*Korean J. of Chem. Eng.*, 13(1), 54-59 (1996)

# CATALYTIC PROPERTIES OF PARTIALLY REDUCED COBALT WIRE IN CO HYDROGENATION

**Hyun Khil Shin, In-sik Nam*, Jae Sung Lee*, Jong Shik Chung* and Sang Heup Moon†**

Dept. of Chemical Engineering, Seoul National University, Shinlim-dong San 56-1, Kwanak-ku, Seoul 151-742, Korea
*Dept. of Chemical Engineering, Pohang University of Science and Technology, P.O. Box 125, Pohang 790-600, Korea

(*Received 4 May 1995 • accepted 27 October 1995*)

**Abstract**—The reaction rate and the ethylene/ethane product ratio in CO hydrogenation increase when cobalt wire, used as a catalyst for the reaction, is reduced to lower extents. The kinetic results obtained with the poorly reduced wire correlate well with temperature-programmed surface reaction (TPSR) and $H_2$ chemisorption results, and are interpreted to be due to electronic modification of the cobalt surface by the unreduced sub-surface cobalt oxide. It has been concluded that the extent of metal reduction is an important variable in determining the catalytic property of cobalt.

*Key words*: *Extent of Metal Reduction, Cobalt, CO Hydrogenation*

## INTRODUCTION

Non-noble metals such as iron, cobalt and nickel are hard to reduce completely even under severe reduction conditions. Therefore, most of the supported catalysts containing the non-noble metals are used as partially-reduced ones. Whether the intrinsic activity of the reduced metal surface is influenced by the unreduced metal oxide in the catalysts or not has been the subject of research in a few laboratories [Moon and Yoon, 1985; Lee et al., 1988; Johnson et al., 1991].

For example, a reaction study with partially reduced $Co/Al_2O_3$ catalysts in CO hydrogenation showed that the olefin/paraffin ratio among the hydrocarbon products increased when the catalysts were reduced poorly and the trend correlated well with the $H_2$ and CO chemisorption behavior of the catalysts [Moon and Yoon, 1985]. Johnson et al. [1991] indicated that the intrinsic activity of their carbonyl-derived $Co/Al_2O_3$ catalysts in CO hydrogenation increased with increasing percentage reduction of the cobalt. On the other hand, Lee et al. [1988] showed that the product distribution in CO hydrogenation was unaffected by the extents of cobalt reduction. Characteristic changes in the reaction rates and the product distribution were also observed with iron catalysts when they were reduced to different extents [Moon et al., 1993].

However, most of the work on this subject including the above examples have been done with supported catalysts, which may cause complications in interpreting the experimental results. That is, the activity of the catalysts may be affected by factors other than the extent of metal reduction. An example is the effect of metal loading which simultaneously modifies the extent of metal reduction and the dispersion of metal particles. When metal particles of different sizes are dispersed on the catalyst support, they experience to different extents both the metal-support interaction [Boudart, 1969] and the crystallite size effect [Hardeveld and Hartog, 1972]. In fact, many previous works [Reuel and Bartholomew, 1984; Fu and Bartholomew, 1985; Lee et al., 1988; Johnson et al., 1991] were designed to include such a particle dispersion effect because the sample catalysts were prepared with different metal loadings.

One method to eliminate the effect of metal dispersion is to change only the reduction conditions of the sample catalyst prepared with an identical metal loading, as done by Moon and Yoon [1985]. Another is to use either metal foil or wire as the catalyst, and reduce or modify it with oxygen under different conditions. An example along this line is the work by Dwyer and Somorjai [1978] who compared the methanation rates on two different iron foils; one foil was ion sputtered to be cleaned of possible contaminants such as oxygen and sulfur, and the other was treated with 4-Torr oxygen at 300℃ for 20 minutes after the sputtering. They observed that the oxygen-treated surface exhibited about twofold higher methanation rates than the clean surface. A similar trend was observed with an oxygen-adsorbed Pt single crystal used for cyclohexene hydrogenation [Smith et al., 1979].

