdCl_2$, temperature and hydrogen pressure. Short induction period occurs but mainly depend on hydrogen pressure.

3) The optimum preparing conditions were found to be at pH of the end solution between 5 and 8, 180℃ of the reduction temperature, 450psi of the hydrogen pressure and 4~8㎎/ℓ of $PdCl_2$.

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From Solution :

$$MSO_4 + nNH_3 + H_2 \longrightarrow M + (NH_4)_2SO_4 + (n-2)NH_3$$

M = Ni, Co, Cu

From Slurry :

$$M(OH)_2 \cdot MCO_3 \cdot xH_2O + 2H_2 \longrightarrow 2M + CO_2 + (x+3)H_2O$$

or

$$M(OH)_2 + H_2 \longrightarrow M + 2H_2O$$

$$NiSO_4 \cdot 6H_2O + NaOH \rightarrow Ni(OH)_2 + Na_2SO_4 + 6H_2O \quad (1)$$

$$Ni(OH)_2 + H_2 \rightarrow Ni + 2H_2O \quad (2)$$

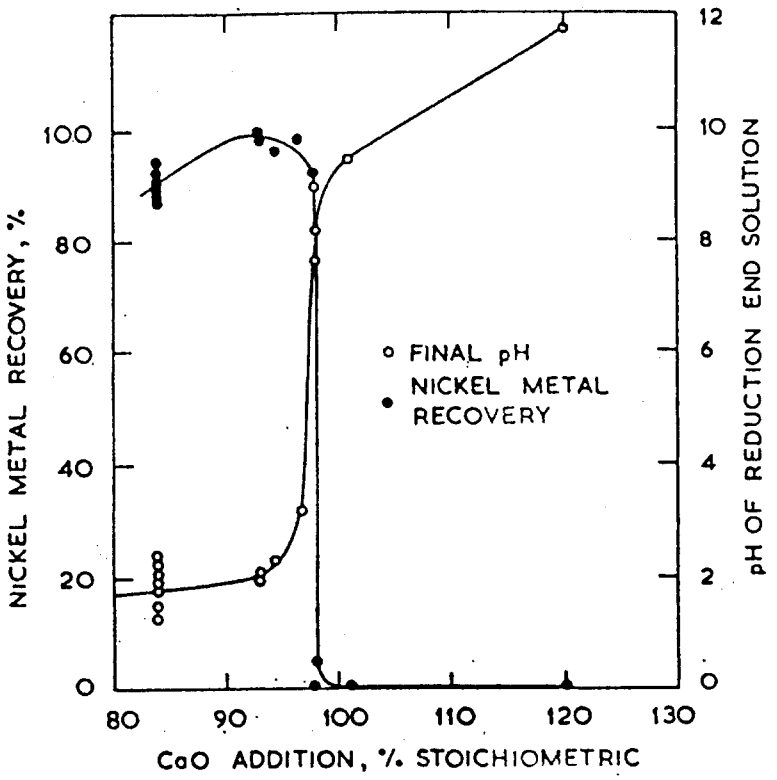


FIG.0 NICKEL RECOVERY IN THE $Ni-SO_4-CaO$ SYSTEM

Content

1. Introduction

reduction of slurries ;

most on Ni, pH <8 (<4 in fact)

pH 5~8 difficult to meet

pH >8 ICM } different design for

few on Co, pH >8 ICM } autoclave & agitator

pH 5~8 (the objective of the present work)

2. Experimental Method

$CoSO_4$ + NaOH $\longrightarrow$ $Co(OH)_2$ $\xrightarrow{PdCl_2\ \&\ CH_3COOH}$ autoclave (180℃, 450psi PH_2, ~30min.) $\longrightarrow$ filtered, washed & dried under N_2

