ENHANCEMENT OF CO HYDROGENATION ACTIVITY ON INCOMPLETELY REDUCED NICKEL WIRE

Sang Heup MOON*, Kwang Euy YOON, and Young Gul KIM

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,

P.O. Box 131, Cheongryang, Seoul, Korea

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Abstract— Enhanced activity of Ni wire in CO hydrogenation has been observed when the metal surface is incompletely reduced. The catalytic behavior has been studied in a flow reactor for different H_2/CO ratios, and the carbon species accumulated on the metal surface during reaction have been analyzed by Temperature-Programmed-Surface-Reaction(TPSR). It has been concluded that the surface or sub-surface oxygen remaining on the catalyst due to incomplete reduction plays an important role in determining the metal catalyst behavior. The extent of metal reduction in addition to the metal surface area has to be considered in estimation of the intrinsic activity of Ni catalysts.

INTRODUCTION

Nickel is a good methanation catalyst, and many studies have been made previously [1-3] for the catalysts of different preparation conditions. Since nickel is relatively difficult to reduce [1], most of the catalysts studied have been reduced only partially. Incomplete metal reduction is particularly significant for the supported catalysts of low metal loading, as are most of the industrial catalysts, because the dispersed metal particles are stabilized by interaction with the support. For example, the percentage reduction of Ni/Al_2O_3 catalysts, after reduction at 450°C for 2 hours, decreases from 97 to 29% as the metal loadings are lowered from 23 to 0.5 wt% [2].

A common view in analyzing the kinetic behavior of partially reduced metal catalysts is to assume that the unreduced metal particles are inert and simply change the metal surface area of the catalysts. Accordingly, comparison of the catalytic activities in most studies has been made on the basis of turnover numbers, which are the conversion rates per surface metal atom.

The assumption of inertness of the unreduced metal particles, however, does not always hold. Instead, the catalytic activities are in some instances significantly modified by existence of the unreduced metal oxides. For example, Palmer and Vroom [3] reported that Ni foil reduced at relatively low temperatures, 525-600°K, showed considerably high activity in methanation as compared to one reduced at higher temperatures,

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* To whom all correspondence should be addressed.
  Mailing Address: Reaction Engineering Laboratory, KAIST, P.O. Box 131, Cheongryang, Seoul, Korea

800-900°K. A similar result, although it was not for Ni, was obtained by Reymond et al. [4] who showed that unreduced Fe_2O_3 was more active in CO hydrogenation than reduced Fe. A recent study of Co/Al_2O_3 in this laboratory [5] has shown that the partially reduced Co catalysts exhibit enhanced methanation activity and higher selectivity to olefinic hydrocarbons than the relatively well-reduced catalysts.

In this work, we have reduced Ni wire under different reduction temperatures and studied its catalytic properties in CO hydrogenation. The metallic state of the Ni wire after reduction treatments has been monitored by measuring its electrical resistance [6], and the percentage reduction of the Ni wire was measured by oxygen titration at 673°K [2].

EXPERIMENTAL

Materials and Reduction Conditions

Nickel wire purchased from Ventron Corporation contained 99.97% Ni, and its diameter was 0.025cm. The purchased Ni wire was cleaned in-situ in the reactor by repeated 5-6 cycles of oxidation with oxygen and reduction with hydrogen at 1000°K. As a final step before the reaction studies, the Ni wire was oxidized at 900°K and then reduced at two different temperatures, i.e., 900°K or 550°K. Both the hydrogen and oxygen flow rates were 20cc/min, and the reactor was purged with helium (25cc/min) for 10 minutes before changing the gases.

Hydrogen (Metheson, 99.999%) and helium (Takachiho, 99.999%) gases were further purified by

1. H. P. 3455A digital voltmeter   2. Furnace
3. Thermocouple   4. Temperature programmer
5. Teflon stopper   6. Nickel wire
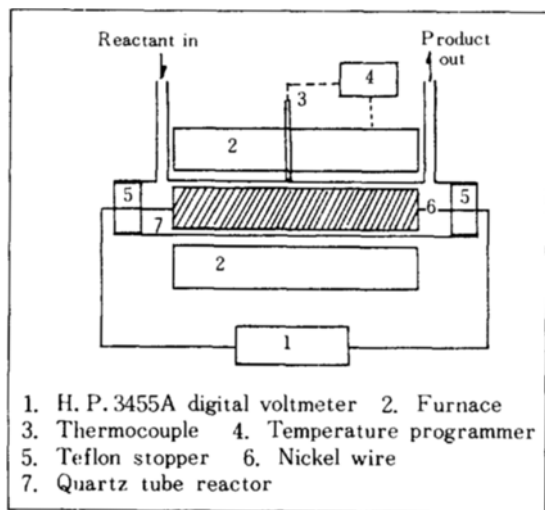7. Quartz tube reactor