Another example similar to these is the work by Moon et al. [1986], who used nickel wire as a catalyst for CO hydrogenation. They reduced the wire at two different temperatures, 550 K and 900 K, before using it in CO hydrogenation. The 550 K-reduced wire was reduced to less than a monolayer of nickel atoms on the surface and the 900 K-reduced one to more than 20 surface layers of nickel atoms, as measured by the oxygen titration method [Bartholomew and Farrauto, 1976]. The methanation rates were enhanced by more than 5 times when the wire was reduced at 550 K instead of 900 K.

Moon et al. [1986] explained that the rate difference occurred because the surface of the 550 K-reduced wire was modified strongly by interaction with the unreduced nickel oxide. In fact, Palmer and Vroom [1977] observed a similar trend with their Co and Ni foils reduced at different temperatures, as did Ignatiev and Matsuyama [1979] with cobalt single crystal. They all explained that the trend was due to an electronic interaction between the metal and the unreduced metal oxide.

This paper reports our work on partially reduced cobalt wire similar to our previous work on nickel wire [Moon et al., 1986]. The work is mostly a kinetic investigation on incompletely-re-

---

† To whom correspondence related to this paper should be made.

**Table 1. Gas uptake by cobalt wires (in μmol/m of wire)**

| Wire | Reduction temperature | $O_2$ uptake at 673 K | Extent of reduction* | $H_2$ chemisorption at 473 K | Percentage exposure of the reduced metal** |
|---|---|---|---|---|---|
| I | 550 K | 14 | 11.8% | 2.2 | 21% |
| II | 800 K | 96 | 79% | 2.3 | 3.2% |

*Estimated by oxygen titration method(14).

**Defined as the amount of surface metal/the amount of reduced metal.

duced cobalt wire in CO hydrogenation. The results are discussed in comparison with previous observations on nickel wire and supported cobalt catalysts.

## EXPERIMENTAL

Cobalt wire obtained from Johnson Matthey Chemicals Ltd. was a thin cylindrical wire of 0.1-mm thickness. It was of ultra-high purity grade, specified as "puratronic" by the vendor, containing 99.9965% of cobalt. The supplier analyzed the wire for impurities to the level of ppm by weight using optical emission arc spectroscopy together with supplementary methods such as UV, Vis, AA, XRF, ICP and wet chemical analysis. The impurity contents were 10 ppm of Si, 7 ppm of Fe, 1 ppm of Al and Ca, and less than 1 ppm of Cr, Cu, Mg and Ag. Other elements were undetected by the above analyses.

As sulfur is a notorious impurity in cobalt, special attention was given in this laboratory to eliminate possible sulfur contamination of the wire, although the vendor claimed no detection of the element. The purchased wire was further purified by repeated 5-6 cycles of oxidation in air and reduction in $H_2$ at 800 K for 1 hour each. The effluent gas during the purification cycles was analyzed for sulfur by a flame photometric detector (FPD, installed in Tracor GC 565 with a sulfur detection limit of about 1 nanogram per μl of sample gas), but no sulfur was detected.

We analyzed the wire surface after each step of oxidation, reduction, and reaction in CO hydrogenation with X-ray photoelectron spectroscopy (XPS) and detected no sulfur on the surface. As the detection limit of XPS for sulfur was relatively high, we also examined the wire surface by the secondary-ion mass spectrometry (SIMS). The SIMS results contained much noise due to a small target area of the sample wire, but again, no sulfur signal was observed.

Based on all these observations, we concluded that the cobalt wire used in this study contained no sulfur impurity, at least within the detection limit of the current analysis methods mentioned above.

After the final oxidation treatment, the wire has been reduced in $H_2$ at either 550 K or 800 K for 20 minutes to be reduced to different extents. The extent of reduction was estimated by oxygen titration method described by Bartholomew and Farrauto [1976], assuming that cobalt was converted $Co_3O_4$ after oxidation at 673 K.

