

## Role of MgO and CaO Promoters in Ni-Catalyzed Hydrogenation Reactions of CO and Carbon

TETSUYA HAGA, JUN-ICHI OZAKI, KYOSUKE SUZUKI,  
AND YOSHIYUKI NISHIYAMA<sup>1</sup>

*Institute for Chemical Reaction Science, Tohoku University,  
2-1-1 Katahira, Sendai 980 Japan*

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The roles of Mg and Ca promoters in Ni-catalyzed hydrogasification of carbon were investigated with emphasis on nickel dispersion and nickel-carbon interactions during gasification. The dispersion of nickel on carbon, which was estimated by means of XRD, H<sub>2</sub>-TPD, and CO methanation test, was (Ni + Mg) ≫ (Ni + Ca) > Ni. The increased dispersions of nickel by the Mg and Ca added were found to result in the enhanced Ni-C interaction, which was monitored through the desorption of CO from oxygen remaining on carbon, and, therefore, in the promotions of Ni-catalyzed lower-temperature gasification at 400 ~ 700°C. The Ca promoter was likely to give surface CaO(COO) species upon heating up to 550°C and release CO<sub>2</sub> above ~650°C. The CO<sub>2</sub> released is efficiently converted by the nickel adjacent to CaO into CO to create Ni-(O)-C species above 700°C, resulting in acceleration of Ni-catalyzed gasification above 700°C. *In situ* oxygen transfer to Ni/C during reaction is the most important role played by the Ca promoter. © 1992 Academic Press, Inc.

### INTRODUCTION

It is well known that the iron-group metals of Fe, Co, and Ni are excellent catalysts for gasification of carbonaceous resources with H<sub>2</sub>, H<sub>2</sub>O, or CO<sub>2</sub> (1) and they catalyze the gasification separately at temperatures lower and higher than 700°C, showing a two-tier type of activity (2-6). We have previously reported that the iron-group catalysts are effectively promoted by small amounts of MgO and CaO added in hydrogasification of carbon (7, 8) and coal char (9); MgO and CaO are themselves inactive for hydrogasification. Interestingly, the lower-temperature catalysis of nickel below 700°C is promoted by both the MgO and CaO added, while the higher-temperature catalysis above 700°C is promoted only by CaO. Electron microscopic observations have demonstrated that the alkaline earth promoters added, particularly MgO, increase the dispersion of nickel particles on

carbon. On the other hand, the effect of CaO on the higher-temperature catalysis of nickel has been suggested to be related to a metal-carbon interaction which dominates the metal catalysis of gasification (10-12).

Our recent works have revealed that there are two kinds of nickel-carbon interactions which suggest the importance of Ni-catalyzed activation of carbon in gasification (13). One is a Ni-(O)-C type of interaction which is responsible for the lower-temperature catalysis of nickel at 400-700°C, and this is accompanied by the thermal desorption of CO from oxygen remaining on carbon at <650°C. Another route of Ni-catalyzed activation of carbon is the dissolution of carbon into nickel followed by internal diffusion and is likely to become evident at >600°C (14-17).

The purpose of this study is to elucidate the roles of Mg and Ca promoters on Ni-catalyzed hydrogasification of carbon. Considering the importance of nickel dispersion and nickel-carbon interaction in the catalysis of gasification, the state of nickel on carbon in

<sup>1</sup> To whom correspondence should be addressed.

the presence and absence of Mg or Ca added is examined using various techniques: X-ray diffraction, temperature-programmed desorption of hydrogen, XPS, CO methanation test, and temperature-programmed decomposition in inert gas. The roles of MgO and CaO promoters in the nickel catalysis of gasification are discussed based on the reaction and characterization results.

#### EXPERIMENTAL

A calcined pitch coke (Nittetsu Chem. Ind.; ash 0.24%) and an activated carbon (Wako Pure Chem. Ind.; ash 3%), which were crushed to 0.25–0.5 mm, were used as carbonaceous reactants. The calcined pitch coke was heated to 750°C to remove about 0.3 wt% of residual volatile matter and was then subjected to the quenching treatment with a distilled water after air oxidation for 6 min at 600°C to enhance the reactivity for catalytic hydrogasification (2, 18). The N<sub>2</sub> surface area of the pitch coke was enlarged by the pretreatment from 0.5 to 3 m<sup>2</sup>/g, and this specimen is hereafter referred to as WPC. The activated carbon, which had a large N<sub>2</sub> surface area of ~1020 m<sup>2</sup>/g, is called AC hereafter. The ashes of WPC and AC specimens essentially consisted of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> only. Besides these carbons, an Australian brown coal, Loy Yang (LY), and the chars prepared by heating the coal in nitrogen were also used for reactivity measurements. The dried LY coal contained 1.0% ash and 66% carbon on a dry ash-free basis and its N<sub>2</sub> surface area was about 200 m<sup>2</sup>/g.

