# Crystallographic and Magnetic Properties of Cobalt Particles Dispersed on Spherocarb Support

**Kwan Kim**

*Department of Chemistry, College of Natural Sciences, Seoul National University,
Seoul 151. Received May 14, 1987*

Nickel has been identified as promising catalyst for steam gasification at 813 K with pure carbon system[1].Nickel, however, shows a rapid loss of catalytic activity after 30-50% carbon gasification[2]. The mechanism of catalyst deactivation is not yet completely understood. Nevertheless, Simoens *et al.*[3] ascribed the deactivation to a strong metal-carbon interaction.

Magnetic measurement has been known to be a useful means to investigate the mechanism of catalyst deactivation[2,4]. In our previous study on the Ni-C system[5], a strong electronic interaction appeared to exist between the nickel and carbon particles. In conjunction with the Ni-C system, we have investigated in this work the magnetic behaviors of dispersed cobalt particles on carbon supports. In a thermogravimetric study, Mckee[6] examined the catalytic effect of cobalt metal on the kinetics of hydrogenation of graphite at temperatures between 873 and 1273 K. He found that metallic Co was also active catalyst for the gasification reaction at temperature above 873 K.

The carbon used in this study was Spherocarb(Analabs Incorporation, GCA 012, 80×100 mesh) which is very pure, high surface area carbon(980 $m^2/g$ by $CO_2$ at 273 K) with less than 0.1% ash. These particles were impregnated with an aqueous solution of cobalt nitrate to give a final loading of two atomic percent Co/C. The aqueous solution of cobalt nitrate was prepared by dissolving a stoichiometric quantity of freshly reduced high purity cobalt (Leico Incorporation, 99.999% purity, reduced in a 15% $H_2$-85% Ar atmosphere at 1123 K for 12 hours) in 3 M nitric acid(Ashland Chemical Company, electronic grade). Spherocarb particles were added to the cobalt nitrate solution, and the mixture was transferred to a vacuum desiccator where the excess water was allowed to evaporate. The sample was then placed into a silica boat which was positioned in the center of a silica reaction tube and purged with dry hydrogen(research grade) for one hour at the flow rate of 100 $cm^3/min$ before the reaction tube was placed in a furnace(set already at appropriate temperature). Six minutes of initial preheating, under a hydrogen atmosphere, were required to bring the temperature of the tube to the actually set furnace temperature. The decomposition of cobalt(II) nitrate hexahydrate and subsequent reaction were allowed to proceed for periods of 10, 30, 60, and 120 minutes. The reaction tube containing each sample was removed from the furnace and quenched by means of wrapping the tube with a wet towel.

X-ray diffraction patterns for the samples thus obtained were taken with a Pillips Norelco Diffractometer using copper radiation( $\lambda CuK\alpha_1 = 1.5405$ Å); data were taken with a graphite monochromator. Crystallite sizes were calculated from the peak width using the Scherrer equation[7].

A vibrating-sample magnetometer(Princeton Applied Research model FM-1) was used to measure the room tempera-

**Table 1. Percent Weight loss of Carbon and Average Crystallite Size of Cobalt Particles**

| Temperature (K) | Time (min) | % Weight Loss of Carbon | Particle Size(Å)[a] |
|---|---|---|---|
| 813 | 10 | 62 | |
| | 30 | 76 | |
| | 60 | 80 | 82 |
| | 120 | 81 | |
| 973 | 10 | 52 | 95 |
| | 30 | 68 | |
| | 60 | 73 | 103 |
| | 120 | 74 | |
| 1073 | 10 | 42 | 113 |
| | 30 | 56 | |
| | 60 | 62 | 132 |
| | 120 | 63 | |

[a] Calculated from the peak width using the Scherrer equation: $D = \dfrac{K\lambda}{\beta\cos\theta}$, where D = Crystallite size, K = Shape factor; a value of 0.94 was used, $\lambda$ = X-ray radiation wavelength (CuK$\alpha_1$ wavelength = 1.5405 Å), $\beta$ = half-height width expressed in radians for the peaks at 2 , corrected for K$\alpha_2$ and instrumental broadening. The cobalt diffraction profiles (200) were recorded for samples reduced under various conditions at a scan rate of 0.25° $2\theta$/min.

ture magnetization at various field strengths, from 100 to 8000 Oe. Sample holders were prepared from Delrin rod. After machining, the holders were soaked in 3 M hydrochloric acid, then washed thoroughly and dried. A single crystal of nickel(Material Research Corporation) was used as a calibration standard. The magnetic measurements were performed immediately after the preparation of samples.

Untreated Spherocarb is amorphous. The dispersed cobalt sample prepared at 813 K contained small amount of cobalt oxide as indicated by x-ray analysis. X-ray analysis of all other dispersed cobalt samples showed the exclusive presence of cobalt particles with varying degrees of crystallinity, which was evidenced by the extent of line broadening of the diffraction peaks. In Table 1 are given the calculated average crystallite sizes of the cobalt particles. These results display an increase in the relative crystallite size of the cobalt particles with increased temperature of reduction.