For the reaction test in CO hydrogenation, the 0.1-mm thick and 5-m long wire was placed in a tubular glass reactor, purified and finally reduced as described above, and then exposed to a stream of $H_2$ and CO at 513 K. The reactant flow rate was changed to obtain various conversions maintaining the $H_2$/CO ratio at 6. The reactant gases were purified before use as described previously [Moon and Yoon, 1985]. That is, $H_2$ was passed through a Deoxo purifier (Engelhard) for oxygen removal and then a Molecular Sieve 5A trap for water removal. CO was purified by flowing the gas sequentially through a Molecular Sieve 5A, MnO, and activated carbon traps. Helium was also purified with Molecular Sieve 5A and MnO traps. The reaction products were analyzed with a G.C. (Hewlett-Packard 5890A) equipped with a 8-foot Porapak Q column and a flame ionization detector.

The amount of $H_2$ chemisorption on the wire was measured in a conventional volumetric adsorption apparatus capable of degassing up to $10^{-5}$ Torr. Temperature-Programmed Surface Reaction (TPSR) of $H_2$ with the surface-deposited carbon species or pre-adsorbed CO was performed in the same reactor unit as used for CO hydrogenation with the heating rate of 15 K/min.

## RESULTS AND DISCUSSION

### 1. Extents of Reduction

When the wire is finally treated in air at 800 K for 1 hour during the purification step, it is oxidized only to a limited depth from the surface with the wire core still remaining as metallic cobalt. According to the amount of oxygen consumption during the final step, the wire is oxidized to 11.0% corresponding to about 43.4 μmols of $Co_3O_4$ per m of wire.

After the subsequent reduction in $H_2$ at either 550 K or 800 K, the wire is reduced to different extents as shown in Table 1. The extent of reduction indicates the percentage that the oxide layer produced during the final oxidation step is reduced to cobalt. As expected, 550 K-reduced Wire(I) is reduced to only 11.8% while the 800 K-reduced Wire(II) is reduced to 79%. In the estimation, it has been assumed that the chemical state of the unreduced cobalt oxide remaining in the sub-surface after reduction is $Co_3O_4$, although it is more logical to consider that part of the oxide layer exists as CoO. Relative errors due to this assumption are within 30%.

Table 1 also shows the results of $H_2$ chemisorption on the wires. Two aspects are to be noted in the results. One is that the amount is much greater than what is expected when $H_2$ is assumed to adsorb on the geometric surface of the wire, i.e., $3.14\times10^{16}$ Å$^2$ corresponding to ca $0.79\times10^{-3}$ mol of Co/m of wire. The other is that the amount of $H_2$ adsorption is almost the same for the two wires.

We may expect an increase in the amount of $H_2$ chemisorption when many cracks develop on the wire surface after reduction. In fact, crack formation is possible because the specific volume of metallic cobalt is smaller than that of cobalt oxide, and therefore cobalt oxide undergoes volume contraction upon reduction. The extent of crack formation, however, seems to be almost the same for the two wires because they adsorb almost the same amounts of $H_2$.

The extents to which cobalt atoms in the reduced layer are exposed to the surface are 21% and 3.2% for Wires I and II, respectively. The amount of surface cobalt atoms has been estimated from $H_2$ chemisorption assuming that hydrogen adsorbs dissociatively on the cobalt surface. The estimated results indicate

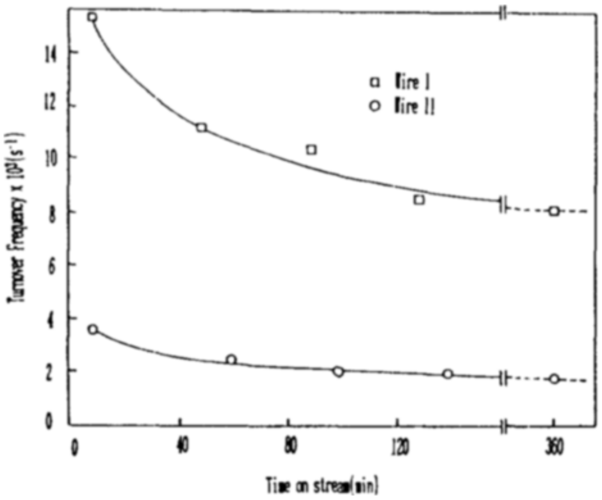

Fig. 1. Changes in the CO hydrogenation rate on cobalt wires reduced under different conditions. Wire I was reduced at 550 K and Wire II at 800 K. TOF was estimated based on $H_2$ chemisorption.