3. Result and Discussion

4. Conclusion

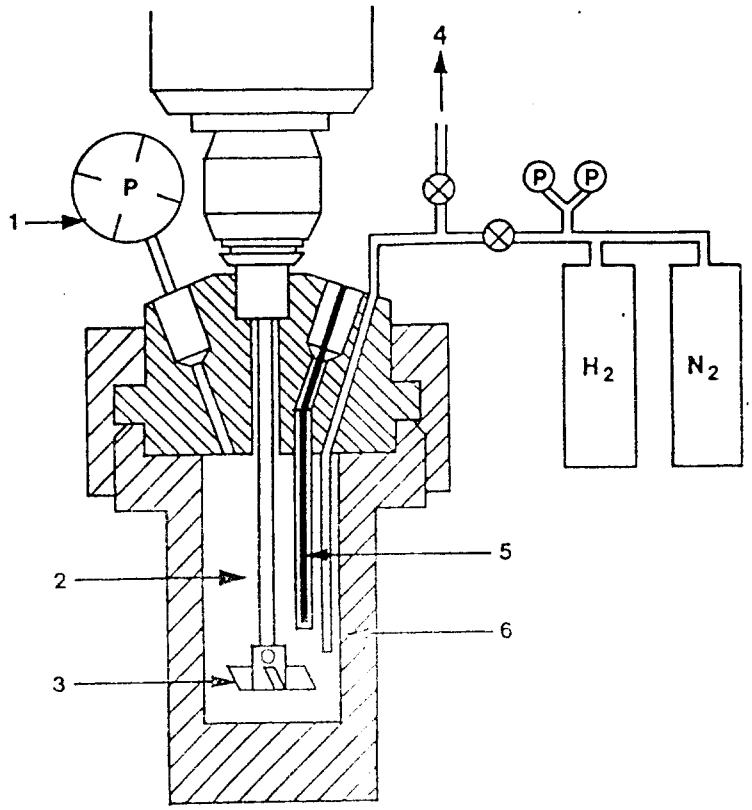


Fig. 2. Schematic diagram of experimental apparatus

1) pressure gage
2) reaction vessel
3) stirrer
4) sampling out
5) temperature controller
6) heating element

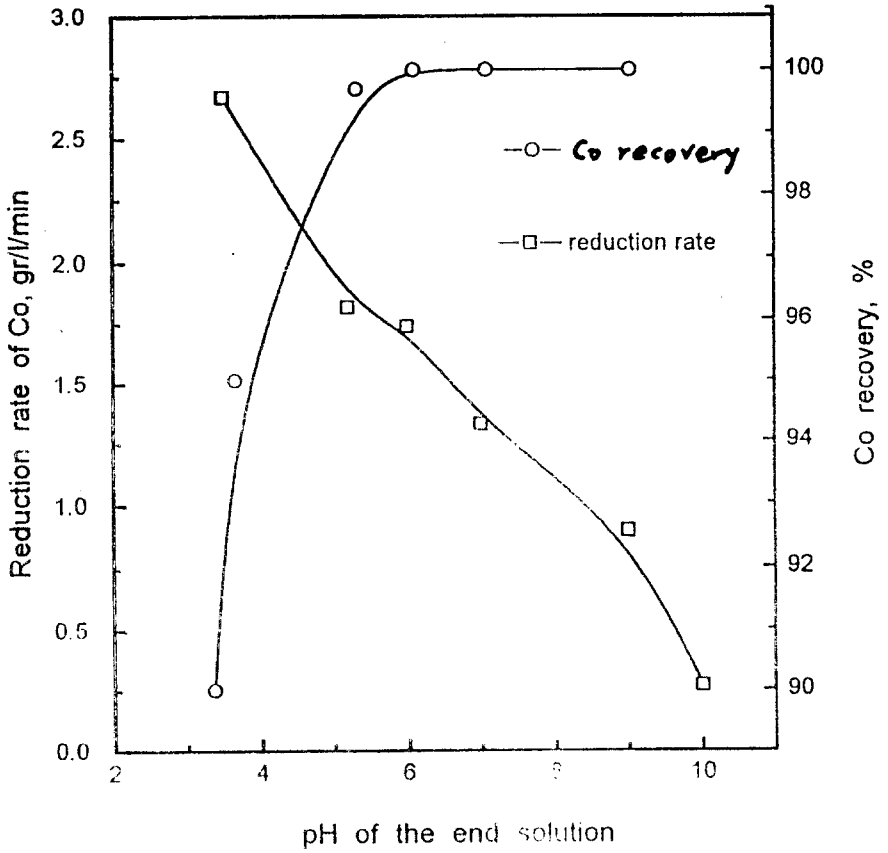


Fig. 1. Co recovery % and reduction rate at different pH of the end solution. { Co ; 40gr/l, PH_2 ; 450psi, 180-190°C, 800rpm, $PdCl_2$; 4mg/l }