Nickel nitrate was loaded on the WPC, AC, and LY specimens by the impregnation from an aqueous solution. The loadings of metallic nickel are 2 wt% on the AC and LY specimens and 5 wt% on the WPC specimen. In preparation of the Ni + Mg and Ni + Ca catalysts, magnesium or calcium nitrate was added to the specimen in a loading of 0.2–1 wt% (as Mg or Ca metal) by the simultaneous impregnation method with nickel nitrate. After the impregnation, the specimen was heated for 1 h at 350°C in pure hydrogen at 1 atm to reduce the nickel on

carbon and was then used for reactivity measurements and characterizations.

Reactions were performed in flowing 100% H<sub>2</sub> and 1% CO + 99% H<sub>2</sub> gases at 1 atm using a fixed-bed reactor made of quartz. The 1% CO + 99% H<sub>2</sub> gas was utilized to *in situ* monitor the CO methanation reaction catalyzed by nickel on carbon during hydrogasification of the carbon (13). The reactions were mostly carried out by temperature-programmed heating to 850–1000°C at a rate of 5°C/min. The effluent gas was subjected to the gas chromatographic analysis of C-containing gases (CO, CO<sub>2</sub>, and CH<sub>4</sub>) to evaluate the conversion rates of CO and carbon, which are expressed on a carbon weight basis in the specimen initially charged.

The state of nickel on carbon was examined by means of temperature-programmed desorption of adsorbed hydrogen (H<sub>2</sub>-TPD), X-ray diffraction (XRD, Shimadzu-XD3A), and X-ray photoelectron spectroscopy (XPS, Shimadzu-ESCA750). In H<sub>2</sub>-TPD, the specimen exposed to hydrogen for 5 min at 300°C and during the cooling period from 300 to 20°C was heated to 300°C at 30°C/min in a flow of pure argon, and the amount of hydrogen evolved was analyzed using a thermal conductivity detector. Some Ni-loaded specimens (~1 g) were also heated to 850 or 900°C at a rate of 5°C/min in flowing helium at ~100 ml/min to detect small amounts of carbon oxides thermally evolved from the surface of specimen. The weight loss upon heating was measured using a thermogravimetric microbalance, and the CO and CO<sub>2</sub> gases desorbed were analyzed by a gas chromatograph using the apparatus for reactivity measurements.

#### RESULTS

##### *Effects of Addition of Mg and Ca on the Dispersion of Nickel on Carbon Examined by XRD, H<sub>2</sub>-TPD, and CO Methanation*

The dispersion state of nickel on the WPC specimens with 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca was explored as a

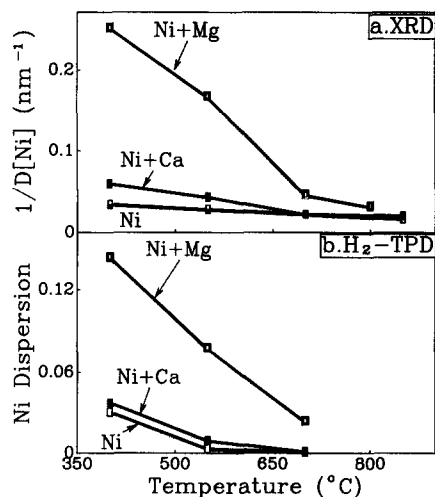


FIG. 1. Nickel dispersions in the 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca catalysts on carbon (WPC), estimated from the average diameter of crystallites determined by XRD (a) and the  $H_2$ -TPD measurement assuming  $H/Ni = 1$  (b).

function of the heat-treatment temperature of specimen in hydrogen. Figures 1a and 1b represent the inverse of the average diameter of Ni crystallites determined by XRD and the dispersion of Ni estimated from  $H_2$ -TPD assuming  $H/Ni = 1$ , respectively. It is seen that the dispersion of Ni is in the order of 5% Ni + 1% Mg > 5% Ni + 1% Ca > 5% Ni on WPC and largely decreases upon heating.

When a 1% CO + 99%  $H_2$  gas was flowed over the Ni/C specimens, CO was found to be substantially converted to methane by the reaction of  $CO + 3H_2 = CH_4 + H_2O$ , which was far faster than the hydrogasification of carbon substrate. Figure 2 compares the methanation rates of CO on the WPC specimens with 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca in 1% CO + 99%  $H_2$ . Methane is formed above 250°C by the methanation; hydrogasification of WPC was also occurring above 400°C at a far slower rate than the CO methanation. No methane was observed over the 1% Mg- and 1% Ca-loaded specimens without nickel. The rate of Ni-catalyzed methanation reaction of CO