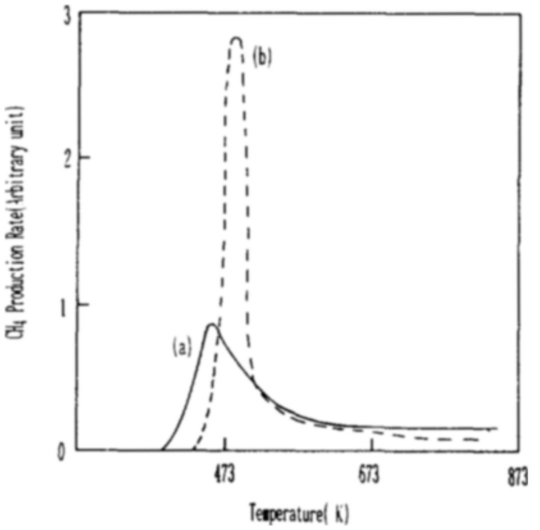

Fig. 2. TPSR spectra of methane production on Wire I (reduced at 550 K) obtained by reacting $H_2$ with the surface deposited species after the wire was used in CO hydrogenation for (a) 30 minutes and (b) 3 hours.

that Wire I is covered with about 4.8 layers of metallic cobalt atoms whereas Wire II is covered with 31.3 layers. As the surface cobalt layer on Wire II is about 7 times thicker than one on Wire I, we may expect that the surface of Wire I is affected more by the sub-surface cobalt oxide than is Wire II.

## 2. Rates of CO Hydrogenation

The kinetic results in Fig. 1 show the following two aspects. One is that the rates of CO hydrogenation decrease during the initial reaction period before reaching the steady-state values, and the other is that the steady-state rate on Wire I is about 3 times higher than the rate on Wire II.

The initial rate decrease on cobalt catalyst is not unusual. For example, Johnson et al. [1991] reported that activities of their $Co/Al_2O_3$ catalysts in CO hydrogenation declined by 10% to 30% over the initial reaction period of 24 hours. The rate decrease in this study is not due to sintering or poisoning of the metallic surface because the reaction temperature, 513 K, is low enough to prevent sintering and the reactant gases have been purified sufficiently as described in the experimental section.

Instead, the rate seems to decrease due to carbon deposition on the wire surface. Fig. 2 shows the TPSR spectra of methane production on Wire I after the wire has been used for CO hydrogenation for different periods. The peak near 473 K is due to hydrogenation of the α-carbon species [McCarty and Wise, 1979]. The peak grows significantly and shifts to higher temperatures after the wire has been used in the reaction test for 3 hours, indicating that carbon accumulates on the surface as the reaction proceeds.

Increase in the CO hydrogenation rate on the relatively poorly reduced Wire I over the well reduced Wire II is of the same trend as observed by others on Ni wire [Moon et al., 1986], Co and Ni foils [Bartholomew and Farrauto, 1976] and Co single crystal [Palmer and Vroom, 1977]. As for the reasons for the rate difference between the two wires, the following three may be considered.

One is that the rate enhancement on Wire I is due to the increase in the metallic surface area. However, this reasoning should be counted out because the amounts of $H_2$ chemisorption are almost the same on the two wires. Another result that denies the above possibility is that the two wires show difference not only in the reaction rate but also in the ethylene/ethane product ratio as discussed in the next section. If the rate increase is caused simply by a change in the metallic surface area, the product distribution should remain unchanged for the two wires.

Secondly, the activity may be modified by a species that is possibly accumulated on the wire surface during the reduction or the reaction step. Contamination by sulfur is not likely because the wire and reactant gases have been purified and the wire surface contains no sulfur as described in the experimental section. Another evidence that disapproves sulfur contamination is that the turnover frequencies of CO hydrogenation observed in this study are of the same order of magnitude as those reported by others for fresh cobalt catalysts [Reuel and Bartholomew, 1984; Johnson et al., 1991]. The wire surface is modified by carbon accumulation during reaction, but again, this is not a reason for the activity difference because Fig. 1 shows that the difference is observed from the beginning of the reaction period.

