

Hydrogasification of Carbon Catalyzed by Nickel

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Introduction

Gasification of coals to produce high-Btu gases is receiving extensive attentions. Catalysis at gasification stage is investigated by several workers(1), but the catalytic processes, especially the interaction between coal and catalyst, are not well understood. In the preceding report from this laboratory, it was shown that some of the transition metals catalyze the hydrogasification of active carbons and that methane was formed in two or three stages. When Ni was used, the first stage reaction occurred at a temperature region around 550°C and the second one above 800°C. It would be interesting if the low temperature reaction can be incorporated in a coal conversion process. In this presentation, a study to clarify the nature of the reactions is described, putting emphasis on the behavior of Ni.

Experimentals

Two types of activated carbon were used; one in a granular form (AC-G) and the other a powder(AC-P). They were impregnated with a Ni salt, normally $Ni(NO_3)_2$, if not stated otherwise, from aqueous solution. Gasification was conducted mainly in a thermobalance and the specimen, 0.1-0.5 g, was heated in an atmospheric flow of hydrogen at a constant heating rate(denoted as HR) up to 1000°C and the amount of methane formed was analyzed by a gas chromatograph. Gasification at elevated pressures were done in a fixed bed reactor. In this case, the temperature was raised to 900°C in 80 min and kept for 1 hr.

The dispersion of Ni on carbon surface was examined using X-ray diffraction, scanning electron microscope and a magnetic measurement. In the last one, the magnetization of the specimen was measured in hydrogen atmosphere by Faraday method using a permanent magnet. The apparant magnetic susceptibility given below, χ_a , is supposed to be proportional to the magnitude of magnetization at a constant field.

Results

Types of reactions concerned

A typical methane formation profile is illustrated in Fig. 1. Of the two active regions, the lower one between 400 and 700°C is referred to as R-1 and the other, the higher one above 800°C, as R-2. In the results given below, conversion to methane is denoted by X.

Features of R-1 reaction

[1] Temperature dependence. One of the marked character of R-1 is its transient nature, i.e., the specimen lost its activity when heated above 650°C whether the heating accompanied gasification or not, but a re-impregnation of Ni to the deactivated specimen restored the reactivity(Table 1). Even when the temperature was kept within the active region, the rate decreased rather rapidly, as shown by one of the broken lines, A, in Fig. 1, as if a limited portion of carbon could be gasified.

[2] Pressure dependence. R-1 had a negative dependence on the hydrogen pressure above 1 atm(Fig. 2).

[3] Dependence on Ni content. Fig. 3 shows that X(R-1) is small up to 2 % of Ni for AC-P and beyond this limit, the conversion increases steeply with Ni content. For another carbon, similar patterns were

observed, but the extent of Ni content within which the activity was insignificant depended on surface state of carbon. For example, a nitric acid treatment of AC-G (in 13.5 N acid at 20°C for 3 hr) increased the amount of inactive Ni to 4 % when this was 1.5 % for untreated specimen (AC-G). The concentrations of surface acidic sites titrated with NaOH were 52 and 9 mmol/100g for treated and untreated carbon, respectively. This suggests that the inactive Ni atoms are trapped at active sites.

[4] Effect of Ni salts. Table 2 shows a comparison of Ni salts used as Ni source. $\text{Ni}_2\text{CO}_7(\text{OH})_4$ from aqueous ammonia solution and $\text{Ni}(\text{NO}_2)_2$ were active for R-1, whereas NiCl_2 was almost inactive under normal conditions. Interestingly, X(R-1) of NiCl_2 -impregnated specimen varied with the condition to reduce the salt. The activity increased by a prolonged reduction at lower temperatures (Table 3). These results can be understood by a variation in the dispersion of Ni.

Features of R-2 reaction

[1] Dependence on temperature and pressure. R-2 is an ordinal reaction in that it proceeds at nearly constant rate at a constant temperature though the rate increased somewhat at the initial period and decreased gradually with the carbon burn-off and that the rate varied reversibly with temperature. R-2 had a positive order with respect to hydrogen pressure (Fig. 2).

[2] Dependence on Ni content. In contrast to R-1, X(R-2) increased with Ni content at first but leveled-off soon, as shown in Fig. 3.

[3] Effect of Ni salt and the surface state of carbon. R-2 had no preference to the species of Ni salt to be impregnated (Table 2). Also, the surface treatment of carbon had negligible effect on X(R-2).

Dispersion of Ni on carbon surface

[1] X-ray diffraction. The breadth of (111) diffraction of Ni showed a trend that the smaller the average crystallite size, the larger the X(R-1), and that growth of Ni crystallites occurred after R-2 took place (Table 2), but this method is insensitive to the smaller part of crystallite and is inappropriate to follow the changes during R-1.

