

Hydrogenation of Carbons Catalyzed by Transition Metals

AKIRA TOMITA AND YASUKATSU TAMAI

*Chemical Research Institute of Non-Aqueous Solutions, Tohoku University
Katahira, Sendai, Japan*

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The catalytic activities of transition-metal catalysts in methane formation from carbons were investigated at temperatures up to 1050°C under atmospheric pressure of hydrogen. The studies in a thermobalance revealed that methane was produced in several stages and the temperature of maximal rate varied from one metal catalyst to another. When the most active metal was used, the methane formation from an active carbon occurred below 200°C and the carbon was completely gasified upon heating up to 1050°C at the rate of 100°C/hr. Without catalyst, carbons of only 10% were gasified under the same condition. The order of activity at the lower temperature region was $Rh \gtrsim Ru \gtrsim Ir > Pt > Ni \gg Pd \gtrsim Co \gtrsim Fe$. The reactivity depended not only on the kind of catalyst, but on the kind of carbon and the preparative method of metal-carbon mixtures. The role of metal catalysis was discussed in connection with the spill-over phenomenon.

INTRODUCTION

As the interactions of the carbon with gases are of fundamental importance in a number of processes where carbon and graphite are used, many mechanistic studies have been carried out, particularly in the interaction with oxidizing gases (1, 2). Very little data are available with respect to the reaction between pure graphitic carbon and hydrogen, because of the very low reaction rate (3-5). Other carbonaceous materials such as a low-temperature char (6), a deposited carbon (7), and a coal char (8) are more reactive towards hydrogen.

We now wish to report the catalytic activity of the group VIII transition metals in the hydrogenation of carbons. The fact that some transition metals can catalyze the hydrogenation of carbonaceous materials has long been known. Randall and Mohammad (9), for example, reported that an equilibrium among graphite, hydrogen, and methane was attained rapidly by using a catalyst such as a nickel-ceria. However, a systematic study of the catalytic activity

of transition metals has not been made to date. It appeared of interest to investigate further the mechanism of this reaction. On the other hand, these reactions are of potential practical interest in connection with the production of more valuable hydrocarbons from carbons. A number of attempts to convert asphaltic residuum into lighter hydrocarbons have been made in the field of petroleum refining.

EXPERIMENTAL

Materials

Three kinds of carbon were employed in this work: an active carbon (AC), a carbon black (HAFn2), and a graphite scale (GS). Most experiments were carried out by using AC which was obtained from Kanto Chemical Co., Inc. It had a surface area of 1230 m²/g, a pore volume of 0.29 ml/g, and a bulk density of 0.31 g/ml. The elemental analysis was as follows: C, 93.5%; H, 0.3%; O (by difference), 6.2%; ash, 0.0%. The surface acidic groups were

determined by the technique of Boehm *et al.* (10). The base consumptions were 0.07, 0.16, and 0.33 mequiv/g for NaHCO_3 , Na_2CO_3 , and NaOH , respectively. The X ray powder diffraction pattern of AC showed the amorphous nature of AC (refer also to Fig. 2). The presence of free radicals was confirmed by ESR spectrum for the sample evacuated at 250°C and 10^{-4} Torr for 24 hr.

A carbon black (HAFn2) was prepared by HNO_3 treatment of a carbon black supplied by Tokai Electrode Mfg. Co. The resulting HAFn2 had the following characteristics: surface area, $78 \text{ m}^2/\text{g}$; pore volume, 0.02 ml/g ; bulk density, 0.33 g/ml ; analysis: C, 96.9%; H, 0.8%; and O, 2.3%; base consumption: NaHCO_3 , 0.02 mequiv/g; Na_2CO_3 , 0.04 mequiv/g; and NaOH , 0.08 mequiv/g. It had a crystallite height of 12 \AA and an interlayer spacing of about 3.68 \AA . A natural graphite scale (GS) had still less surface area, pore volume, density, and surface acidity. GS had a crystallite height of 330 \AA and an interlayer spacing of about 3.37 \AA .

Reagent grade metal chlorides were used as obtained from Wako Pure Chemical Ind., Ltd. Electrolytic hydrogen was purified by passing it over palladium asbestos to remove trace amounts of oxygen and through tubes packed with drying agents, calcium chloride, and a molecular sieve.

