

탄소에 분산된 니켈 입자의 자기 특성

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Magnetic Properties of Spherocharb Supported Nickel Particles

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요 약. 540°C에서 탄소에 분산된 니켈 입자를 제조하여 니켈 덩어리 및 산화 마그네슘에 지지된 니켈 입자의 자기 특성과 상호 비교 검토하였다. 환원대기에 무관하게 니켈은 탄소와 반응함을 알 수 있었다. 또한 니켈-탄소간의 상호작용 가능성에 관하여 논의하였다.

ABSTRACT. Dispersed nickel particles on Spherocharb were prepared at 540°C in various reaction atmosphere. Magnetic properties of these samples were determined, and results were compared with those of unsupported and MgO supported nickel particles. It was shown that nickel react primarily with carbon regardless of reducing atmosphere. In addition, apparent possibility of nickel-carbon interaction was discussed.

INTRODUCTION

The group VIII transition metals are well known to be active catalysts for the C-H₂ and C-H₂O reactions and have often been studied using graphite as the carbonaceous material. In a thermogravimetric study Mckee² examined the catalytic effects of a number of metals on the kinetics of hydrogenation of graphite at temperatures between 600 and 1000°C. Weight-change measurements at a linearly increasing temperature rate in a stream of dry hydrogen indicated that metallic Fe, Co, and Ni were active catalysts for the gasification reaction at temperatures above 600°C.

Potentially large incentives for methane production at a lower gasification temperature

of 425~540°C have focused attention on possible catalysts for this process. At these temperatures, methane is favored thermodynamically over CO/H₂, and this could improve process economics by reducing or eliminating costly cryogenic separations and CO/H₂ recycle. Nickel and cobalt have been identified as promising catalysts for steam gasification at 540°C with pure carbon systems.¹

Both nickel and cobalt, however, show a rapid loss of catalytic activity after 30~50% carbon gasification.¹ Deactivation of nickel catalysts in steam gasification of carbon is well known phenomenon in the literature.^{2~9} The loss of catalytic activity has been attributed to encapsulation of the nickel particles with a layer of inactive amorphous carbon,^{3~4} loss of

carbon-nickel contacts,⁵⁻⁶ agglomeration of the nickel particles,⁷ formation of inactive nickel oxide,² and loss of active surface species.⁸⁻⁹ Comparison among these different studies are very difficult to make due to variations in the physical and chemical properties of the catalysts and carbon substrates, the different temperature regimes, and the various reaction conditions. At any rate, very little evidence is presented in these studies to support any of these proposed mechanisms of nickel deactivation. Recent work at high temperatures shows that deactivation under these conditions is the result of a strong nickel-carbon interaction.¹⁰

The goal of the present study was to show the nickel-carbon interaction in nickel catalyzed gasification of carbon. Since the crystallinity and structure of the carbon and the presence of inorganic impurities are the major factors that influence the rate of the gasification reaction of carbon, an extremely pure, high surface form of amorphous carbon, Sphero-carb, has been chosen in the present study as the support for the nickel particles. The present study is primarily concerned with the magnetic behaviors of dispersed nickel particles on Sphero-carb supports at various reduction atmosphere. These are compared with the properties of unsupported and MgO supported nickel samples.

EXPERIMENTAL

The carbon used in this study was Sphero-carb (Analabs Incorporation, GCA012, 80×100 mesh) which is very pure, high surface area carbon (980 m²/g by CO₂ at 0°C) with less than 0.1% ash. These particles were impregnated with an aqueous solution of nickel nitrate to give a final nickel loading of two atomic percent Ni/C. The aqueous solution of nickel nitrate was prepared by dissolving a stoichiometric

quantity of freshly reduced high purity nickel (Gallard-Schlesinger Corporation, 99.999% purity, reduced in hydrogen at 600°C for 3 hours) in 3M nitric acid (Ashland Chemical Company, electronic grade) to make a 2M solution of nickel nitrate. To 2 ml of this solution were added 2.4g of Sphero-carb, and the mixture was then transferred to a vacuum desiccator, and the water was allowed to evaporate. The impregnated Sphero-carb was shaken for one hour using a Spex Wig-L-Bug in order to assure homogeneity of the sample.