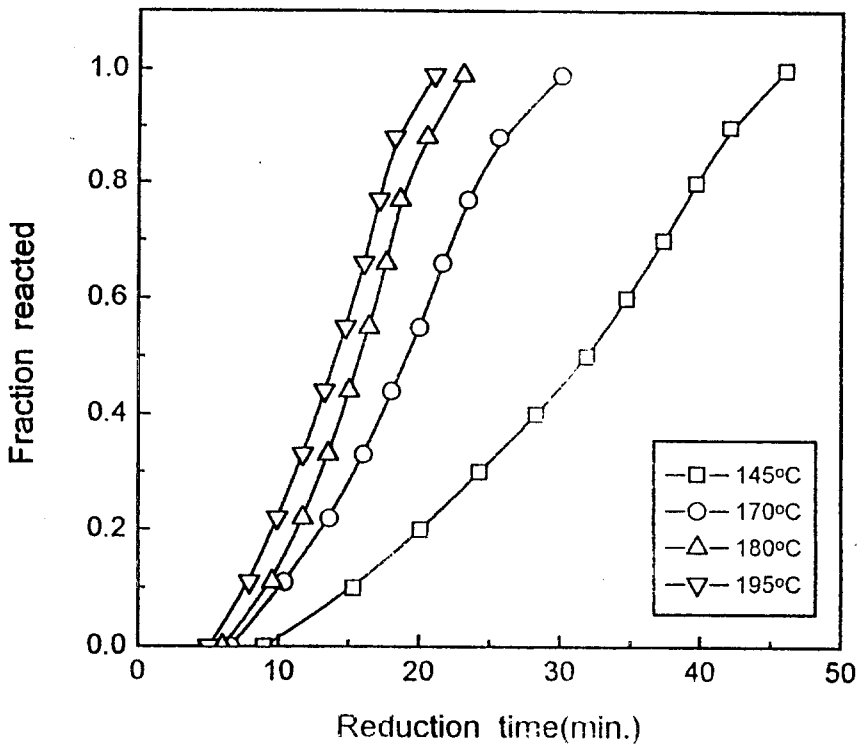


Fig. 2. Fraction reacted at different temperature.
{ Co ; 40gr/l, pH ; 6.1-6.3, PH_2 ; 450psi,
$PdCl_2$; 4mg/l, 900rpm }