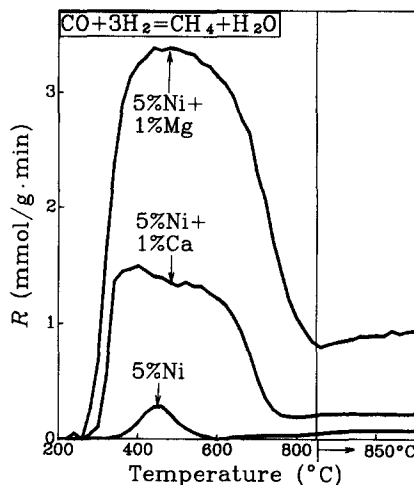


FIG. 2. The methanation rates of CO on the 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca catalysts on carbon (WPC) in 1% CO + 99%  $H_2$ .

is in the order of 5% Ni + 1% Mg > 5% Ni + 1% Ca > 5% Ni, and this is the same order as that in dispersion of nickel. It is obvious that the Mg and Ca added increases the dispersion of Ni on carbon and therefore enhances the catalytic activity of Ni for the methanation reaction of CO.

Table 1 compares the turnover frequencies of Ni, Ni + Mg, and Ni + Ca catalysts, which were estimated from the nickel dispersions (Fig. 1b) and the methanation rates (Fig. 2). It is found that the dual catalysts yield higher turnover rates than the single

TABLE I

Turnover Frequencies (TOF) of the Ni, Ni + Mg, and Ni + Ca Catalysts on Carbon for the Methanation of CO

Catalyst	400°C	550°C	700°C
5% Ni	0.09	0.29	0.95
5% Ni + 1% Mg	0.46 (4.9)	0.88 (3.0)	2.08 (2.2)
5% Ni + 1% Ca	0.82 (8.7)	3.00 (10.4)	11.13 (11.8)

Note. The values in parentheses represent the ratio of  $TOF[Ni + Mg \text{ or } Ni + Ca]$  to  $TOF[Ni]$ .

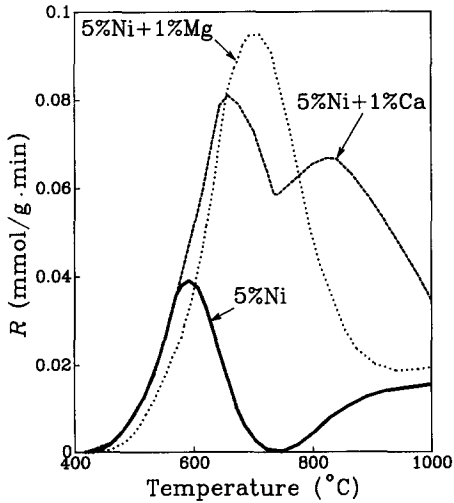


FIG. 3. Temperature-programmed hydrogasification of the carbons (WPC) with 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca.

catalyst of Ni. It is also noted that the effect of Mg promoter on the turnover rate decreases with temperature and that of Ca promoter increases with temperature.

#### Temperature-Programmed

#### Hydrogasification of Carbon Using the Ni, Ni + Mg, and Ni + Ca Catalysts

Figure 3 shows the rate profiles of methane formed when the WPC specimens with 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca were heated to 1000°C in pure hydrogen. It is seen that a two-tier type of activity of Ni is observed and enhanced by the Mg and Ca added in respectively different ways. The hydrogasification rates of the 1% Mg- and 1% Ca-loaded WPC specimens were quite negligible. Considering that the lower-temperature catalysis of Ni is transient in nature (2, 19, 20), the WPC specimens with Ni, Ni + Mg, and Ni + Ca after gasification were again subjected to temperature-programmed hydrogasification. Figures 4a and 4b give the rate differences between the first and second runs and the methane formation profiles in the second run, respectively, which are considered to estimate the contributions of lower- and higher-tempera-

ture catalyses of nickel to the methane formation by the first run, respectively. It is seen from Fig. 4a that the order in catalytic activity of nickel for lower-temperature hydrogasification is  $(\text{Ni} + \text{Mg}) > (\text{Ni} + \text{Ca}) \sim \text{Ni}$  and similar to the order in dispersion of nickel on carbon. In contrast to this, Fig. 4b reveals that the Ni-catalyzed higher-temperature reaction is effectively enhanced by the Ca added.