A 0.6g of sample was then placed into a small silica tube which was positioned in the center of a silica reaction tube and purged with dry nitrogen for one hour at the flow rate of 100 cm³/min before the reaction tube was placed in a furnace and heated to 540°C. The dimensions of the tubes, as well as their arrangement are shown in Fig. 1. Six minutes of initial preheating, under a nitrogen atmosphere, were required to bring the temperature of the tube to 540°C. The decomposition of nickel(II) nitrate hexahydrate and subsequent reaction were allowed to proceed for 15 minutes under an atmosphere of dry nitrogen, and then for 15 minutes under an atmosphere of either dry or wet hydrogen (or nitrogen) at a flow rate of 100 cm³/min. The reaction tube containing each

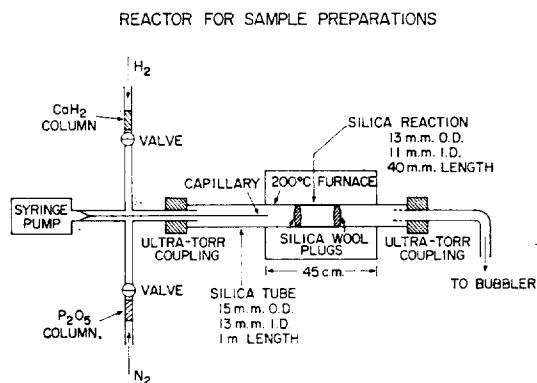


Fig. 1. Apparatus for reduction of samples in various atmosphere.

sample was removed from the furnace and quenched under a stream of dry nitrogen by means of wrapping the tube with a wet towel. The water vapor was introduced by injection of distilled water from a syringe pump (Sage Instrument Model 355). In order to achieve a mole ratio of water-to-carrier gas of 1:1, an injection rate of 4.82 cm³/hr of water was maintained. The complete reactor as well as the point of injection, which was kept at or above 200°C, is shown in *Fig. 1*.

Separately, three different nickel samples were prepared; unsupported, Sphero carb supported, and MgO supported nickel samples. The Sphero carb supported nickel sample was prepared as described above. The unsupported and MgO supported nickel samples were obtained by the reduction of nickel(II) nitrate hexahydrate and MgO-NiO mixture, respectively. Initially, the aqueous solution of nickel nitrate, prepared as described above, was evaporated to dryness, yielding a green product of nickel(II) nitrate hexahydrate, and 2.0 g of MgO (Reagent Grade) and 74.1 mg of NiO (Reagent Grade), yielding two molecular percent of NiO/MgO, was shaken with a Wig-L-Bug for 1 hour before reduction. For three samples above, reduction was accomplished at 540°C under a dry hydrogen atmosphere for 15 minutes (gas flow rate=100 cm³/min) along with 15 minutes of initial preheating at 540°C in a dry nitrogen atmosphere.

The magnetic measurements were performed immediately after the preparation, since the finely dispersed particles were readily oxidized on exposure to air.¹¹ A vibrating-sample magnetometer (Princeton Applied Research Model FM-1) was used to measure the room temperature magnetization at various field strengths, from 100 to 8000 Oe. Sample holders were prepared from Delrin rod. After machin-

ing, the holders were soaked with 3M hydrochloric acid, then washed thoroughly and dried. In order to verify the absence of any magnetic contribution of impurities, empty sample holders, as well as a pure Sphero carb sample, were also measured. Sample holders containing various samples under investigation were tightly secured with glue, thus minimizing air-oxidation during the measurement. A single crystal of nickel (Material Research Corporation) was used as a calibration standard. In addition, a Faraday balance,¹² operated at approximately 700 Oe under 40 torr of helium, was used to study the temperature dependence of the magnetization for various nickel samples.

