論 文 内 容 要 旨

Chapter 1: Introduction

For last decade, metal nanoparticles have attracted many researchers' attention because of their superior chemical and physical properties, such as catalytic, optical, electrical, and magnetic properties. Several synthesis methods have been reported to produce metal nanoparticles. However, large amount of organic solvents and highly reactive reducing agents are required in most syntheses. Since considerable cost is required to treat wasted organic solution and to recycle organic solvents, those synthesis methods are still difficult task to be applied in industry. Thus, environmentally benign solvents are required to replace organic solvents.

Reductive supercritical hydrothermal synthesis is one of the most prospective environmentally benign processes to produce metal nanoparticles. Water can satisfy both economic and environmental points of view, since water is clean, inexpensive, and recyclable with relatively low cost. Most importantly, supercritical water can provide high concentrated reaction condition. At near the critical point of water, the dielectric constant of water dramatically decreases, thus water can act as organic solvents. In this reaction condition, precursor, reducing agent, and organic modifier used as capping agent make a homogenous phase. Then, mono-dispersible organic modified metal nanoparticles can be synthesized. Although supercritical water has many advantages as solvent for producing metal nanoparticles, few reports on the synthesis of metal nanoparticles have been reported. Also, the reaction mechanism of synthesizing metal nanoparticles under supercritical water condition has not yet reported.

In this study, metal nanoparticles such as Co and Ni, were synthesized with/without organic surface modifiers, using reductive supercritical hydrothermal synthesis. The reaction mechanism was also elucidated by using thermodynamic tools. Finally, continuous synthesis of cobalt nanoparticles was developed on the basis of the reaction mechanism and theoretical results obtained from thermodynamic analysis.

Chapter 2: Back Ground of Research

To analyze the redox reaction of metal and to estimate the required amount of reducing agent,

thermodynamic analysis is required. The Ellingham diagram is a well known thermodynamic tool to determine the direction of the redox reaction between metal and metal oxide. The main chemical equation is described as follows

$$\text{MeO}(s) + \text{A} \xrightarrow{K_{eq}} \text{Me}(s) + \text{A}' \tag{1}$$
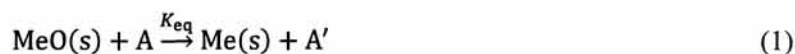
where MeO represents metal oxide, A represents $H_2(g)$, $C(s)$, or $CO(g)$, Me represents metal, and A' represents $H_2O(g)$, $CO(g)$, or $CO_2(g)$. K_{eq} represents the equilibrium constant of reaction.

When the value of K_{eq} is obtained, the required amount of reducing agent for forward reaction can be estimated. The Ellingham diagram is generally used for several metal-metal oxide systems, but solvent effect on each component is not taken into account. The revised HKF EOS (Helgeson, Kirkham, and Flowers equation of state) model [1] is applied to calculate the solvent effect on each component at supercritical water condition.

The HKF EOS provides precise values of the standard partial molar Gibbs free energies of formation, of each aqueous species, $\Delta \bar{G}_f^\circ$, including electrolytes, ions and neutral materials. With summation of the Gibbs free energy of formation of each species, the standard partial molar Gibbs free energy of reaction, $\Delta_r \bar{G}^\circ$, is calculated, and then the value of K_{eq} is can be obtained by following equation.

$$K_{eq} = e^{-\Delta_r \bar{G}^\circ/(RT)} \tag{2}$$

By using the revised HKF EOS, the precise value of the equilibrium constant of reaction can be obtained even under the supercritical condition. However, the multiphase effect on the batch reactor system is not considered. When we use hydrogen obtained from the decomposition of formic acid, amount of dissolved hydrogen gas in liquid water should be considered, since most of hydrogen gas immediately goes to gas phase during the heating process. The amount of dissolved hydrogen gas in liquid water has to be identified to design and optimize the reaction system. To calculate these values, PSRK EOS (predictive Soave Redlich Kwong EOS) [2] was applied.