The above considerations lead us to the third reasoning that the rate difference is due to modification of the cobalt surface by the sub-surface cobalt oxide. The surface may be affected by electronic interaction between cobalt and cobalt oxide at their contacting interface where reduction has proceeded.

Concerning the nature of the interaction, it is noteworthy that CoO and $Co_3O_4$ are p-type semiconductors forming a Schottky-type metal-semiconductor contact with metallic cobalt. Accordingly, electrons may transfer from cobalt to cobalt oxide across the interface, thus reducing the strength of $H_2$ and CO adsorption on the cobalt surface. The surface modification is expected to be more significant on Wire I than on Wire II because the former has a thinner surface cobalt layer than the latter.

Fig. 3 shows a TPSR result of methane production obtained by reacting $H_2$ with CO pre-adsorbed on the wire surface. Lee and Bartholomew [1989] have proposed in their study with $Co/Al_2O_3$ catalysts that the peak near 473 K, A, is due to hydrogenation of an active carbon, commonly referred to as α-carbon [McCarty

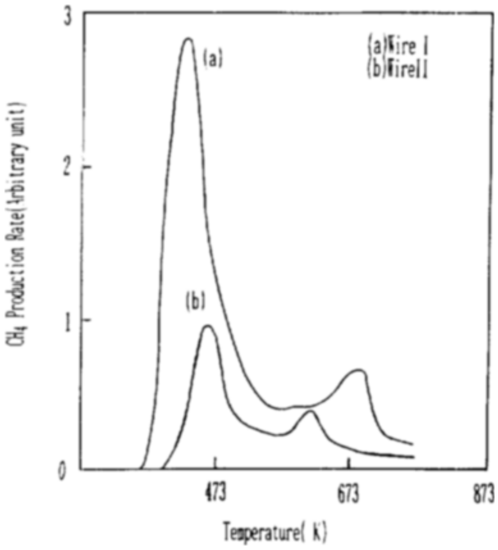

**Fig. 3. TPSR spectra of methane production obtained by reacting $H_2$ with CO pre-adsorbed on cobalt wires at room temperature. (a) Wire I reduced at 550 K and (b) Wire II at 800 K.**

and Wise, 1979], produced by dissociation of CO on cobalt metal sites, and the peak near 673 K, B, is due to decomposition of the $CH_xO$ species formed on the support. Peak A appears smaller than Peak B on the supported catalysts, but the wire catalysts of this study show the opposite relative intensity. This is an obvious result because the wire has no oxide surface corresponding to the support and therefore formation of the $CH_xO$ species is hindered. Accordingly, Peak A is responsible for most of the methanation activity of the wire catalyst.

The 550 K-reduced Wire I shows a larger Peak A than Wire II, in agreement with the reaction results. It is also to be noted that the position of Peak A on Wire I is at a lower temperature by about 20 K than on Wire II. This is not due to increased carbon coverage on Wire I because in such a case, the peak shifts to higher temperatures as observed by Lee and Bartholomew [1989]. The peak shift in this study suggests that the surface α-carbon on Wire I is more reactive for hydrogenation than on Wire II.

One explanation for the enhanced activity is that a significant weakening of CO adsorption on Wire I, induced by the electronic effect of the sub-surface cobalt oxide, promotes formation of the active carbon species on the cobalt surface. In fact, this is possible because CO usually retards the methanation rate on most transition metals by its strong adsorption on the metal surface relative to hydrogen [Vannice, 1977].

Weakening of the CO and $H_2$ adsorption on Wire I than on Wire II has been confirmed by separate TPD experiments in this laboratory. That is, the $H_2$ desorption peak is located at 398 K for Wire I and at 405 K for Wire II. The CO peak is centered at 383 K for Wire I and at 423 K for Wire II. The trend in the adsorption strength change is the same as observed in similar studies with supported Co and Fe catalysts [Moon and Yoon, 1985; Moon et al., 1993].