It can be seen from Table 1 that there was appreciable weight loss of carbon at 813 K, and hence significant gasification occurred. The extent of gasification decreases, however, as the reduction temperature increases. An observed increase in the particle size appears to correlate with the carbon weight loss. Nevertheless, cobalt appears to be a more active catalyst than nickel for the carbon gasification. For the dispersed nickel particles on Spherocarb, percent weight loss
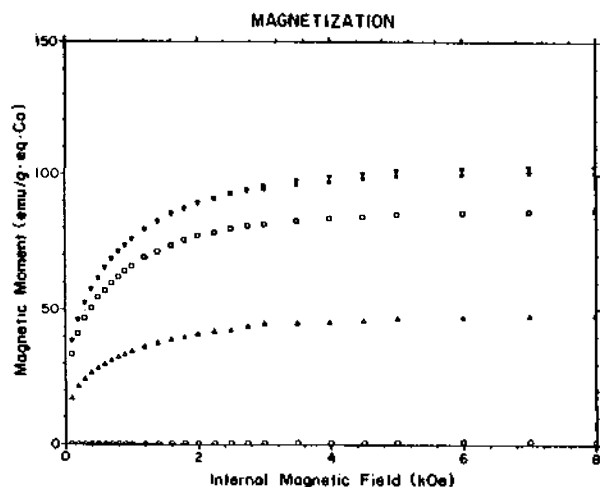
**Figure 1.** Field dependence(at 300 K) of the magnetic moments of samples reduced at 813 K in hydrogen atmosphere. $\circ$ ; $Co(NO_3)_2$ $6H_2O$, $\triangle$ ; 10 min., $\square$; 30 min., $\star$ ; 60 min., $\triangledown$ ; 120 min.
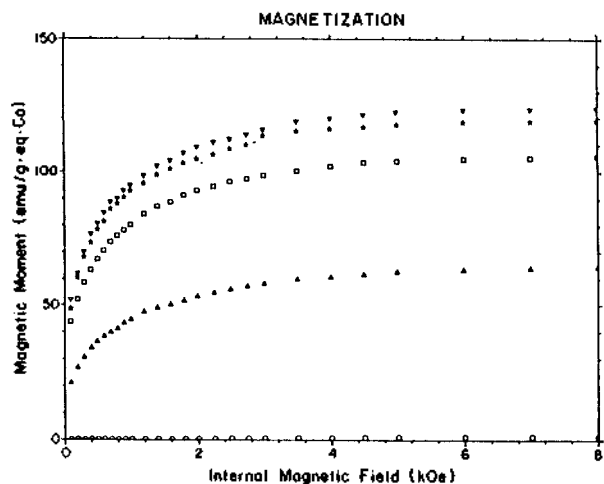


**Figure 2.** Field dependence(at 300 K) of the magnetic moments of samples reduced at 1073 K in hydrogen atmosphere. $\circ$ ;$Co(NO_3)_2$ $6H_2O$, $\triangle$ ; 10 min., $\square$; 30 min., $\star$; 60 min., $\triangledown$ ; 120 min.

of carbon at 813 K was 46% for 30 minutes reduction[4]. As can be seen from Table 1, the amount of weight loss for the dispersed cobalt sample is 76% at the same condition.

The results of the magnetization curves for the samples obtained at 813 and 1073 K are shown in Figure 1 and 2, respectively. It can be seen from the Figures that undecomposed cobalt nitrate on Spherocarb does not exhibit ferromagnetic behavior. However, ferromagnetism is observed after reduction in hydrogen for just 10 minutes. Treatment for 30 minutes shows an increase in both the saturation moment and the initial slope of the magnetization curve. An apparent equilibrium saturation moment is approached with increased time of gasification. This behavior is in accord with the decomposition of paramagnetic cobalt nitrate and the formation of metallic cobalt. The magnetic moments at 8 kOe show the

same trend as the particle sizes for the samples. The knees of the curves are more sensitive to the variation in particle size, as is clearly evident in Figure 1 and 2 at lower fields (approximately 1 kOe).

As the reduction temperature is increased, the saturation moment increases as well. Such an increase appears to be correlated with the increase in crystallite size. However, the observed magnetic saturation moment for the catalyzed Spherocarb samples remains appreciably below the moment for a freshly prepared pure cobalt($\sim$160 emu/g) even after treatment for 120 minutes.

A sample gasified in hydrogen for 60 minutes and then heated under vacuum for 3 hours at 573 K shows an increase ($\sim$10%) in ferromagnetic moment. The reduction in saturation moment upon chemisorption of hydrógen is a well documented phenomenon[8]. Therefore, the observed lowering of the saturation moment between the hydrogen reduced samples and the fresh metal may be ascribed in part to the interaction of hydrogen with the dispersed cobalt particles. Since the difference in the saturation moment between the reduced sample and the pure cobalt is not entirely due to the hydrogen chemisorption, it seems appropriate to assume the possibility of a strong electronic interaction between cobalt and carbon particles, as reported for the nickel-carbon systems[3,5].

In summary, the crystallographic and magnetic properties of finely divided cobalt particles on Spherocarb supports were used in this work to characterize the metal as a function of reducing conditions. As gasification proceeded and the cobalt catalyst became deactivated, the saturation moments were observed to increase. This was accompanied by an increase in crystallite size. Magnetic measurement resulted in a much lower ferromagnetic moment than that of pure crystalline cobalt. This behavior was mainly attributed to the interaction between cobalt and carbon particles. Finally, cobalt appeared to be a more active catalyst than nickel for the carbon gasification.

## References

1. K. S. Colle, Exxon Research Report COR. 5KW. 81 (1981).
2. K. S. Colle, A. Wold, K. Kim, and V. S. Nguyen, Exxon Research Report COR. 2KW. 83 (1983).
3. A. J. Simoens, E. G. Derouane, and R. T. K. Baker, J. Catal. **75**, 175 (1982).
4. K. Kim, R. Kershaw, K. Dwight, A. Wold, and K. S. Colle, Mat. Res. Bull. **17**, 591 (1982).
5. K. Kim, J. Kor. Chem. Soc. **27**, 376 (1983).
6. D. W. Mckee, Carbon **12**, 453 (1974).
7. H. P. Klug and L. E. Alexander, X-Ray Diffraction Procedures, Wiley, New York, N. Y. (1974).
8. P. W. Selwood, Chemisorption and Magnetization, Academic Press, New York, N. Y. (1975).