Chapter 3: Reductive Supercritical Hydrothermal Synthesis of Metal Nanoparticles and Development of the Reaction Mechanism

Cobalt nanoparticles were synthesized at near the critical point of water with batch reactor. An aqueous solution of cobalt (II) acetate tetrahydrate (0.1 M) was used as a precursor and formic acid was used as a source of hydrogen gas that acts as a reducing agent. The experiments were conducted at low and high temperatures around the critical point of water. The crystallographic phases were investigated by using XRD analysis, and the obtained cobalt peak intensity from the XRD peak patterns was described in Figure 1. It describes the Co peak intensity percentage obtained from comparison
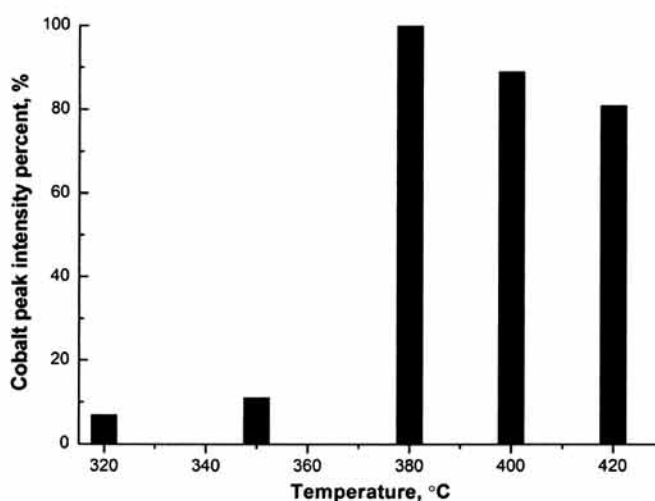

Figure 1 Cobalt peak intensity percent at various reaction temperatures.

between fcc Co and CoO. At low temperature condition, small amount of cobalt nanoparticles was synthesized. However, at near the critical point of water, only cobalt nanoparticles were obtained, since all the produced H_2 could take part in the reduction. Over the critical point, Co peak intensity percent was decreased. Lack of amount of H_2 causes the formation of CoO. Since the reaction is exothermic, the more amount of H_2 gas is required.

Figure 2 Schematic diagram of reaction mechanism under the reductive supercritical hydrothermal synthesis

On the basis of the results, the reaction mechanism was elucidated. The schematic diagram of the reaction mechanism is described in Figure 2. In the batch reactor system, the reaction temperature increases slowly because of long heating process, which takes 6 min to reach 380 °C. During the heating process, CoO is expected to be formed. Since most of hydrogen gas, from the decomposition of formic acid cannot dissolve in the liquid water, only small portion of the hydrogen can take part in the reduction.

At near the critical point of water all the hydrogen gas can take part in the reduction, since a homogenous phase is formed in the reactor. However, large amount of hydrogen gas is required to produce cobalt nanoparticles, because metal oxide is already formed during the heating process. Thus, high concentration of hydrogen gas is required as the reaction temperature is increasing. Therefore, near-critical condition provides better environment for the synthesis of cobalt nanoparticles by making a homogenous phase.

Chapter 4: Surface Modification for Organic Modified Cobalt Nanoparticles in the Reductive Supercritical Hydrothermal Synthesis