It is worth mentioning here that the trend of rate change with the extent of reduction observed in this study is opposite to the one reported by Johnson et al. [1991] for their carbonyl-derived $Co/Al_2O_3$ catalysts. Our trend, however, agrees with the results of other works reported previously with $Co/Al_2O_3$ [Moon and Yoon, 1985; Lee et al., 1988], Co foil [Bartholomew and Farrauto, 1976] and Co single crystal [Palmer and Vroom, 1977].

**Table 2. Product distribution and the ethylene/ethane ratio among products of CO hydrogenation on cobalt wires**

| Wire[a] | Conversion[b] | Hydrocarbon distribution (mol%)[c] | | | | Ethylene |
|---|---|---|---|---|---|---|
| | | $C_1$ | $C_2$ | $C_3$ | $C_4$ | Ethane |
| I | 2.34 | 70.0 | 10.5 | 14.0 | 5.5 | 1.55 |
| | 2.27 | 71.4 | 10.9 | 14.1 | 3.7 | 1.10 |
| | 1.06 | 72.9 | 10.5 | 11.6 | 4.8 | 2.90 |
| | 1.00 | 72.7 | 10.6 | 11.5 | 5.2 | 3.36 |
| | 0.81 | 71.9 | 10.9 | 12.0 | 5.2 | 4.73 |
| | 0.58 | 72.5 | 10.8 | 11.5 | 5.1 | 4.99 |
| | 0.44 | 71.8 | 10.9 | 11.9 | 5.3 | 6.20 |
| II | 2.06 | 73.6 | 10.4 | 12.4 | 3.6 | 0.83 |
| | 1.90 | 74.2 | 10.3 | 11.7 | 3.8 | 0.66 |
| | 1.84 | 73.1 | 10.3 | 12.5 | 4.1 | 0.91 |
| | 0.75 | 75.7 | 11.4 | 12.9 | - | 2.06 |
| | 0.55 | 76.7 | 11.2 | 12.0 | - | 2.68 |

[a] Wire I was reduced at 550 K and Wire II at 800 K.

[b] Various conversions were obtained by changing the space time in reaction experiments with the $H_2/CO$ ratio of 6 and at 513 K.

[c] Including olefins and paraffins.

The major difference between the work by Johnson et al. [1991] and the other two [Moon and Yoon, 1985; Lee et al., 1988] for the $Co/Al_2O_3$ catalysts is that the former changed the metal loading to obtain different extents of reduction while the latter changed only the reduction conditions with a fixed metal loading. As mentioned in the introduction section and also by Lee et al. [1988], the activity of CO hydrogenation may be affected by both the size of the dispersed particles and the extent of reduction. It has been demonstrated by another experiment in the work of Johnson et al. [1991] that the activity is unaffected by the metal dispersion when the metal loading and the percentage reduction are relatively high. However, when the metal loading is low, e.g., below 3 wt% as in the above case of Johnson et al. [1991], the dispersed particles may be affected through interaction with the support.

In other words, the activity of the cobalt catalysts prepared by Johnson et al. [1991] may have been modified by both the support effect and the extent of reduction. The catalysts prepared in the other two works [Moon and Yoon, 1985; Lee et al., 1988] are almost free from the support effect because the metal loading is relatively high, 10 wt%, and the size of the dispersed particles has not changed during the reduction step [Lee et al., 1988]. Accordingly, the result with the cobalt wire in this study is better correlated with the latter two works [Moon and Yoon, 1985; Lee et al., 1988].

### 3. Product Distribution in CO Hydrogenation

Table 2 shows that the fractions of the hydrocarbon products of specific carbon numbers remain almost unchanged on the two wires for various conversions obtained by adjusting the space time in the reaction experiments. The decrease in the ethylene/ethane ratio with conversion is a well-known phenomenon characteristic to CO hydrogenation, as reported by Amelse et al. [1981].