Fig. 1.   Schematic diagram of reactor.

flowing through Oxytrap (Alltech) and Molecular Sieve 5A trap consecutively. Carbon monoxide (Takachiho, 99.95%) was also flowed through Molecular Sieve 5A trap for water removal. Oxygen (Matheson, UHP 99.99%) was used without purification.

Chemisorption and O_2 Titration

CO chemisorption and H_2 adsorption were performed in a conventional volumetric adsorption apparatus capable of easily degassing up to 10^{-5} Torr. Pressure changes during adsorption measurements were monitored with a capacitance monometer (M.K.S. Instrument Inc., 170 M). The amount of CO chemisorption was estimated as a balance of the total and reversible uptakes at 273°K after the results were extrapolated to zero pressure. The H_2 adsorption was measured simply at 100 Torr of H_2 pressure because the amount of irreversible H_2 uptake varied sensitively with the evacuation period, being almost negligible after 30 min evacuation.

The percentage reduction of Ni wire was measured by oxygen titration at 673°K as was used by Bartholomew and Farrauto [2]. It was assumed that Ni reacted with oxygen to produce NiO.

CO Hydrogenation and Temperature-Programmed Surface Reaction (TPSR)

Activity of the Ni wire in CO hydrogenation was measured in a flow reactor made of 11-mm I.D. quartz tube. Ni wire was wound around a 9-mm dia. quartz rod which was placed in the reactor as shown in Fig. 1. The wire was reduced in-situ in the reactor under the reduction conditions described above, before the reactant stream (typically $H_2/CO = 6/1$ in mole ratio) was flowed into the reactor for reaction. Typical flow rate of the reactant was 35 cc/min (controlled by a flow controller, Brooks model 5841), and the temperature was maintain-
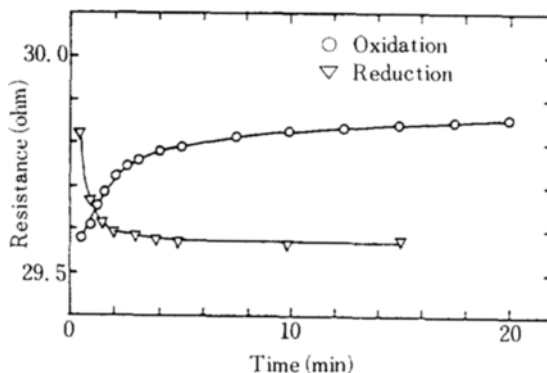

Fig. 2.   Electrical resistance change during reduction or oxidation of Ni wire at 900°K.

ed at 550°K.

After about 9-hour reaction, the reactor was cooled to room temperature, purged with hydrogen for 1 hour, and then heated again at 10°K/min in hydrogen stream (40 cc/min) for TPSR. Methane produced during TPSR was analyzed by a G.C. (Hewlett-Packard 5840A) with 6-feet, Porapak Q column and FID detector.

RESULTS AND DISCUSSION

Reduction of Ni Wire

Fig. 2 shows changes in electrical resistance of the Ni wire measured during the final step of oxidation or reduction at 900°K. The overall changes in the electrical resistance during oxidation or reduction are almost same, 0.25 ± 0.03 ohm, which suggests that the treatments are basically reversible processes. In Fig. 3, resistance of the Ni wire after final reduction at two different temperatures, 550 and 900°K, has been compared as measured between 540 and 560°K. It is clear from Fig. 3 that the Ni wires are in different metallic states, or with different extents of reduction, after reduction at different temperatures.

The metallic states of the two different Ni wires have been studied by O_2 titration, CO chemisorption, and H_2 adsorption at 100 Torr. In Table 1, the results of O_2 titration obtained at the O_2 pressures of 250 Torr and at the zero pressure extrapolation are listed. In both cases, the wire reduced at 900°K (Wire II) shows higher O_2 uptake than one reduced at 550°K (Wire I). The amount of O_2 uptake increases with O_2 pressure for Wire II, whereas the amount is unaffected by O_2 pressure for Wire I.