RESULTS AND DISCUSSION

The results of the magnetization curves for dispersed nickel particles on Sphero carb supports are shown in *Fig. 2*. It is rather surprising to notice that samples obtained at various reaction atmospheres are much alike in their magnetic behaviors. The saturation moments approach an apparent equilibrium value (~38 emu/g at 300K), which is, however, significantly lower than the saturation moment for pure nickel (54.39 emu/g at 293K).¹³ For the samples held in wet or dry hydrogen or wet nitrogen, such a difference might be attributed to hydrogen chemisorption on nickel particles as reported by Selwood.¹⁴ However, that may not be an appropriate explanation, for the sample exposed only to dry nitrogen has almost the same saturation moment as others. As reported in the previous paper,¹¹ treatment of the sample under wet or dry hydrogen or wet nitrogen results in a significant increase in particle size, about 1.5 times greater, in comparison with that under dry nitrogen (~50 Å for dry nitrogen and ~75 Å for other atmosphere). It is, then, clearly evident that the difference in the

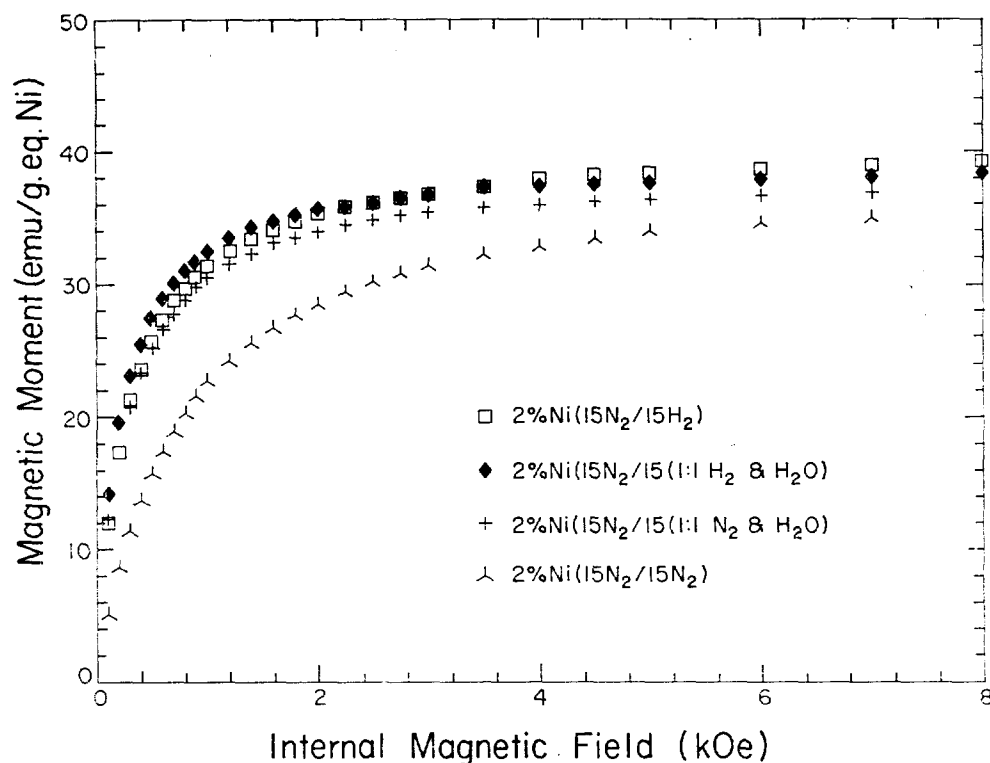


Fig. 2 Magnetization at 300K of nickel particles dispersed on Spherocharb by reducing at 540°C under various reducing atmospheres.

observed saturation moment and the saturation moment for pure nickel is not solely due to either hydrogen chemisorption or particle size. Therefore, in order to explain the experimental fact that the sample obtained under dry nitrogen not only has the same saturation moment as others but also has a significantly lower value than pure nickel, it may be appropriate to assume the possibility of a strong electronic interaction between nickel and carbon particles, consistent with the result reported by Simoens et al.¹⁰

It has also been reported previously¹¹ that dispersed nickel samples treated at 540°C were completely reduced to nickel particles regardless of the atmosphere used. Although no gasification occurred with dry nitrogen, there was appreci-

able carbon weight loss(gasification), 30~40% in 15 minutes, under all other atmospheres. However, as noted above, the sample prepared under dry nitrogen has the same saturation moment as others. Above observation indicate that, regardless of reaction atmosphere, the reaction, $\text{NiO} + \text{C} \rightarrow \text{Ni} + \text{CO}(\text{g}) \uparrow$, may be the most favorable process for the nickel particles in this system. Other possible reaction process involving either H_2 or H_2O might be unfavorable in comparison with above mechanism.