[2] Microscopic observation. From observations by a SEM, slight change in the distribution of Ni was noted after the completion of R-1. Upon heating to R-2 region, visible Ni particles appeared on the whole surface (Fig. 4).

[3] Magnetic measurement. Fig. 5 demonstrates typical changes in χ_a at the initial and the final stage of R-1. The turns at 70-200°C was ascribed to the adsorption of hydrogen at lower temperatures. The figure indicates that Ni in unreacted specimen is in a superparamagnetic state (3), which was converted into a ferromagnetic state by heating. The χ_a at 100°C from descending curve or its extrapolation was used as a measure of the dispersion of Ni and is given as χ^0 in Table 4, together with the activity in R-1. The conversion into a ferromagnetic state occurred even without gasification reaction. If a plot is made from Table 4, it can be shown that the remaining activity of specimens preheated to various degrees is nearly proportional to the change in χ^0 by further heating. In another experiment, a specimen was heated repeatedly to the predetermined temperature which was raised in succession and the weight and χ_a were measured at room temperature (Fig. 6). Both of these changed concurrently at the same temperature regions. The χ_a decreased during or after R-2, which seems to suggest a change in the bonding state of Ni, probably due to the dissolution of carbon or some component of ash concentrated on carbon surface.

Discussions

From the results given above, it can be concluded that the deactivation by heating above the R-1 region is due to a change in the dispersion of Ni, i.e., an aggregation to a larger particles. Fig. 6 and Table 4 seem to suggest that the catalytic action is related to the migration of Ni atoms and smaller particles on carbon surface. The migration itself is, perhaps, a thermal motion, not associated with the gasification reaction. The dependence of R-1 activity on Ni content indicates that those atoms strongly held at active sites are immobile and are inactive for R-1. Ni particles continue to grow during R-2, but this seems to be caused by the disappearance of the substrate.

Two types of possible mechanism of catalytic gasification are frequently discussed: (A) hydrogen dissociates on the catalyst surface and spills over to carbon surface, and (B) catalyst modifies the C-C bonds to enhance the reactivity. The present results are insufficient to draw a conclusion about the mechanism, but it seems improbable that (A) type action is working in R-1, as this has negative dependence on hydrogen pressure. For R-2, on the other hand, (A) type action can account the pressure dependence as well as the insensitiveness to Ni content and to the state of dispersion, although other possible explanations may exist. The decrease in χ_c at R-2 region need further study and it is not clear at present whether this change has any correlation with the gasification reaction.

References

- (1) J. L. Johnson, *Cat. Rev.*, **14**, 131 (1976).
- (2) A. Tomita and Y. Tamai, *J. Cat.*, **27**, 293 (1972).
- (3) P. W. Selwood, "Adsorption and Collective Paramagnetism", Academic Press, New York (1962).

Table 1 Activities in R-1*

Specimen	X(R-1)
Unreacted	30.2 %
Reacted once	0.7
Re-impregnated	27.7
Preheated in He**	3.1

* AC-P, 5 % Ni. HR=5°C/min.

** at 600°C for 2 hr.

Table 2 Comparison of Ni salts*

Salt	Ni content	X(R-1)	X(R-2)	Crystallite size after reduction	
				R-1	R-2
Ni(NO ₃) ₂	4.3 %	5.8 %	7.0 %	35 Å	40 Å 260 Å
NiCl ₂	4.1	0.8	6.4	200	200 230
NiBr ₂	4.3	0.9	5.4	200	- 490
Ni ₃ CO ₃ (OH) ₄ **	4.1	6.3	4.8	260	300 320
(CH ₃ COO) ₂ Ni**	3.9	1.2	6.8	165	- 190

* AC-G, HR=2.3°C/min.

** Impregnated from aqueous ammonia solution.

Table 3 Effect of reduction temperature

Conditions	X(R-1)	Crystallite size
240°C, 5 hr	1.2 %	- Å
257°C, 14.7 hr	2.7	125
263°C, 8 hr	1.1	135
284°C, 3 hr	0.8	140
const. rise**	0.9	200

* AC-G impregnated with NiCl₂ (4.1 % Ni).

** HR=2.3°C/min.

Table 4 \bar{X}° and R-1 reactivity*

Ni content	Treatment**	\bar{X}°	X(R-1)
1 %	300°C, 2 hr	3.2 esu/g Ni	1.2 %
1	450°C, 2 hr	3.7	0.5
1	600°C, 2 hr	5.5	0.1
5	300°C, 2 hr	2.3	30.2
5	450°C, 0 hr	3.9	25.2
5	450°C, 2 hr	4.2	24.0
5	600°C, 2 hr	8.0	0.7
5	600°C, 2 hr in He	8.9	3.1

* AC-P, HR=5°C/min.