Since the Ni wire is 35 m long and 0.025 cm thick, its total surface area is 280 cm², and this is equivalent to 0.7 μmole of surface Ni atoms. For Wire II, the amount of O_2 uptake at zero pressure is equivalent to 22.8 layers of reduced Ni and at 250 Torr, to 50.0 layers. The amount of O_2 uptake on Wire I is equivalent only to 0.86 layer of
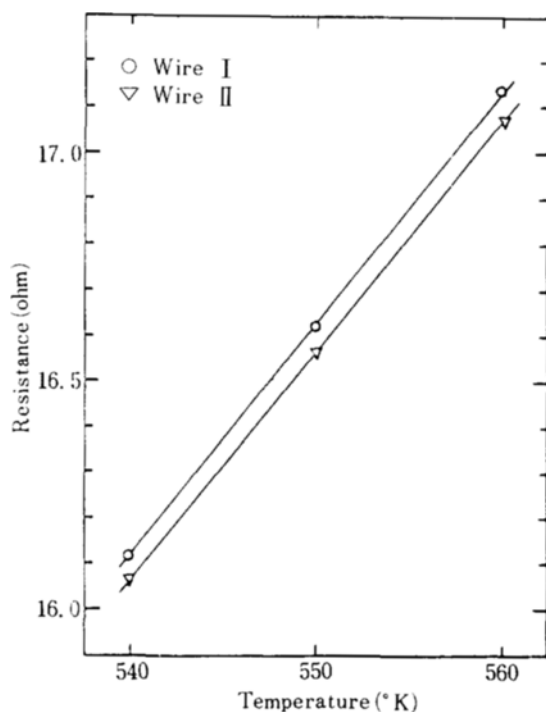
Fig. 3. Electrical resistance of Ni wire in He atmosphere after different reductive treatments.

Ni atoms, and furthermore the amount is unaffected by O_2 pressure. The result indicates that the Ni wire is almost completely reduced to the inner part when it is reduced at 900°K, whereas it is only partially reduced on the surface at 550°K. Accordingly, Wire I is expected to have surface or subsurface nickel oxides.

The CO chemisorption data in Table 1 show that Wire II adsorbs more CO than Wire I. This suggests either that Wire II has a higher metal surface area than Wire I or that CO adsorption on Wire I is suppressed due

Table 1. Gas uptake data of nickel wires(in μmole/35m Ni).

	H_2 Uptake[a] at 298 °K	CO Uptake[b] at 273 °K	O_2 Uptake[c] at 673 °K	O_2 Uptake[d] at 673 °K
Wire I	n	0.2 ± 0.1	0.3 ± 0.2	0.3 ± 0.2
Wire II	0.3 ± 0.1	0.5 ± 0.1	8.0 ± 0.2	17.5 ± 0.2

a: Value at 100 Torr H_2 pressure
b: Difference between total adsorption and reversible adsorption
c: O_2 uptake at zero oxygen pressure
d: O_2 uptake at 250 Torr oxygen pressure
n: Too small to detect

to modification of the metal surface by interaction with the unreduced nickel oxides. We believe that suppression, or weakening, of CO adsorption by surface modification is a more plausible explanation for the reason described below.

In Table 1, suppression of gas adsorption due to reduction at 550°K is more serious for H_2 adsorption. That is, the amount of H_2 adsorption on Wire I is almost undetectable even under the H_2 pressure of 100 Torr, whereas the amount is significant on Wire II which corresponds to about monolayer coverage of the surface. Since measurements of the percentage reduction of the wire indicate that Wire I is still considerably reduced on the surface, i.e., about 0.86 surface layer is reduced, it is not correct to explain that the undetectable H_2 adsorption is due to negligible metal surface area. In this respect, modification of the Ni surface by interaction with the unreduced Ni oxides is a more reasonable explanation. Similar trend of H_2 suppression has been observed by Moon and Yoon [5] for Co/Al_2O_3 catalysts of relatively poor reduction.

