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# Regeneration of Nickel Catalyst on Carbon

TETSUYA HAGA AND YOSHIYUKI NISHIYAMA[1]

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

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Catalytic activity of nickel for carbon gasification is initially high at 500–700°C, but it disappears when the reaction is repeated or the specimen is preheated in an inert atmosphere above 700°C. The deactivated catalyst was found to be regenerated by a treatment with steam at 700–800°C and subsequent reduction at 350°C. The surface state of nickel on carbon was inferred by temperature-programmed desorption of hydrogen, and a correlation was found between the TPD patterns and the catalytic activity for gasification. Catalytic activity of the nickel for $CO_2$ conversion in $1\%CO_2+99\%H_2$ mixture deactivated, and the catalyst was regenerated in a similar way as that observed for gasification. Redispersion of nickel and, possibly, removal of contaminants are thought to be responsible for the observed catalyst regeneration.

## INTRODUCTION

It is well known that some transition metals such as nickel and cobalt catalyze carbon gasification in two temperature regions: the lower one between 400 and 700°C and the higher one above 750°C (*1*, *2*). The lower temperature reaction (LTR) takes place nearly in the same temperature region irrespective of the nature and pressure of gasifying agent (*3*), and the reaction rate is reported to decrease from 600 to 700°C (*4*, *5*). This is different from the higher temperature reaction (HTR), which proceeds without serious deactivation as long as carbon substrate remains (*6*, *7*). A similar deactivation to that observed for the LTR was seen in hydrogenation of CO or $CO_2$ catalyzed by nickel on carbon during gasification in a somewhat wider temperature region of 500–700°C (*8*). The sintering of nickel particles and carbon deposition onto or into nickel are possible causes of deactivation.

The carbon conversion in LTR can be enhanced by modifying the reaction system (*9*–*13*). Here, we tried to regenerate the catalytic activity of nickel in the LTR region during hydrogasification, and found that it can be restored by a steam treatment and subsequent reduction in hydrogen.

## EXPERIMENTAL

A calcined pitch coke, supplied by Nittetsu Chemical Industry Co., was crushed to 0.25–0.5 mm and heated to 750°C to remove residual volatile matter (0.3 wt%). As the surface state of this carbon was not suitable for catalyst loading, the carbon was treated at 850°C for 1 h with $50\%H_2O$–He, which caused a weight decrease of about 1% and an enlargement in surface area measured by nitrogen adsorption from 0.5 to 3 $m^2/g$ (*9*). The treated specimen is hereafter referred to as SPC. The SPC was impregnated with nickel nitrate to load 5 wt% of nickel, and dried at 50°C in vacuum. The nitrate was reduced to nickel at 350°C by hydrogen before use.

In the present study, three temperature-programmed methods were employed. In hydrogasification, referred to as $H_2$-TPG, approximately 1 g of the Ni-loaded sample was packed in a quartz tube of 15 mm I.D., and was heated up to 1000°C at a rate of 5°C/min in a flow of pure hydrogen, 100 $cm^3/min$ (20°C, 1 atm). In another temperature-programmed reaction, designated as $1\%CO_2/H_2$-TPR, about 0.1 g of the speci-

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[1] To whom correspondence should be addressed.

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men was heated in a flow of 1%$CO_2$+99%$H_2$ under the same temperature and flow rates as $H_2$-TPG. The state of nickel was inferred by temperature-programmed desorption of hydrogen ($H_2$-TPD). In $H_2$-TPD, the specimen was exposed to hydrogen for 5 min at 300°C and 1 atm and cooled in hydrogen to 25°C. Then, after the hydrogen in the gas phase was purged, the specimen was heated to 300°C at 30°C/min in a flow of pure argon, 30 $cm^3$/min (20°C, 1 atm), and the amount of hydrogen evolved was quantified using a thermal conductivity detector (TCD).