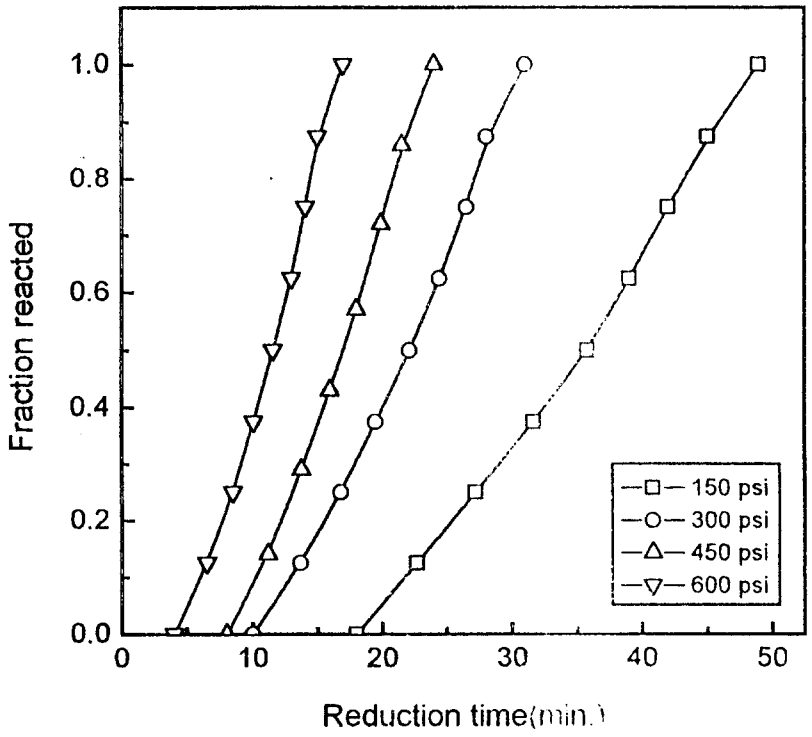


Fig. 3. Fraction reacted at different hydrogen pressure.
{ Co ; 30gr/l, pH ; 5.5-5.6, 170-175°C, 800rpm,
$PdCl_2$; 4mg/l }

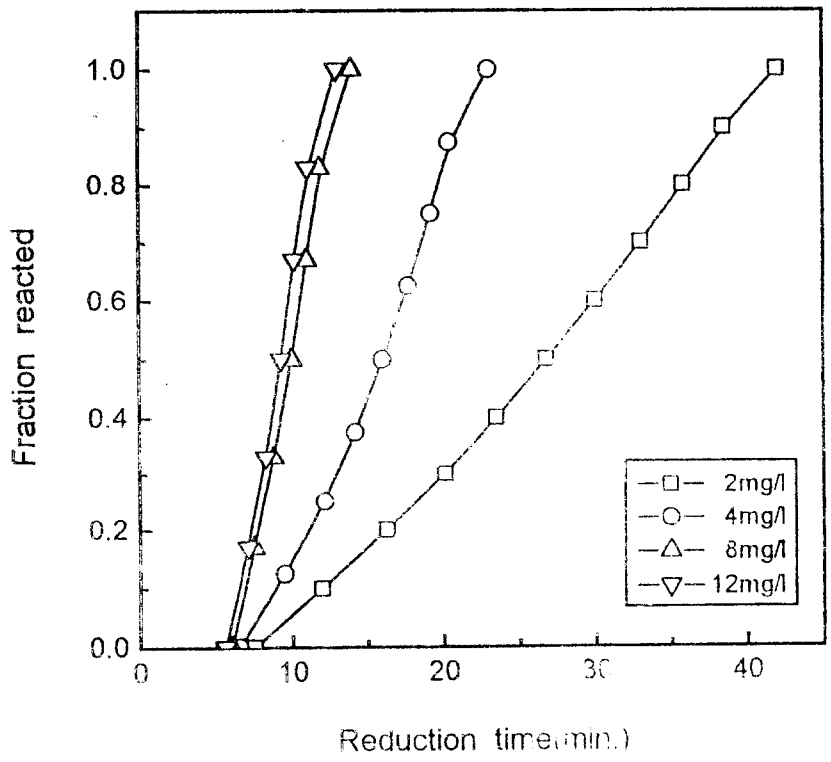


Fig. 4. Fraction reacted at various amounts of $PdCl_2$.
{ Co ; 30gr/l, pH ; 5.5-5.7, 175-185°C, 800rpm,
PH_2 ; 430psi }