#### Kinetic Features of Ni-Catalyzed Higher-Temperature Gasification in the Presence and Absence of Ca

The Ni-catalyzed higher-temperature gasification, which is promoted by the added Ca, was studied in detail using the AC and LY specimens, which were higher in reactivity than the WPC specimen. No pretreatment, except the heat treatment in inert gas, was made on these specimens to minimize the lower temperature reaction. Figure 5 shows the rate profile of carbon converted when a heat-treated activated carbon with 2% Ni is gasified at 10 atm and 850°C in 100%  $\text{H}_2$  and at 1 atm and 850°C in 50%  $\text{H}_2\text{O} + 50\% \text{H}_2$ , together with the surface area changes of carbon with the progress of reac-

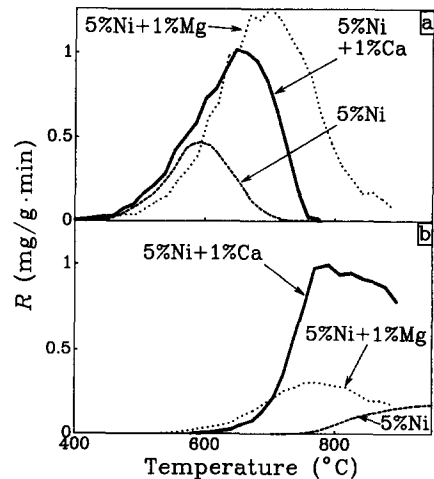


FIG. 4. The rate difference between the twice-repeated hydrogasification runs of the carbons (WPC) with 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca (a) and the rate of second run (b).

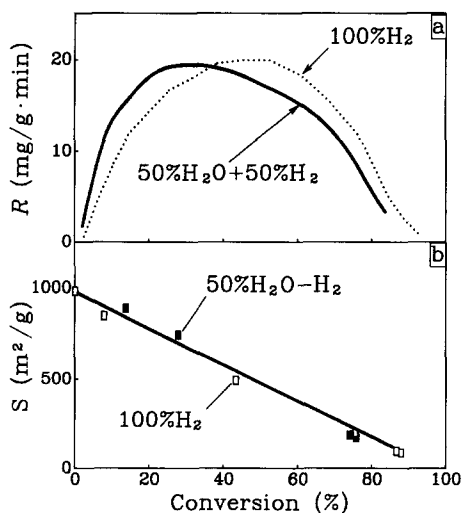


FIG. 5. The rate profiles (a) and the changes in surface area of specimen (b) during the reactions of an activated carbon with 2% Ni at 850°C with 100% H<sub>2</sub> at 10 atm and 50% H<sub>2</sub>O + 50% H<sub>2</sub> at 1 atm.

tion. The product gas is CH<sub>4</sub> in H<sub>2</sub> and the mixture of CO and H<sub>2</sub> in H<sub>2</sub>O + H<sub>2</sub>, and the noncatalytic gasification rate is negligibly small in both gases. It is seen that the isothermal catalytic gasification is accelerated

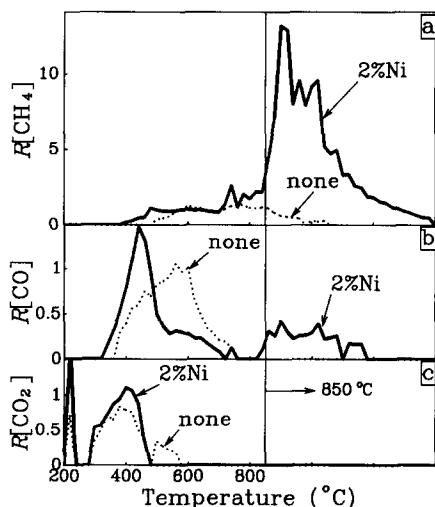


FIG. 6. The formation rates with the unit of mg/g·min of CH<sub>4</sub> (a), CO (b), and CO<sub>2</sub> (c) in hydrogasification of the Loy Yang coal with and without 2% Ni.

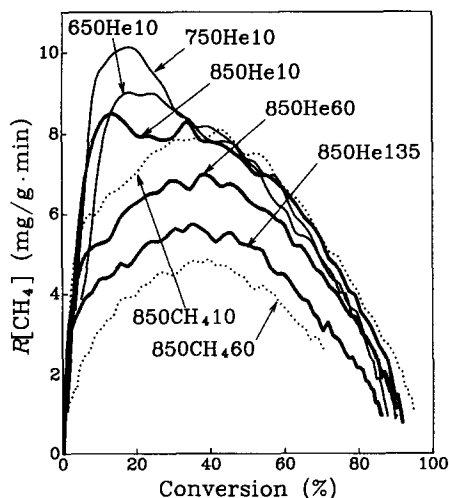


FIG. 7. Hydrogasification profiles (850°C) of the Loy Yang coal heat-treated at different conditions. The heating conditions of coal are shown; e.g., 650He10 and 850CH<sub>4</sub>60 represent the coals heated for 10 min at 650°C in He and for 60 min at 850°C in 15% CH<sub>4</sub> + 85% He, respectively.

to give a maximum rate at ~50% of carbon conversion and the observed phenomenon of "acceleration" is independent of the change in surface area of specimen during gasification (21).