Methanation Activity and Product Distribution

The Ni wires reduced at two different temperatures have been tested for methanation as shown in Fig. 4. Turnover numbers have been calculated based on $6.5A^2/Ni$ atom $(1.54\times10^{15}$ atom/cm$^2)$ assuming that a constant metal dispersion is obtained regardless of the reduction conditions. The steady state turnover number of Wire II is 0.09 sec^{-1}, which is in the range of values for supported Ni catalysts, 0.035-0.095 sec^{-1}, as reported by Vannice [1].
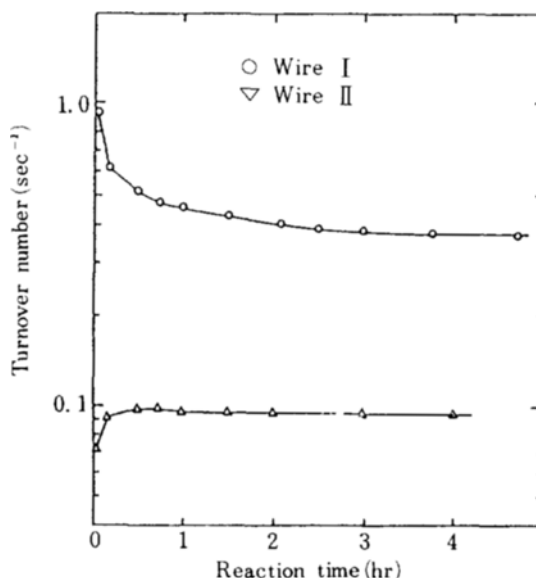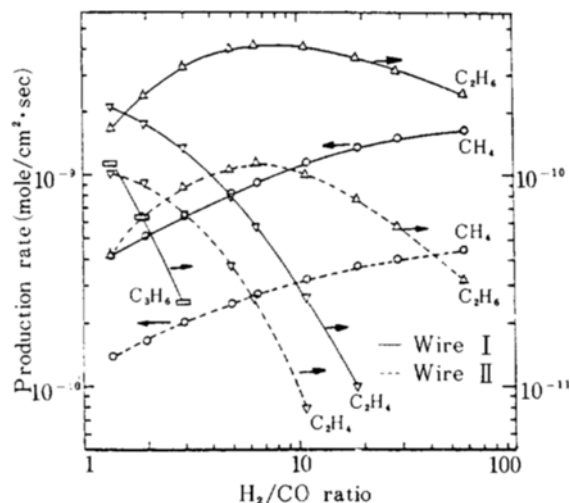

Fig. 4. Methanation turnover number vs. reaction time.

Fig. 5. Product distribution vs. H_2/CO ratio.

Fig. 6. TPSR spectra from Ni wire after 9 hour reaction.

The activity, however, is enhanced considerably, by about 5 times, when the wire is reduced at 550°K (Wire I). If CO chemisorption is used as a basis for turnover number calculation, the enhancement is even greater. This result should be compared with that of Palmer and Vroom [3], who also observed about 10-fold increase in activity for their incompletely reduced Ni foil. It is therefore clear that incomplete metal reduction is beneficial to enhanced methanation activity of Ni. The origin of the activity enhancement will be discussed later related to the TPSR result.

Reasons for the transient activity drop and increase during the initial reaction period, as observed in Fig. 4, are not clear at present. It is possible, however, that carbon deposited or H_2O generated during the initial reaction period modifies the catalyst surface.

Under the reaction conditions of Fig. 4, methane is the main product and only small fractions of ethylene and ethane are produced. The product distribution, however, changes as the H_2/CO ratio is varied between 35/25 and 59/1. In Fig. 5, Wire I shows higher activity for all the hydrocarbon products than Wire II. Nevertheless, the characteristic trend in activity for each hydrocarbon product seems unchanged with the H_2/CO ratio for both wires. That is, the methanation rate increases with the H_2/CO ratio, ethane formation goes through a maximum at about $H_2/CO = 7.0$, and ethylene decreases when the H_2/CO ratio increases. Propylene is detected only on Wire I, but the rate decreases rapidly with increase in the H_2/CO ratio. In case of Wire II, the production of propylene is too small to detect.