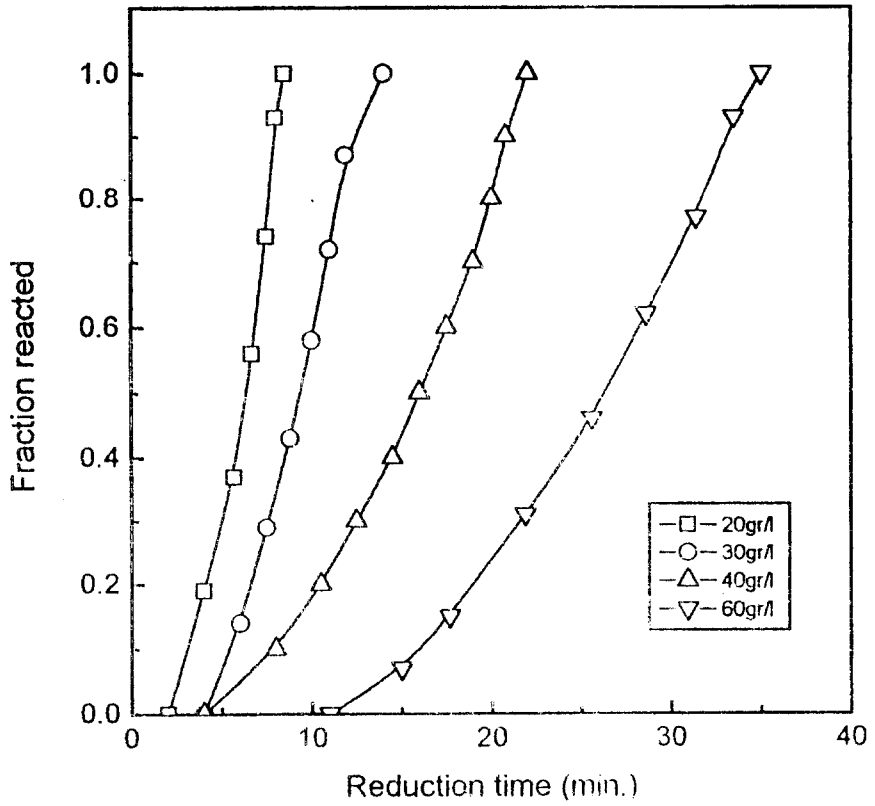


Fig. 5. Fraction reacted at various cobalt concentrations.
{ pH ; 5.2-5.6, 180-190°C, 800rpm, PH_2 ; 400psi,
$PdCl_2$; 4mg/l }

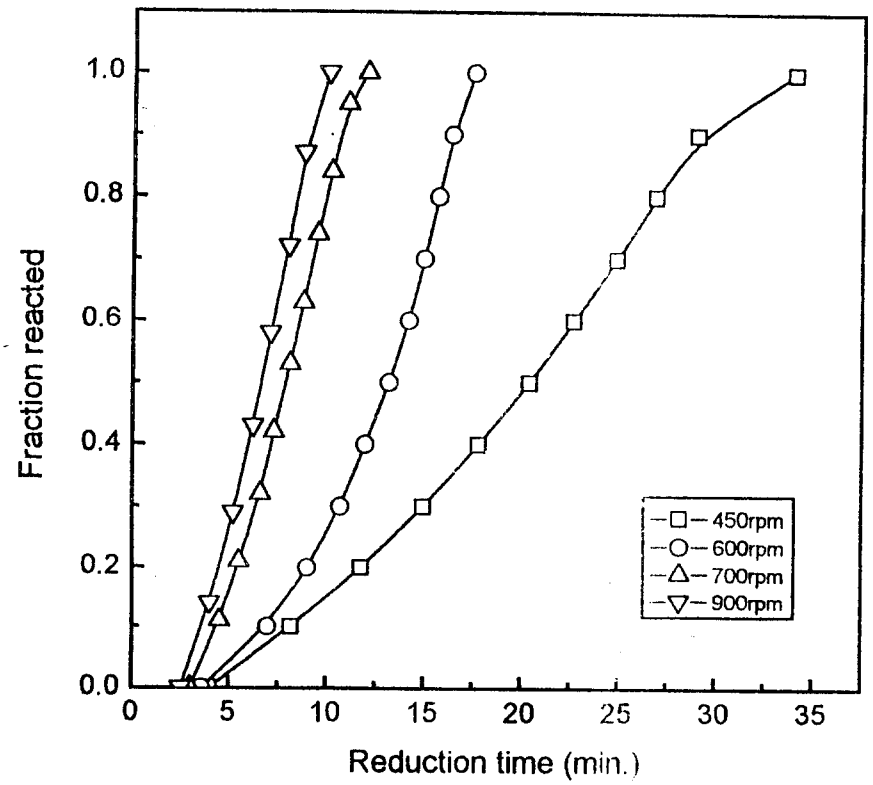
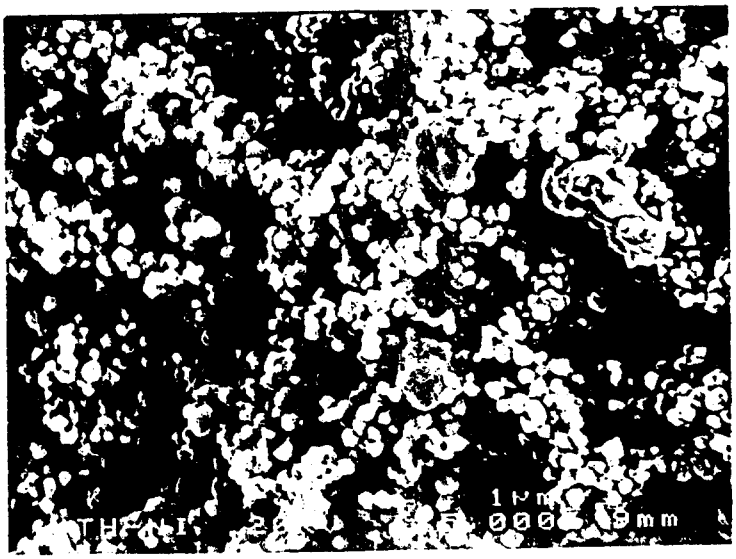