Figure 6 shows the rate profiles of methane formed when the LY coal with and without 2% Ni were heated to 850°C at a rate of 5°C/min in an atmospheric flow of hydrogen. After the temperature reaches 850°C, the rate acceleration is evidently observed in the presence of nickel. Again, such an acceleration cannot be explained by the change in surface area of the LY coal during gasification. To remove any influence of volatile matters, the 2% Ni-loaded LY coal was heat-treated at 850°C for different times in helium and was then subjected to isothermal hydrogasification at 850°C. The result is given in Fig. 7 and shows that the Ni-catalyzed hydrogasification of LY gives peaks in rate at about 20 and 50% conversions. By the heat treatment for longer times in helium, the peak at  $X = 20\%$  becomes small, the peak at  $X = 50\%$  is nearly unchanged, and as a result, the gasification profile ap-

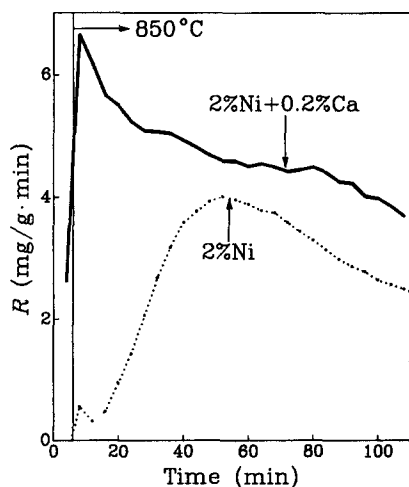


FIG. 8. Hydrogasification profiles of the Loy Yang coal with 2% Ni and 2% Ni + 0.2% Ca at 1 atm and 850°C.

proaches that of the activated carbon. Again, the formation of a small amount of CO was observed at the early stage of isothermal hydrogasification at 850°C. The CO formation during hydrogasification gave a maximum rate at 5–10% of conversion in catalytic reaction of the LY coals heat-treated for a short time (10 min), suggesting that the evolution of CO induces the activation of nickel at 20% conversion (13).

Figure 8 compares the profiles of atmospheric hydrogasification of the 2% Ni-LY coal with and without calcium. It is seen that the LY coal with Ni + Ca shows only a continuously decreasing rate with the progress of reaction, without acceleration. We have already reported that the Ni-catalyzed hydrogasification of activated carbon and some coal chars at 10 or 30 atm give monotonically decreasing and steadily increasing rates in the presence and absence of Ca added, respectively. Modification of gasification profile due to an accelerated activation of nickel catalyst was another effect attained by the addition of calcium, other than the enhancement of catalyst activity, which becomes pronounced under elevated pressures of hydrogen (8, 9). It might be

important that the initial highest activity seen in Ca-promoted Ni-catalyzed gasification above 700°C is a feature common to Ni-catalyzed lower-temperature gasification and Ca-catalyzed steam gasification.

#### Thermal Decomposition and Desorption Experiments

The thermal decompositions of magnesium and calcium nitrates in the absence of nickel were investigated in helium and hydrogen gases. The decomposition behavior of magnesium or calcium nitrate was not different in helium and hydrogen gases. Figure 9a displays the weight losses of 1% Ca salts unsupported and supported by WPC and of 1% Mg salt on WPC upon heating in hydrogen, which were measured using a thermomicrobalance (Shimadzu Seisakusho Ltd., TG30). The magnesium salt on carbon decomposes into MgO at 300–400°C; the existence of crystalline MgO particles was ascertained by the X-ray method. In the case of calcium nitrate, the unsupported salt decomposes into CaO at 500–700°C, but the salt on carbon decomposes in two stages: at

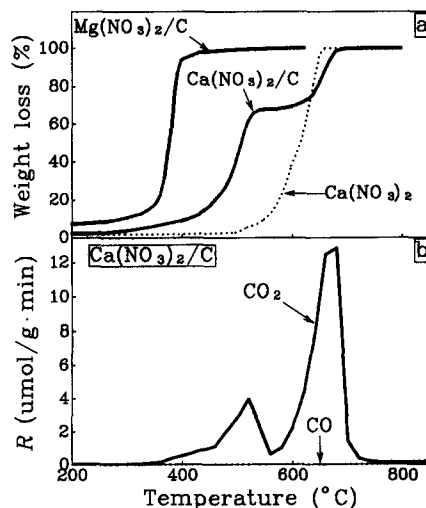


FIG. 9. Thermogravimetric curves of decomposition of the magnesium and calcium nitrates on carbon (WPC) and unsupported calcium nitrate (a), and the CO and CO<sub>2</sub> gases evolved in decomposition of calcium nitrate on WPC (b).