The cobalt nanoparticles were modified by using nine organic modifiers. Trioctyl-phosphine oxide, oleic acid, lauric acid, oleylamine, and decylamine provided cobalt nanoparticles without any impurities. However, trioctyl-phosphine (TOP), sodium dodecylbenzene sulphonate, diethyl-decylphosphonate, and 1-dodecanthiol couldn't produce cobalt nanoparticles without any impurities. The effect of organic modification on the reduction is also investigated by using oleic acid. In the previous chapter, the formation of metal oxide is confirmed during the heating process. To suppress growth of the metal oxide, oleic acid was employed. By employing oleic acid, the required amount of formic acid
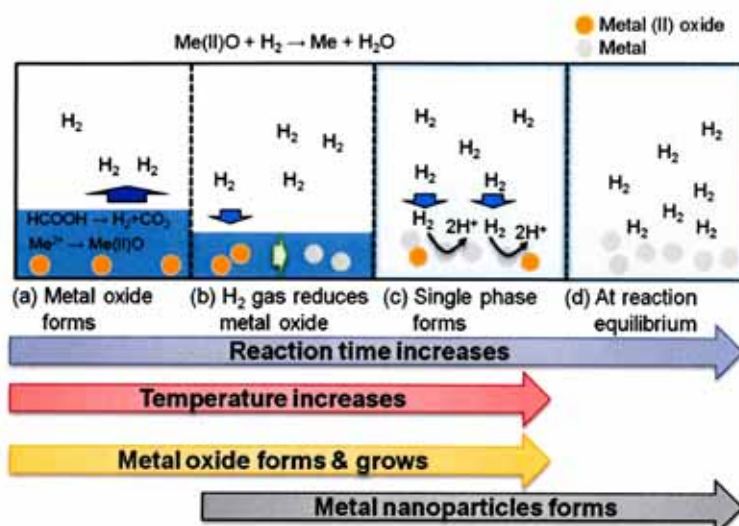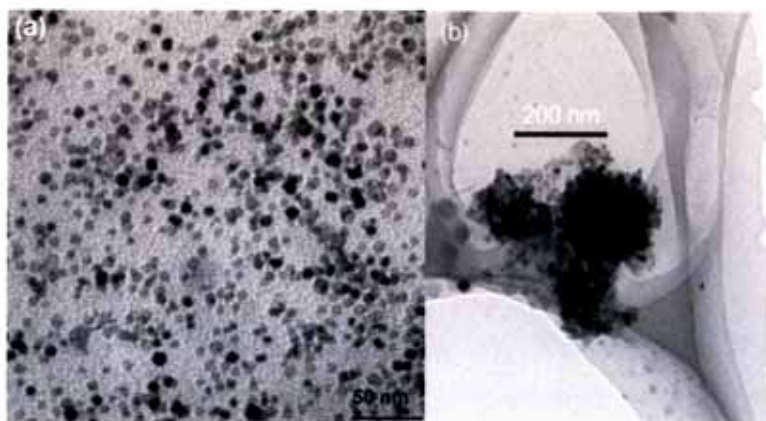

Figure 3 Oleic acid modified cobalt nanoparticles (a) after pH adjustment (b) before pH adjustment.

was reduced. To increase the interaction between oleic acid and cobalt nanoparticles and that between oleic acid and CoO, pH condition was adjusted for the reaction. The electric charge is increased by thinking conditions of pKa of oleic acid, isoelectric point (IEP) of CoO and IEP of Co together. At pH 5.2, the electric charge was maximized because of highly deprotonated oleic acid and positively charged surface of cobalt and CoO. The required amount of formic acid was reduced from non-pH adjusted reaction system. The TEM images of the synthesized oleic acid modified cobalt nanoparticles were shown in Figure 3. The morphology and size of the particles are observed in the images. Figure 3 (a) shows oleic acid modified cobalt nanoparticles after pH adjustment, and (b) shows oleic acid modified cobalt nanoparticles before pH adjustment.

Chapter 5: Development of flow reactor system for the reductive hydrothermal synthesis of the cobalt nanoparticles

On the basis of the results of previous chapters, cobalt nanoparticles were continuously synthesized by using a flow type reactor. By calculating the equilibrium constant of the reaction using the PSRK EOS, the required amount of hydrogen gas was estimated [3]. The estimated required amount of formic acid was described in the Figure 4. The experimental results of batch reactor system were plotted in the same figure for the comparison. The required amount of formic acid in the flow reactor was well matched with the estimated value. In addition, surface modification of the cobalt nanoparticles developed by using trioctyl-phosphine (TOP). The performance of the modification was increased with increasing amount of TOP.
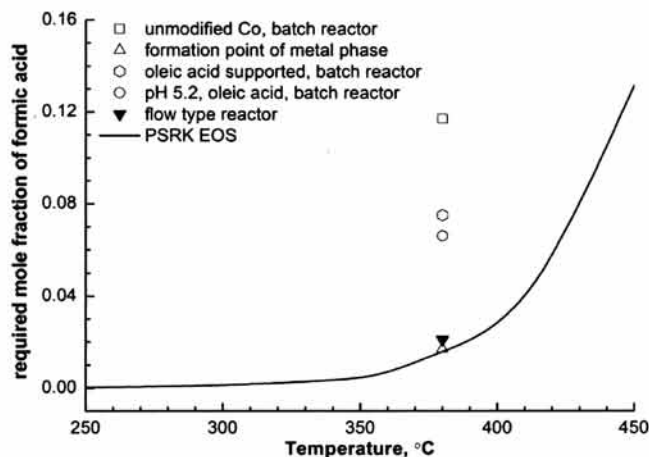

Figure 4 Estimation of the required amount of formic acid for producing cobalt nanoparticles. The symbols show experimental data.