A notable result in Table 2 is that the ethylene/ethane ratio on Wire I is about 2-3 times higher than on Wire II. The difference in the ethylene/ethane ratio between the two wires is

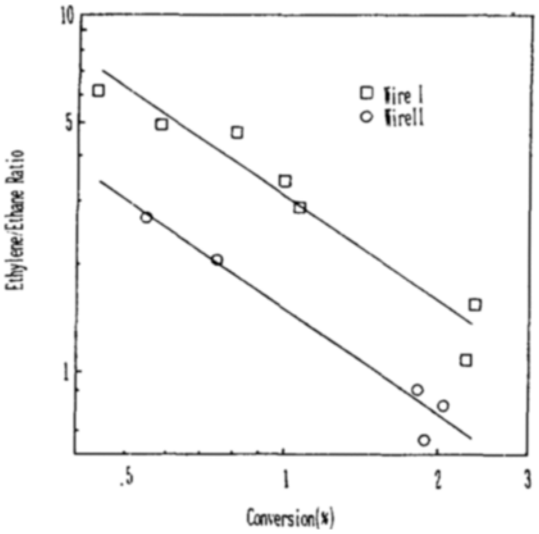

**Fig. 4. Changes in the ethylene/ethane ratio among the products in CO hydrogenation on cobalt wires. Wire I was reduced at 550 K and Wire II at 800 K.**

clear when the data are plotted versus conversion as in Fig. 4. This trend is the same as the result obtained with supported cobalt catalysts [Moon and Yoon, 1985], which also shows that the olefin/paraffin ratio increases when the catalysts are reduced poorly. In the case of supported catalysts, the trend has been correlated with a decrease in the relative amounts of $H_2$ and CO chemisorption, i.e., the $H_2$/CO ratio, with lower extents of catalyst reduction [Moon and Yoon, 1985]. In this study, however, such a correlation is not obtained because the amount of CO adsorption is too small to be measured by a volumetric chemisorption unit in this laboratory.

Nevertheless, the TPSR result of Fig. 3 suggests that the same correlation holds true in the case of the cobalt wire. It is obvious from Fig. 3 that more CO is adsorbed on Wire I than on Wire II. Since the amount of $H_2$ chemisorption is almost the same on the two wires as shown in Table 1, the $H_2$/CO adsorption ratio is lower on Wire I than on Wire II, in agreement with the reaction results.

CO hydrogenation on metal catalysts proceeds through two major steps: carbon-carbon chain growth and hydrogenation of the surface carbon species [Paal and Menon, 1988]. The former step determines the distribution of the hydrocarbon products of specific carbon numbers and the latter step, the relative distribution of olefinic and paraffinic products. According to the results of this study, the extent of metal reduction seems to influence mostly the hydrogenation step instead of the carbon-carbon chain growth step.

## CONCLUSION

The present work consists mostly of reaction studies on cobalt wire, and therefore many possibilities have been considered to explain the experimental results.

A unique aspect of this work is that the experiments have been designed to investigate the effect of the sub-surface cobalt oxide while eliminating possible complications that can arise from the support. It has been confirmed experimentally that the catalytic property of cobalt wire changes with the extent of metal reduction, and particularly that the CO hydrogenation rate and the ethylene/ethane ratio among products increase when the wire is poorly reduced.

The results of this study agree well with most of the previous works on cobalt foil, single crystal, and supported catalysts. Accordingly, it is concluded that the extent of metal reduction is an important variable in determining the catalytic behavior of non-noble metals.

## ACKNOWLEDGEMENTS

This work was supported by the Korea Science and Engineering Foundation under the program of "Goal-oriented Fundamental Research" H.K. Shin appreciates the financial supports from Yukong Ltd. and Lucky Ltd.

## APPENDIX

One of the reviewers of this paper indicated a possibility that CoO might be present on the wire surface either after the reduction step or during CO hydrogenation. We do not exclude the possibility particularly because Fig. 3 shows small peaks near 673 K, which are due to the $CH_xO$ species formed on oxides [Lee and Bartholomew, 1989]. Nevertheless, this does not invalidate the conclusion of this paper. That is, the catalytic behavior of cobalt in CO hydrogenation is affected by the extent of metal reduction.