<550°C and 600–700°C. It is noted that the calcium salt on carbon begins to decompose at a lower temperature than the unsupported salt, suggesting that the calcium salt interacts with carbon in the first stage of decomposition. The analysis of gases evolved showed that CO<sub>2</sub> was evolved from the 1% Ca–WPC specimen in both the first and second stages of decomposition, as shown in Fig. 9b. CO<sub>2</sub> was the only gas produced at 600–700°C, although such gases as N<sub>2</sub>, O<sub>2</sub>, NO<sub>x</sub>, and H<sub>2</sub>O, which could not be detected precisely, were formed by the decomposition at <450°C. It is suggested that calcium nitrate reacts with carbon to form fine carbonate particles (CaCO<sub>3</sub>) at ~550°C and then these decompose into the oxide (CaO) at 600–700°C in both helium and hydrogen (7).

To see the decomposition of oxygen remaining on WPC with 5% Ni, 5% Ni + 1% Mg, or 5% Ni + 1% Ca after being heated for 1 h at 350°C in hydrogen to reduce the nickel, about 1 g of specimen was heated to 900°C at a rate of 5°C/min in flowing helium (100 ml/min) and the gas evolved was analyzed using a gas chromatograph. CO was found to be formed above ~400°C from all the three specimens; from WPC with 5% Ni + 1% Mg, CO<sub>2</sub> was initially formed and tended to be substituted by CO above 450°C. Most interesting was that not CO<sub>2</sub> but CO was only evolved from the specimens with 5% Ni + 1% Ca. Figure 10 compares the formation rates of CO (the sum of CO and CO<sub>2</sub> for the Ni + Mg catalyst) upon heating in helium among the specimens with 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca. The 5% Ni catalyst on WPC is found to show a two-tier type of activity for CO formation with a minimum at ~700°C, similar to the observations of methane formation by Ni-catalyzed gasification. It is seen that the specimens with Ni + Mg and Ni + Ca release larger amounts of carbon oxides than does the specimen with Ni alone and the promotions of CO desorption by the Mg and Ca added are very similar to those observed for the methane formation by hydrogasifi-

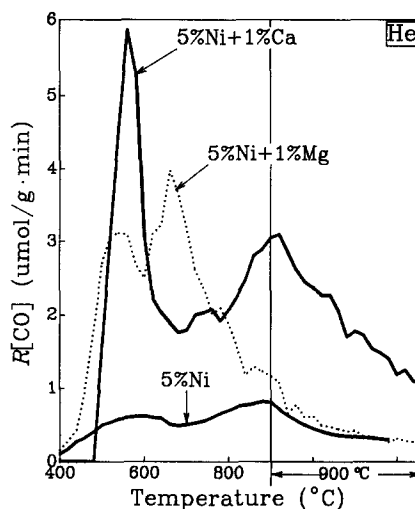


FIG. 10. The rates of carbon oxides, mostly CO, evolved from the carbons (WPC) with 5% Ni, 5% Ni + 1% Mg, and 5% Ni + 1% Ca upon heating in helium.

cation. That is, the amount of CO, partly CO<sub>2</sub>, evolved from the specimen with Ni + Mg is larger than that of the specimen with Ni alone at temperature lower than ~900°C, while the Ca added enhances the CO formation at both lower and higher temperatures. An irregular profile of carbon oxides desorbed at 450–650°C from the (Ni + Mg)/C specimen, probably due to a poor contact between MgO and Ni, as suggested by the initial formation of CO<sub>2</sub>. It is evident that the promotion of Ni-catalyzed higher-temperature hydrogasification by Ca, as well as the Mg- and Ca-promoted lower-temperature reactions, are accompanied by the thermal desorption of CO from oxygen remaining on Ni/C (13).

To elucidate the occurrence on the WPC with 5% Ni + 1% Ca above 700°C, the conversions of carbon into carbon oxides upon heating in helium were compared in Fig. 11 among the WPC specimens with 1% Ca, 5% Ni, and 5% Ni + 1% Ca. It is seen that the conversion of carbon to CO in the presence of 5% Ni + 1% Ca corresponds to two times the conversion of 1% Ca-loaded carbon to CO<sub>2</sub>. This means that CO<sub>2</sub> released from the

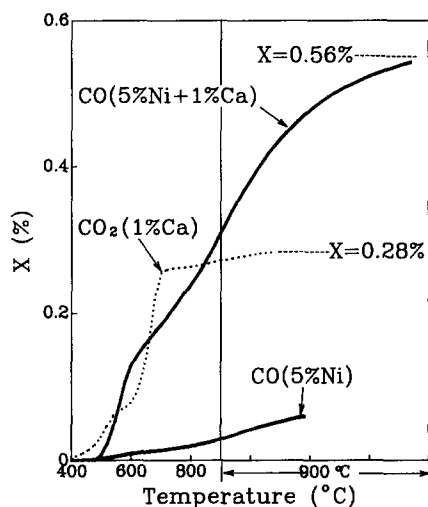


FIG. 11. The conversions of the carbons (WPC) with 5% Ni, 1% Ca, and 5% Ni + 1% Ca into CO (Ni and Ni + Ca) and CO<sub>2</sub> (Ca) upon heating in helium.