Chapter 6: Summary

In this thesis, novel synthesis method for metal nanoparticles was introduced by using supercritical water. At near the critical point of water, the reduction occurred by hydrogen gas was promoted, since supercritical water condition provides a homogenous phase. The reaction mechanism was also elucidated by calculating amount of hydrogen gas in liquid water phase. Organic modification for cobalt nanoparticles were also succeeded with oleic acid, and pH adjustment was conducted to increasing electric charge between modifier and Co and that between modifier and CoO. Finally, based on the estimation of the required amount of formic acid, cobalt nanoparticles were continuously synthesized with and without organic modifier (TOP).

Reference [1] Tanger IV et al., *Am. J. Sci.* **288** (1988) 19-98. [2] Holderbaum et al., *Fluid Phase Equilib.* **70** (1991) 251-265. [3] Seong et al., *J. Supercritical fluid* **60** (2011) 113-120.

論文審査結果の要旨

　本論文は、優れた物理化学特性による触媒や磁性材料そして導電性材料への応用が期待される金属ナノ粒子の合成を対象とし、有機溶媒で表面を修飾したハイブリッド金属ナノ粒子の合成プロセスの開発に取り組んだものである。

　第1章では本研究の背景の概要を述べ、ナノ金属の物性を整理した。さらに、既往の金属ナノ粒子合成方法を紹介し、本研究で提案する合成方法の必要性を述べ、研究目的を設定した。

　第2章では、既往の水熱合成法と超臨界合成法を整理し、本研究の位置付けを明確にした。続いて金属の酸化還元反応で用いる熱力学的な理論をまとめた。さらに、超臨界水の溶媒効果を表現するため、修正HKF式を用いた。これらの枠組みを示すことで、本研究が究めて高い独自性を有することを示した。

　第3章では、還元場制御による超臨界水熱合成法を用いて、金属ナノ粒子を合成した結果を述べている。水素ガスを還元剤として用いると、臨界点近傍でもっとも金属ナノ粒子を合成しやすいことを見出した。これは、低温では水素ガスと水溶液が相分離する一方、均一相を形成する超臨界場では低温ほど金属生成反応の平衡が有利となるためである。高圧状態とすれば、亜臨界状態でも均一相で反応を進行させうることを確認した。また、本反応場における反応機構についても、反応の初期過程では酸化物ナノ粒子が生成し、反応後期で金属に還元されることを明らかにした。

　第4章では、還元場制御による超臨界水熱合成法に表面修飾剤を加え、有機無機ハイブリッドコバルトナノ粒子の合成に挑戦した。様々な修飾剤を用い、その種類による結晶相の変化を評価した。また、修飾剤を用いることで酸化物の生成が抑制されることを確認し、修飾剤の利用で金属ナノ粒子の合成に必要な水素の量を減らせることを実証した。さらに、pHを調整して表面修飾剤と金属ナノ粒子表面の相互作用を増加させることで、金属ナノ粒子の合成に必要な水素の量を減らすことに成功した。さらに、生成する金属ナノ粒子に、より多くの修飾剤分子を結合させることで金属ナノ粒子を溶媒中で分散安定化させることに成功した。

　第5章では、流通式反応装置を用いて金属コバルトナノ粒子の連続合成を行った。3章の機構によれば、初期に生成する酸化物ナノ粒子の粒子径を小さくできれば、還元反応に必要な水素量を削減できると考え、流通式装置を用いた急速昇温法により金属ナノ粒子の合成を行った。その結果、還元に必要な水素量は、反応のギブズ自由エネルギーから評価される理論的水素量とほぼ等しいことを確認した。

　第6章では、まとめと考察を行った。

　以上、本論文は、これまでにまったく報告されたことのない反応メカニズムを明確にするとともに、反応条件を最適化し、有機表面修飾されたコバルトナノ粒子の連続合成を実現した。また、有機表面修飾剤を利用して反応中に生成する酸化物を抑制することで必要な還元剤の量を減らすことに成功した。これらの成果は究めて独自性が高く、全く新しい研究分野の開拓につながるものであると判断でき、化学工学の発展に寄与する所が少なくない。

　よって、本論文は博士(工学)の学位論文として合格と認める。