Increase of the methanation rate with the H_2/CO ratio is obvious considering that the rate-determining step (RDS) of methanation is hydrogenation of the surfa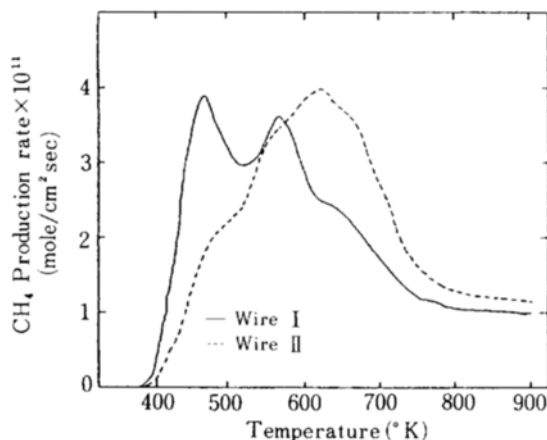ce carbon species and that the hydrogenation will be enhanced under high H_2 partial pressure. The high H_2 pressure, however, is not beneficial to formation of olefins such as ethylene and propylene. The olefin formation, on the other hand, is enhanced under the H_2-poor environment, i.e., for lower H_2/CO ratio, which suggests that the RDS in this case is propagation of the surface carbon species instead of their hydrogenation. As for the ethane formation, the rate is suggested to be determined by a balance between the hydrogenation and the carbon propagation rates, showing a maximum at the intermediate H_2/CO ratio.

Maintenance of the above characteristic activity dependence on the H_2/CO ratio regardless of the reduction conditions of the Ni wire suggests that the nature of the surface active intermediates is not altered by different extents of metal reduction. Only the surface population of the active intermediates changes due to different metal reduction, which results in higher overall activity for Wire I than for Wire II.

TPSR Study of Deposited Carbon

To understand the reasons for the enhanced activity of Wire I over Wire II, we have made TPSR on both wires after the reaction study. Since methane is the only product observed in TPSR, its concentration has been monitored vs. the programmed temperature as shown in Fig. 6. The spectra in Fig. 6 show three major peaks appearing at $475 \pm 10°$K, $560 \pm 10°$K, and $650 \pm 20°$K, respectively.

According to McCarty and Wise [7], four types of surface carbon are deposited on Ni/Al_2O_3 during methanation. In the order of reactivity toward hydrogenation, the carbon species are classified as chemisorbed carbon atom (α), bulk nickel carbide, amorphous carbon (β), and crystalline elemental carbon. The temperature ranges for hydrogenation of these carbon species are $473 \pm 20°$K for α-carbon, about $550°$K for nickel car-

bide, and $680 \pm 30°K$ for β-carbon. Crystalline elemental carbon is almost inactive to hydrogenation below 873°K.

Following the above analyses, we may conclude that the peak appearing at about 475°K in Fig. 6 originates from the active α-carbon. This assignment is also in accordance with the results of our methanation study because Wire I, which is more active than Wire II at 550°K, shows a higher intensity for the α-carbon peak than Wire II. An opposite result is observed for relative intensities of the peak corresponding to β-carbon, which is inactive for methanation at 550°C. Carbon species corresponding to the 560°K peak do not seem to be major species to determine the overall activity, although they certainly participate in reaction at 550°K, because the peak intensity is almost unchanged for Wire I and Wire II. Accordingly, we may conclude that the high activity of Wire I comes from a large surface concentration of the active α-carbon, instead of the inactive β-carbon, whereas the opposite reason holds for the low activity of Wire II.

As to the reasons for abundancy of the α-carbon species on Wire I, we do not have a clear explanation yet. However, it is certain that the surface or sub-surface oxygen on the incompletely reduced Ni wire allows formation of more α-carbon than β-carbon. The effect of oxygen on the Ni surface may be an electronic modification. In this case, the reduced Ni metal (Ni^0) in contact with the Ni oxides (Ni^{+2}) tends to become similar to Ni^{+2}, and this results in weakening of CO adsorption as has been observed in Table 1. Geometric blocking of Ni clusters by Ni oxides should also be considered as a possible interaction although no direct evidence is obtained in this study. Nature of the interactions between the reduced surface metal and the unreduced metal oxides has to be further studied in the future, and we welcome more work by other scholars in this area.

CONCLUSIONS

As evident from the experimental results described above, the extent of Ni reduction is an important variable in determining kinetic behavior of Ni. The activity of Ni in CO hydrogenation is enhanced by incomplete metal reduction, and this is due to accumulation of the relatively active α-carbon species than the β-carbon on the poorly reduced Ni surface. It is suggested that the conventional practice of using turnover number, reaction rate/surface metal atom, for the intrinsic activity of Ni catalyst has to be reconsidered because the extent of metal reduction is also an important variable to determine the activity.

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