Fig. 6. Effect of stirring speed on the reduction.
{ pH ; 6.4-6.9, 180-190°C, Co ; 40gr/l, PH_2 ; 450psi, $PdCl_2$; 4mg/l }

$Co(OH)_2$
irregular

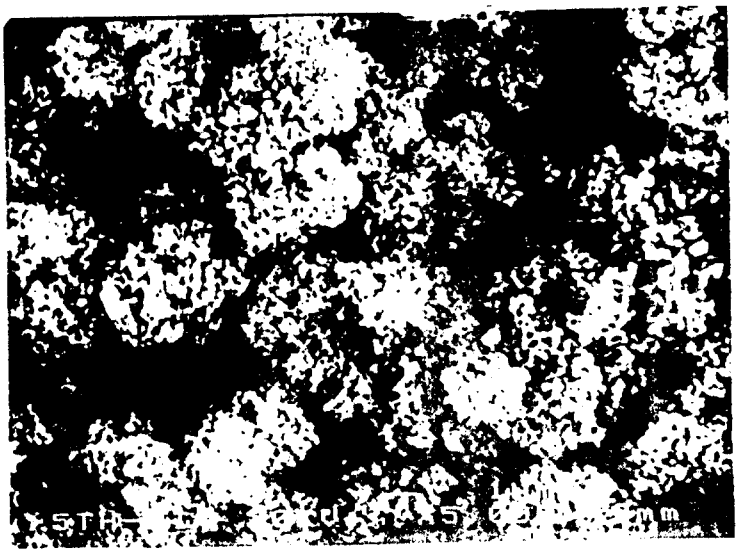
Co
at $PdCl_2$ 2 mg/l
pH 5.6

~ 0.5 μ



Co
at $PdCl_2$ 12 mg/l
pH 5.7

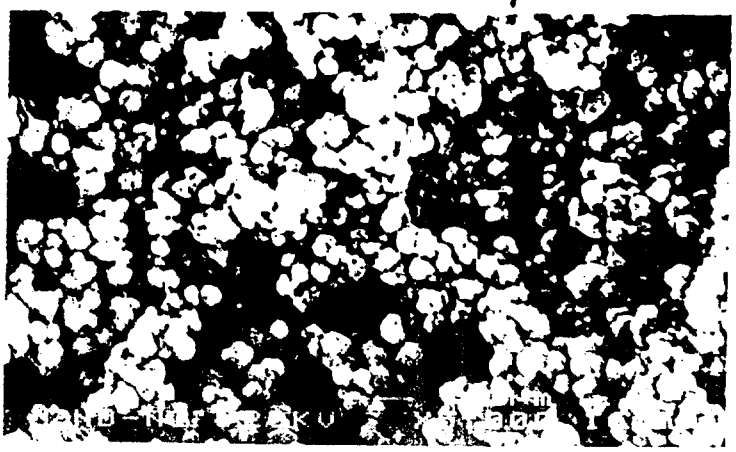
0.1 ~ 0.2 μ



$PdCl_2$ 4 mg/l

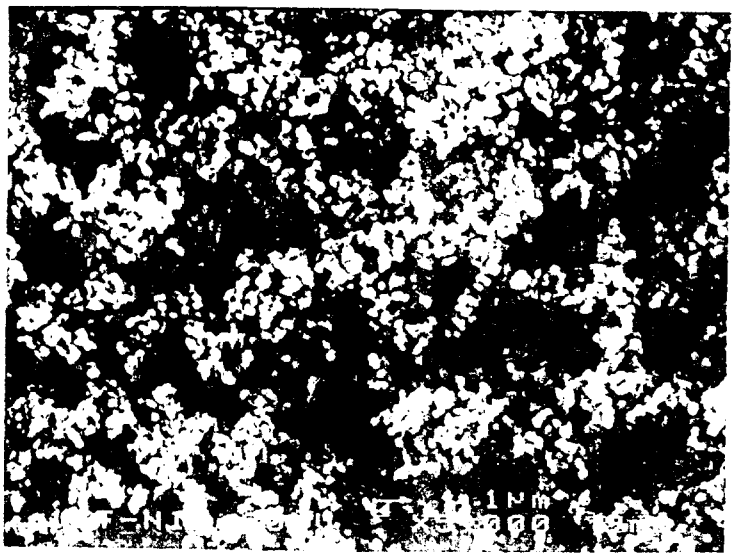
Co
pH 3.2

~ 1 μ



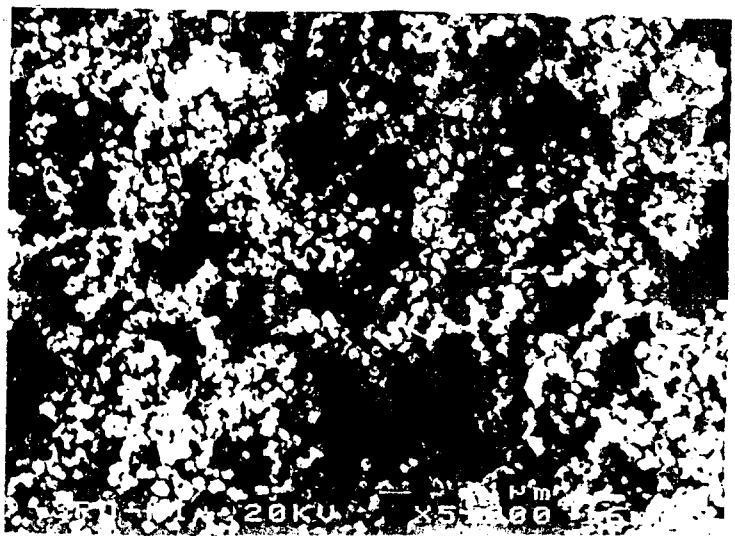
Co
pH 6.5

~0.3 μ



Co
pH 9.8

~0.3 μ



Conclusion

The fine Co powder with an average particle size of less than 1㎛ was prepared by hydrothermal reduction with hydrogen under pressure from $Co(OH)_2$ slurry obtained by mixing the solutions of $CoSO_4 \cdot 7H_2O$ and NaOH.

The following results are summarized ;

1) The optimum preparing conditions were found to be at pH of the end solution between 5 and 8, 180℃ of the reduction temperature, 450psi of the hydrogen pressure, 60gr/ℓ of Co or less, 4~8㎎/ℓ of $PdCl_2$ and 800rpm of the speed.
2) The satisfactory control of pH between 5 and 8 was achieved by adding a little acetic acid into the $Co(OH)_2$ slurry to form a buffer system together with a small excess amount of NaOH.
3) The reduction rate was mainly a function of pH of the end solution, the amount of $PdCl_2$, temperature and hydrogen pressure. Short induction period occurs but mainly depend on hydrogen pressure.