surface CaO(COO) species is completely converted to CO by Ni-catalyzed Boudouard reaction:  $C + CO_2 = 2CO$ . More important is that CO<sub>2</sub> evolved from calcium carbonate species at <550°C is immediately converted to CO by nickel on carbon but CO<sub>2</sub> evolved at 600–700°C is converted to CO very slowly, suggesting that CO<sub>2</sub> or O species is once trapped on Ni or at the Ni–C interface. If a complex such as Ni–(O)–C is formed, the nickel could catalyze the gasification in a manner similar to the lower-temperature catalysis of nickel and probably to the catalysis occurring at the early stage of higher-temperature gasification of LY coal and char. It is believed that the role of Ca added in Ni-catalyzed hydrogasification is to increase the dispersion of nickel and to *in situ* supply active oxygen to the Ni–C interface during reaction to promote the nickel catalysis.

#### XPS Analysis of Nickel Surface

XPS analyses have been performed for the AC samples with Ni, Ni + Mg, and Ni + Ca before and after hydrogasification at 800°C. Ni 2p<sub>3/2</sub> spectra observed, which are given in Fig. 12, show that an extra peak

or shoulder at 855–857 eV appears for the 2% Ni + 1% Ca catalyst on AC before reaction and after reaction for a short time, suggesting a partial oxidation of nickel surface. It was also shown that the relative surface concentration of nickel and calcium decreases and increases with reaction time, respectively, suggesting a pitting mode of Ni-catalyzed gasification (22, 23). However, a significant difference between the Ni + Ca and Ni + Mg catalysts was observed in neither Ni 2p<sub>3/2</sub> spectrum nor surface composition. It seems to be very difficult to speculate the difference in the working state of Mg and Ca promoters from the XPS result of gasified specimen after cooling (24).

#### DISCUSSION

Our previous works have shown that the Ni-catalyzed lower- and higher-temperature gasifications of carbon are different from each other in dependences on the structural properties of carbon (2, 18, 25–27) and the nature and the pressure of the gasifying agent (6, 8, 9, 12). Nevertheless, it is likely certain that nickel–carbon interactions are important in both the lower- and higher-temperature catalyses of nickel, rather than

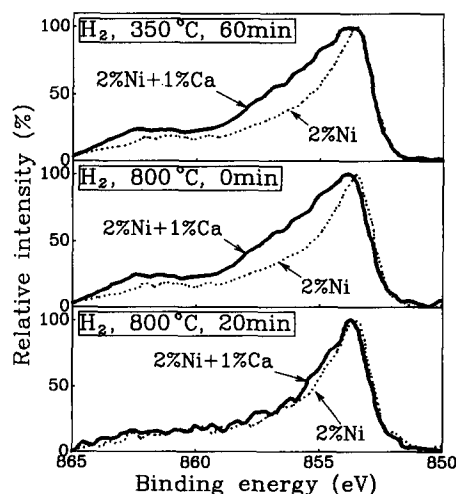


FIG. 12. Effect of Ca promoter on XPS spectra of Ni 2p<sub>3/2</sub> after hydrogen reduction at 350°C and carbon (AC) hydrogasification at 800°C.



gas-nickel interactions (28-30). We have recently clarified that the Ni-catalyzed lower-temperature gasification at 400-700°C occurs when highly dispersed nickel particles migrate on carbon to grow into larger particles. It has also been found that the reaction is mostly accompanied by evolution of a small amount of CO, suggesting that a Ni-(O)-C type of interaction promotes the nickel catalysis. The role of Mg promoter in Ni-catalyzed hydrogasification is likely to be intimately related to the catalyst dispersion and the Ni-(O)-C interaction. This is seen from the following results:

—The Mg salt added increases the dispersion of nickel and, therefore, enhances the methanation reaction of CO, as well as the lower-temperature gasification of carbon.

—The Ni + Mg catalyst on carbon releases a larger amount of CO upon heating in helium than the Ni/C catalyst, giving a maximum rate of CO evolved at ~600°C.

We speculate that the Ni-O-C species contribute to maintain a high nickel dispersion and accelerate the Ni-catalyzed activation of carbon. However, the Mg promoter had a minor effect on the higher-temperature gasification above 700°C, suggesting that the higher-temperature catalysis of nickel is different than the lower-temperature catalysis. Some kinetic examinations on isothermal higher-temperature gasification gave the following results:

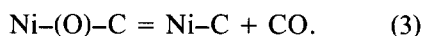
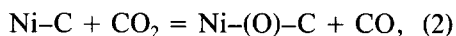
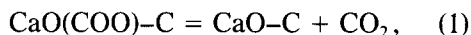
—The Ni-catalyzed higher-temperature gasification of LY coal or char gave two peaks of rate at about 20 and 50% conversions, other than at the initiation of reaction.