** In hydrogen except for the last line.

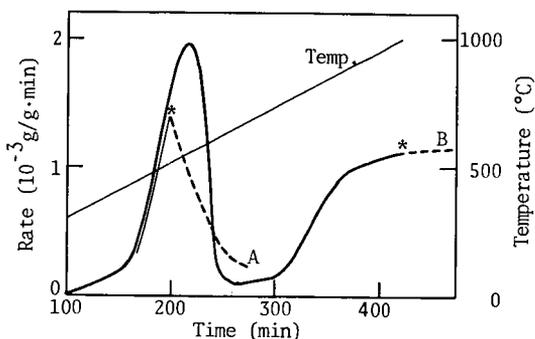


Fig. 1 Methane formation profile (AC-G)

Solid line: HR=2.3°C/min,

Broken lines: Temperature was kept constant

from the points marked by asterisks. A at

560°C and B at 1000°C.

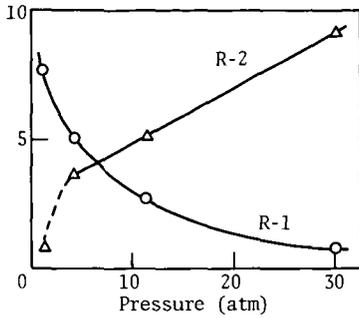


Fig. 2 Pressure dependence (AC-G, 7%Ni)
 R-1: conversion in %.
 R-2: maximum rate at 900°C in 10^{-5} g/g.min.

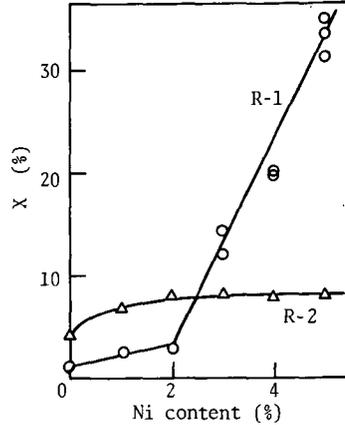


Fig. 3 Conversion vs. Ni content
 Specimen: AC-P, HR=5°C/min.

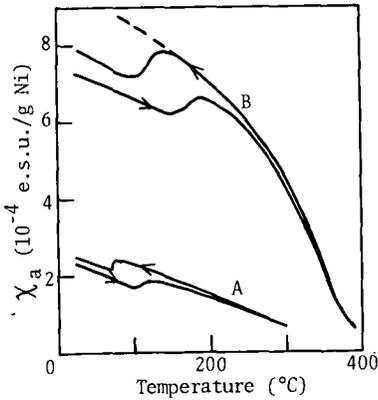


Fig. 5 Apparent magnetic susceptibility of AC-P with 5% Ni
 Specimens were heated in hydrogen for 2 h, A: at 300°C, B: at 600°C before measurement.

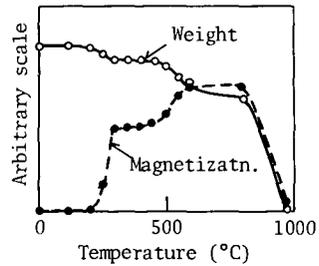


Fig. 6 Changes in weight and magnetization
 Specimen: NiCl₂-impregnated (5% Ni)

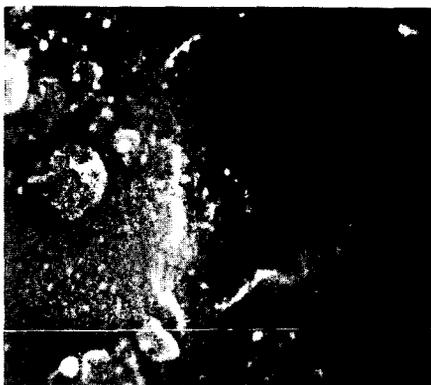
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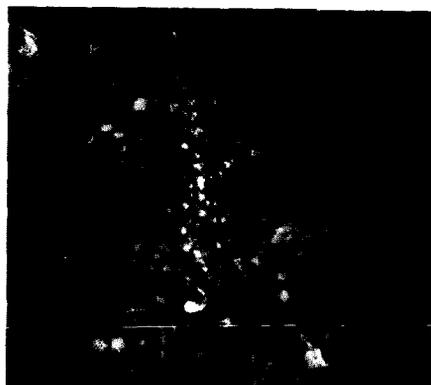
(a) Heated to 350°C.



(b) Heated to 670°C.
X=5.1 %



(c) Heated to 1000°C.
X=11.4 %



(d) Kept at 1000°C for 25 min.
X=18.9 %

Fig. 4 Photographs of an AC-G specimen with 7 % Ni (as an average for a batch of the specimen), heated repeatedly in hydrogen HR=5°C/min.