After a reaction, either $H_2$-TPG or 1%$CO_2$/$H_2$-TPR, the specimen was treated with 50%$H_2O$–He at 1 atm for various times at temperatures between 300 and 800°C to alter the state of nickel. After the treatment, nickel (nickel oxide) was reduced by hydrogen at 350°C and 1 atm for 1 h. The 50%$H_2O$ treatment and the succeeding reduction are hereafter referred to simply as "steam treatment" and denoted by a code such as T(700,3), which express the temperature (°C) and the duration (h) of exposure to 50%$H_2O$–He. During all the reactions and treatments, C-containing components (CO, $CO_2$, and $CH_4$) in the effluent gases were monitored by a gas chromatograph, from which reaction rates ($R$) were calculated. These are expressed on a basis of mol converted per unit weight of catalyst on the carbon specimen.

## RESULTS

### *Hydrogasification Runs Repeated with Intermediate Steam Treatment*

The $H_2$-TPG of the 5%Ni-SPC specimen was repeated with intermediate steam treatment, varying the treating temperature and duration. The profiles of methane formation in $H_2$-TPG are depicted in Fig. 1. The fresh specimen is gasified in the temperature ranges 400–700°C(LTR) and above 700°C(HTR) as described above. Noncatalytic hydrogasification occurred only above 750°C at a small rate. The carbon conversion in the initial run was about 3%. The methane formation profile in the second or later runs, when the $H_2$-TPG was repeated without intermediate steam treatment, is shown by a dotted line in Fig. 1a as "Deactivated." The LTR is totally lacking, indicating a change in the reaction system. As the deactivation is also caused by heating in helium or $CO_2$, the notation is used regardless of the heating atmosphere.

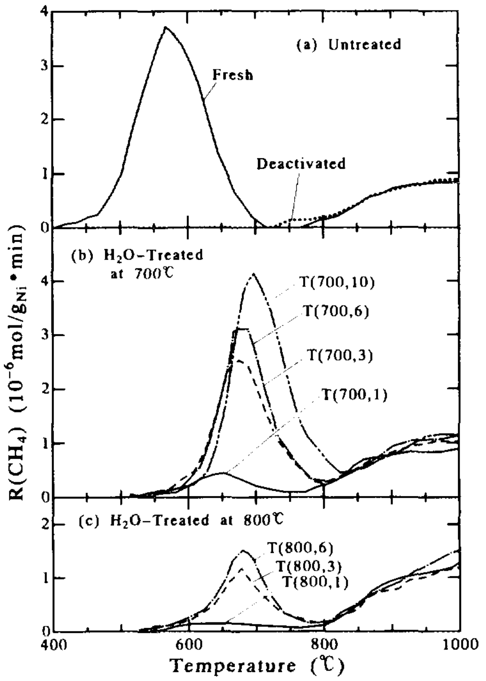

FIG. 1. Methane formation profiles in $H_2$-TPG of 5%Ni-SPC for a series of gasification–steam treatment experiments. (a) Untreated, (b) treated at 700°C, and (c) treated at 800°C. The $H_2$-TPGs were conducted in the order (a), (b), (c), and from shorter duration to longer ones.

Methane formation profiles after the steam treatment below 500°C were the same as that of the deactivated. By raising the treatment temperature to 700°C or higher, LTR was observed again as seen in Fig. 1, though methane was formed in a temperature range a little higher than that of the fresh sample. Thus, the nickel catalyst deactivated in LTR can be regenerated by treating the specimen with steam at a temperature between 700 and 800°C and reducing at 350°C. The methane formation profiles after regeneration depend somewhat on the history of the specimen, but the main features are the same irrespective of the deactivation–regeneration sequence. Also, the steam treatment at 700°C appears to be more effective than that at 800°C. Carbon conversion in $H_2$-TPG after regeneration was less than 2%.

It is important that a similar treatment of the deactivated specimen with 100% $CO_2$ at 1 atm for 1 to 10 h at temperatures from 300 to 800°C did not cause any regeneration. The weight losses in the steam treatment were less than 1%, while a larger weight loss was observed during $CO_2$-treatment at 700°C.