## REFERENCES

Amelse, J. A., Schwartz, L. H. and Butt, J. B., "Iron Alloy Fischer-Tropsch Catalysts. III. Conversion Dependence of Selectivity and Water-Gas Shift", *J. Catal.*, **72**, 95 (1981).

Bartholomew, C. H. and Farrauto, R. J., "Chemistry of Ni-$Al_2O_3$ Catalysts", *J. Catal.*, **45**, 41 (1976).

Boudart, M., "Catalysis by Supported Metals", *Adv. Catal.*, **20**, 153 (1969).

Dwyer, D. J. and Somorjai, G. A., "Hydrogenation of CO and $CO_2$ over Iron Foils. Correlations of Rate, Product Distribution, and Surface Composition", *J. Catal.*, **52**, 291 (1978).

Fu, L. and Bartholomew, C. H., "Structure Sensitivity and Its Effects on Product Distribution in CO Hydrogenation on Cobalt/Alumina", *J. Catal.*, **92**, 376 (1985).

Ignatiev, A. and Matsuyama, T., "Relationship of Surface Composition to Enhanced Methanation Activity over Cobalt Single Crystals", *J. Catal.*, **58**, 328 (1979).

Johnson, B. G., Bartholomew, C. H. and Goodman, D. W., "The Role of Surface Structure and Dispersion in CO Hydrogenation on Cobalt", *J. Catal.*, **128**, 231 (1991).

Lee, W. H. and Bartholomew, C. H., "Multiple Reaction State in CO Hydrogenation on Alumina-Supported Cobalt Catalysts", *J. Catal.*, **120**, 256 (1989).

Lee, J.-H., Lee, D.-K. and Ihm, S.-K., "Independent Effect of Particle Size and Reduction Extent on CO Hydrogenation over Alumina Supported Cobalt Catalyst", *J. Catal.*, **113**, 544 (1988).

McCarty, J. G. and Wise, H., "Hydrogenation of Surface Carbon on Alumina-Supported Nickel", *J. Catal.*, **57**, 406 (1979).

Moon, S. H., Park, C. W. and Shin, H. K., "New Frontiers in Catalysis (Guczi, L. et al.)", 2757, Akademiai Kiado, Budapest (1993).

Moon, S. H. and Yoon, K. E., "Kinetic Behavior of Partially Reduced Co/$Al_2O_3$ Catalysts in CO Hydrogenation", *Applied Cata-*

*lysis*, **16**, 289 (1985).

Moon, S. H., Yoon, K. E. and Kim, Y. G., "Enhancement of CO Hydrogenation Activity on Incompletely Reduced Nickel Wire", *Korean J. of Chem. Eng.*, 3(1), 61 (1986).

Paal, Z. and Menon, P. G., "Hydrogen Effects in Catalysis", p. 543 Marcel Dekker, Inc., New York, NY (1988).

Palmer, R. L. and Vroom, D. A., "Mass-Spectrometric Measurements of Enhanced Methanation Activity over Cobalt and Nickel Foils", *J. Catal.*, **50**, 244 (1977).

Reuel, R. C. and Bartholomew, C. H., "Effect of Support and Dispersion on CO Hydrogenation Activity/Selectivity Properties of Cobalt", *J. Catal.*, **85**, 78 (1984).

van Hardeveld, R. and Hartog, F., "Influence of Metal Particle Size in Nickel-on-Aerosil Catalysts on Surface Site Distribution, Catalytic Activity, and Selectivity", *Adv. Catal.*, **22**, 75 (1972).

Smith, C. E., Biberian, J. P. and Somorjai, G. A., "The Effect of Strongly Bound Oxygen on the Dehydrogenation and Hydrogenation Activity and Selectivity of Platinum Single Crystal Surfaces", *J. Catal.*, **57**, 426 (1979).

Vannice, M. A., "The Catalytic Synthesis of Hydrocarbons from $H_2$/CO Mixture over the Group VIII Metals. V. The Catalytic Behavior of Silica-Supported Metals", *J. Catal.*, **50**, 228 (1977).