—The activity peak observed at 20% conversion was accompanied by the evolution of CO, and the maximum rate at 50% conversion was also observed in Ni-catalyzed gasification of activated carbon.

These suggest a simultaneous occurrence of two kinds of catalytic reactions above 700°C. One is the nickel catalysis of gasification promoted by the Ni-(O)-C interaction, similar to the lower-temperature reac-

tion at 400-700°C. The other, i.e., the gasification showing an autocatalytic behavior, is probably related to a direct Ni-C interaction such as carbon dissolution and diffusion (14-17). If so, the Ni-catalyzed gasification can be expressed as a sequential reaction of  $C[\text{bulk}] \rightarrow C[\text{Ni, dissolved}] \rightarrow C[\text{ad}] \rightarrow \text{CH}_x[\text{ad}] \rightarrow \text{CH}_4$ . The direct Ni-C interactions, by which intermediate  $C[\text{Ni, dissolved}]$  species are formed, probably prefer to occur on a clean (oxygen-free) carbon surface obtained at a later stage of hydrogasification. This may be one of possible explanations for an autocatalytic behavior of reaction above 700°C (2, 18). Alternatively, the catalytic activity of nickel can be related to the thermal stability of intermediate species, such as  $C[\text{Ni, dissolved}]$ .

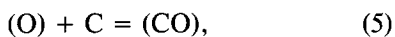
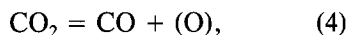
The Ca promoter was not as effective as the Mg promoter for increasing the nickel dispersion but strongly enhanced the Ni-catalyzed gasification of coal and carbon above 700°C. Now, our main concern is to clarify whether the Ca promoter influences the Ni-(O)-C or Ni-C type interaction above 700°C. The present work showed that the calcium nitrate on carbon decomposed through  $\text{CaO}(\text{COO})$  species into CaO and that the  $\text{CO}_2$  evolved above ~700°C was very slowly converted by the Ni/C system into 2CO. This indicates that the Ni-catalyzed C-CO<sub>2</sub> reaction occurs during hydrogasification:



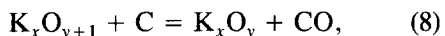
Step (1) is faster than the CO formation, and step (2) is generally faster than step (3) (1). Thus, the slow conversion of  $\text{CO}_2$  to 2CO formation means that the Ca promoter supplies active oxygen to the Ni/C system and replenishes the Ni-(O)-C type structures above 700°C. The active oxygen supplied from the carbonate-like species of Ca may be consumed partly to remove carbonaceous contaminants (coke) formed on nickel

at 600–700°C (13). It is evident that the Mg promoter cannot have the same effect. The present work revealed also that the Ca-promoted nickel catalyst was rapidly activated in the higher temperature gasification and no longer showed the acceleration phenomenon. The initial highest activity of nickel is similar to the lower-temperature gasification, accelerated by Ni–(O)–C interactions. Thus, it can be said that the Ca-promoted higher-temperature gasification is such a case that the nickel-catalyzed gasification is accelerated by the Ni–(O)–C interactions above 700°C.

It is interesting to compare the Ni-catalyzed C–H<sub>2</sub> reaction with the K–salt-catalyzed C–CO<sub>2</sub> or C–H<sub>2</sub>O reaction. Kapteijn and Moulijn (31) have recently presented a useful summary of the mechanisms proposed for the K-catalyzed carbon gasification. A general reaction scheme of gasification is likely to be as,

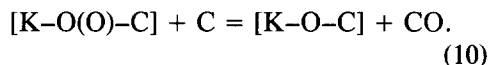
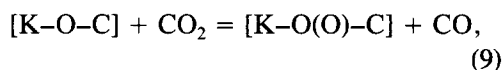


which is compatible to all theories proposed for the action of catalyst. The catalyst promotes reaction (4), (5), or (6). Reference (31) concludes that the active species is not metallic and is generally described as K<sub>x</sub>O<sub>y</sub>, which operates by the following redox scheme:



Mims and Pabst (32) propose that active potassium catalysts are highly dispersed on carbon substrate, and that K–O–C type structures form on the carbon surface and behave as active sites during gasification. The evidence from the IR spectra obtained by Yuh and Wolf (33) for the existence of such K–O–C structures is consistent with the proposals of Mims and Pabst (32). The K–O–C type structure could contribute to keeping high-dispersed K species and un-

dergo the following redox reactions to promote the C–CO<sub>2</sub> reaction:



It is also believed that in the C–H<sub>2</sub> reaction, the Ni–O–C type structures form on the carbon surface and behave as active sites during hydrogasification. However, we believe that the active species is essentially metallic nickel particles highly dispersed on carbon and that surface oxygen species act as a powerful promoter of Ni-catalyzed gasification. The Ni–(O)–C type structures probably maintain a high dispersion of nickel and mediate the activation of carbon by nickel.

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