### *The $H_2$-TPD Study*

As a probe of the changes in the state of nickel on carbon, the $H_2$-TPD experiments were conducted on fresh, deactivated, and steam-treated specimens. Figure 2 displays the $H_2$-TPD profiles for the specimens after hydrogasification up to a temperature between 400 and 700°C. The pattern for a freshly prepared specimen is almost the same as that of the specimen heated to 400°C. The profiles indicate the existence of at least two kinds of hydrogen-adsorbing sites. Also drawn in Fig. 2 are $H_2$-TPD profiles of two steam-treated specimens. They have a small peak at 100°C and a sharp rise near 300°C, and resemble somewhat those of the specimens gasified up to 500 or 550°C, suggesting that the state of nickel after the steam treatment is similar to those on partially gasified specimens.

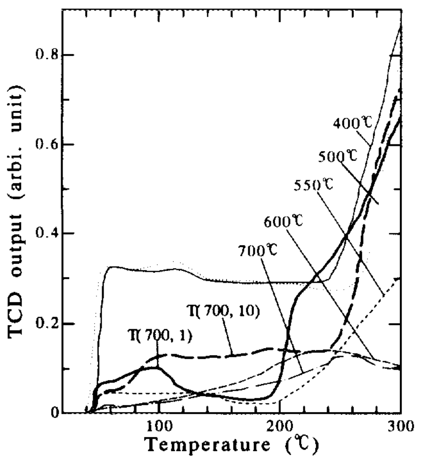

FIG. 2. $H_2$-TPD profiles of 5%Ni-SPC heated in hydrogen up to the temperature shown in the figure. The steam treatments were conducted for specimens gasified up to 700°C.

### *The 1%$CO_2$/$H_2$-TPR Study*

The deactivation and the regeneration of nickel on carbon were also examined for $CO_2$ hydrogenation catalyzed by the nickel using 1%$CO_2$/$H_2$-TPR method. In 1%$CO_2$+99%$H_2$, $CO_2$ was converted into CO and $CH_4$ by the reverse shift and methanation reactions, respectively. We estimated the rate of individual reactions, by using the observed rates of disappearance of $CO_2$, formation of CO and $CH_4$, and hydrogasification measured separately. In doing so, assumptions were made about the additivity of the rates and the inhibition of the Boudouard reaction in a large excess of hydrogen (*8*). In Fig. 3, parts of the results are presented. $R(-CO_2)$ is the rate of disappearance of $CO_2$ and $R(CH_4^*)$ is the difference in the rates of methane formation between 1%$CO_2$+99%$H_2$ run and 100%$H_2$($H_2$-TPG); the former is believed to correspond to the activity for reverse shift reaction and the latter to methanation of CO and $CO_2$.

The nickel on SPC as prepared is very active for converting $CO_2$ in the range of 350 to 600°C, but loses its activity after heated above 700°C, similar to the deactivation in gasification. The catalytic activities for $CO_2$ conversion and methane formation are also regenerated by the steam treatment. It is again noted that the active region shifted to a higher temperature side after the steam treatment. It was observed that the rate of conversion after regeneration is somewhat affected by the maximum temperature of preceding reaction; heating to a higher temperature resulted in a lower rate

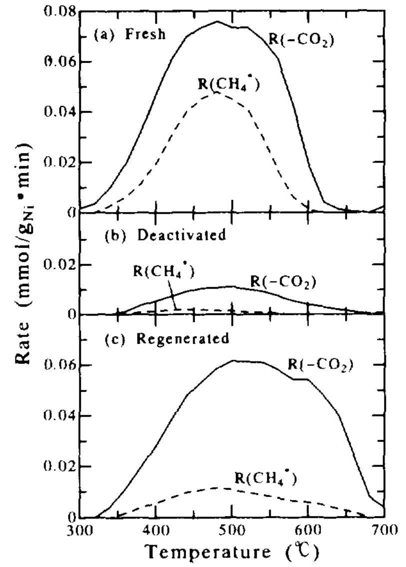

FIG. 3. The rates of disappearance of $CO_2$ [$R(-CO_2)$] and methane formation other than hydrogasification [$R(CH_4^*)$] on the 5%Ni-SPC in 1%$CO_2$+99%$H_2$. (a) Fresh, (b) after $H_2$-TPG up to 700°C, and (c) regenerated by a steam treatment [T(700,1)].

even after the regeneration, as illustrated in Fig. 4.