It can also be noticed from Fig. 2 that the variation of the value of magnetization with magnetic field differs in shape for various samples. This may be due to the fact that, whereas at high magnetic fields one observes

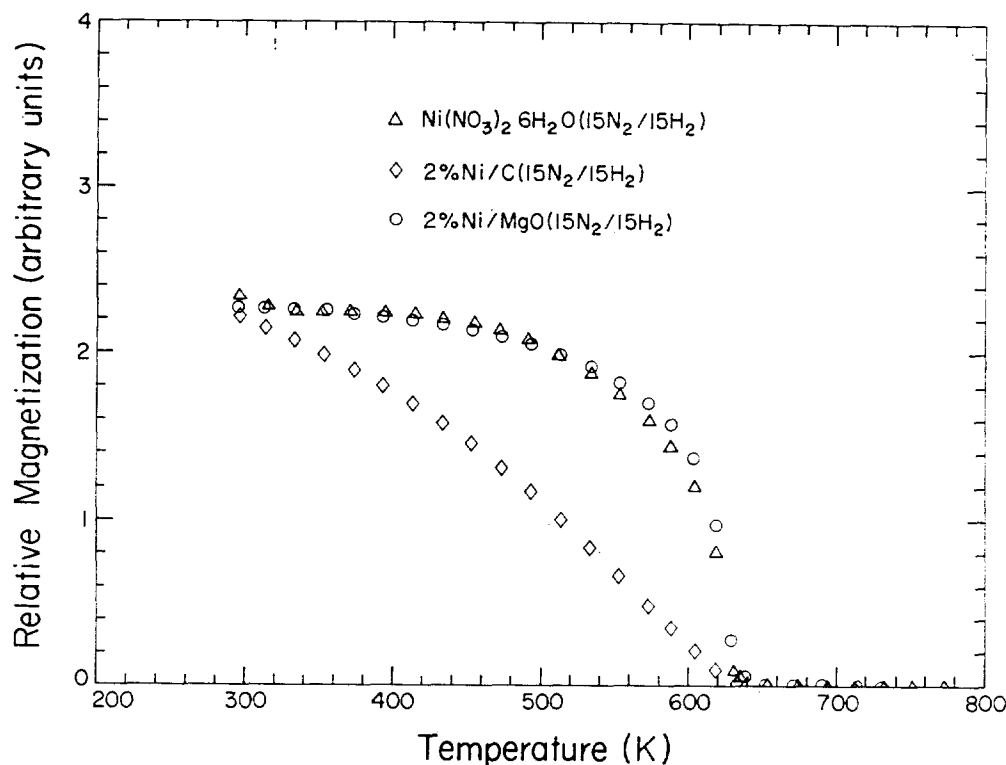


Fig. 3 Temperature dependence of the relative magnetizations of samples reduced at 540°C under a dry hydrogen atmosphere(see text).

essentially the actual moment characteristic of the sample, the low field data are influenced in detail by the particle distribution and crystallite orientations, since nickel metal possesses a very large magnetic anisotropy. Samples prepared under dry nitrogen show more field dependency at low fields than others. Therefore, the observed magnetic properties of Sphero carb supported nickel samples at low fields may indicate the complex nature of these materials, suggesting that strong nickel-carbon interaction is influenced some extent by the presence of hydrogen and/or water vapor resulting in changes of particle size, particle distribution, and crystallite orientation.

Separate measurement has been performed to examine the possibility of any distinct correlation between Curie temperature and carbon

dissolution in nickel. The magnetic behavior of unsupported, MgO supported, and Sphero carb supported nickel samples was investigated as a function of temperature using a Faraday balance. This technique is sensitive to variations in particle size. The results in Fig. 3 show a reduced slope for the Sphero carb supported nickel sample compared to other samples. This would be, primarily, due to the smaller nickel crystallites of Sphero carb supported sample¹⁴; nickel crystallite size of Sphero carb supported sample was about 1/3 compared to other samples as determined by previously reported method.¹¹ Shifts in the values of Curie temperature are generally indicative of incomplete reduction or alloying, possibly also of metal support interaction. The Curie temperature estimated from extrapolation method was observed, however,

to be very similar to that observed for pure nickel ($T_C=631K$ for pure nickel¹³), suggesting that Curie temperature might not have any distinct correlation with dissolution of carbon in nickel. However, to determine whether or not this rationalization is proper, of course, would require more precise information than that provided here.

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