## DISCUSSION

The present work showed that a nickel catalyst deactivated by hydrogasification or in a 1%$CO_2$+99%$H_2$ mixture at temperature up to 700°C can be regenerated by the steam treatment. In this system, three possible reasons for the deactivation are agglomeration of nickel or loss of contact to carbon, encapsulation or embedding into the substrate, and/or a change in the chemical form such as carbide formation.

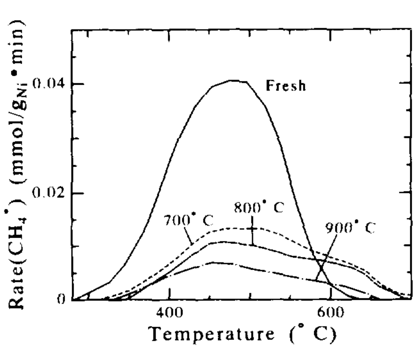

FIG. 4. Dependence of methane formation rate [$R(CH_4^*)$] on the prior history of heating. Specimens were heated in 1%$CO_2$+99%$H_2$ flow up to the temperature indicated in the figure and then steam treated at 700°C for 1 h, except for the fresh specimen.

Though a definite conclusion cannot be drawn from the present study alone, we think it most feasible to suppose that the deactivation is caused by the sintering of nickel which was initially well dispersed, and the steam treatment results in a redispersion of nickel. At the same time, some contribution may occur from removal of carbon contamination, either covering over or dissolving into nickel (*14*). The results of $H_2$-TPD are in accord with the above view. We suppose that the agglomerated nickel in a metallic state was oxidized by steam, spread over the carbon substrate, and was reduced there, resulting in a redispersion. In another study of nickel on silica, we also noted the redispersion of nickel by oxidation–reduction treatment (*15*). It was found that the redispersion was accomplished at some limited temperature program; treatment at higher temperature reduced the effect similarly to the present results. These results might be explained by supposing that the spreading in the oxide form is balanced with their own coalescence, and is sensitive to the treatment temperature. It is possible that oxygen was incorporated with the carbon surface by the steam treatment, so that some alteration of the carbon surface may contribute to the restoring of the activity. Baker *et al.* (*16*) reported the change in the state of nickel on graphite by steaming. In another study, nickel wetted the graphite surface more in steam when hydrogen was absent (*17*).

Removal of carbon contaminants may contribute to some degree to the regeneration, but the nature of contamination is not clear. At least this cannot be the deposition from the gas phase, as the deactivation took place under conditions where nickel is catalyzing carbon gasification. The carbon removal did not appear to be the main reason for the regeneration, as the $CO_2$ treatment which gasifies carbon does not cause regeneration. In $CO_2$, the surface state of carbon as well as the chemical form of nickel would be different from that in steam.

So far, in considering the behavior of nickel, we did not discriminate between gasification, $CO_2$ conversion, and methanation, but they are not the same, and there are some differences in the temperature range and the degree of deactivation as well as the degree of regeneration for the same treatment. Naturally, the activity or turnover frequency of a catalyst is determined by a number of parameters, depending on the nature of reaction, e.g., activity for gasification may be more sensitive to the number of contacts between carbon and nickel, while methane formation from carbon oxides may be sensitive to the surface structure of nickel. The similarity in the change of activities can be taken to indicate that there is one dominate parameter.

Although the catalytic activity for lower temperature reactions is restored by the steam treatment, the nickel-loaded carbon after regeneration is not totally the same as the fresh one, and the reaction occurred at some higher temperature ranges. The $H_2$-TPD after the regeneration resembles somewhat that on the specimen heated up to 550°C in hydrogen. It may be that the steam-treated sample no longer contains very small nickel particles, and incomplete redispersion of nickel by the treatment resulted in the shift in the active temperature region.

It is interesting to add that the activity for HTR is always the same regardless of the state of nickel (Fig. 1). This can be understood by the carbon-dissolution-into-nickel mechanism in which the surface state of nickel is not the controlling factor.

## ACKNOWLEDGMENTS

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