Catalyst Preparation

In most cases metal-carbon mixtures were prepared by impregnation of AC with aqueous solutions of the group VIII transition-metal chlorides: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, PdCl_2 (in aqueous HCl), IrCl_3 , and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. The resulting materials were mixed thoroughly and dried at 90°C *in vacuo*. The sample contained 4.8 weight % metal when it was completely reduced in a stream of hydrogen. Some other combinations of metal-carbon were also prepared. The effect of carbon structure on the reactivity was studied by using HAFn2 and GS in place of AC. In order to examine the effect of the preparative method of a metal-carbon mixture, a Rh(form)-AC was prepared by the reduction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with formal-

dehyde and sodium hydroxide. Furthermore, the reactivity of a $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -AC system was compared with a $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ -AC and a Ni(powd)-AC which was prepared merely by mixing a nickel powder of about 100 mesh with AC in a mortar.

Microbalance Studies

The course of the gasification reaction of the carbon was studied in a flow reactor (Fig. 1). A quartz basket containing 120 mg of a metal-carbon mixture was hung by a quartz spring. The sensitivity of the spring was 5.40 mg/mm . Weight changes accompanying hydrogenation at various temperatures were followed by using a cathetometer. All runs were carried out in flowing hydrogen at atmospheric pressure. The hydrogen flow-rate was 60 ml/min . A linear temperature rise rate of 100°C/hr was used unless otherwise stated. The reaction products were analyzed by gas chromatograph containing a 2-m molecular sieve 5A column and/or a 2-m activated carbon column. The chromatographic unit was connected directly to the outlet of the thermobalance.

The thermal decomposition of surface oxides on carbon yields carbon dioxide and carbon monoxide (11). Little attention was paid to these side reactions, because the amount of oxides was relatively small. Formation of carbon monoxide was ob-

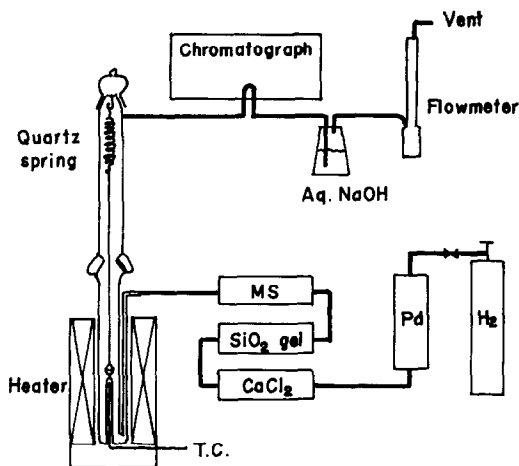


Fig. 1. Schematic diagram of the apparatus.

served above 700°C in every run. The analytical condition was unsuitable for the quantitative determination of carbon dioxide.

Fixed-bed Reactor Studies

Some qualitative experiments were carried out in a fixed-bed reactor. The reactor was a horizontally mounted Pyrex tube, and was surrounded by an electrical heater. The $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ -AC mixture was supported on a porcelain boat. The reaction temperature was maintained constant for 2 hr. Gaseous products were analyzed as described above, and the evolution of hydrogen chloride was evidenced by passing the exit gas through an aqueous solution of sodium hydroxide.

RESULTS

Fixed-bed Reactor Studies

Table 1 shows the overall weight decrease of a $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ -AC system after 2 hr in flowing hydrogen at different temperatures. The weight decrease due to the liberation of hydrogen chloride and the water of crystallization was also included in these values, as well as the weight decrease due to the hydrogenation of the carbon. Included in Table 1 for comparison is the weight decrease of AC in the absence of a rhodium salt. The catalytic activity of the metal was evident from these results. The X ray powder diffraction-patterns of the samples treated with hydrogen for 2 hr at different temperatures are illustrated in arbitrary units in Fig. 2. The peaks at $2\theta = 41.3$ and

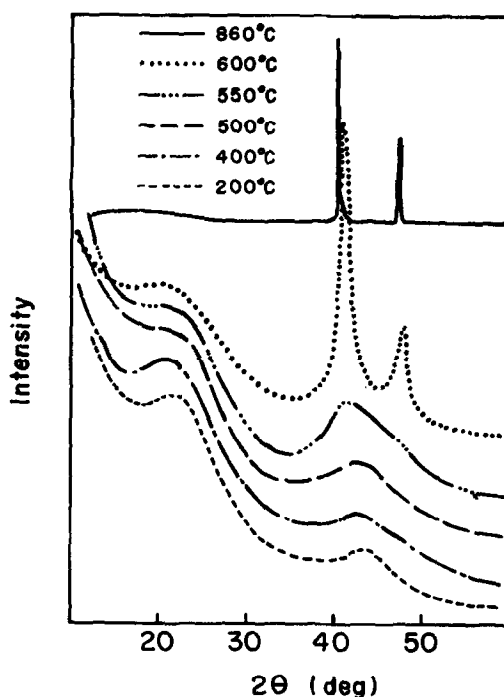


Fig. 2. X ray diffraction patterns of Rh-AC prepared by the hydrogen treatment of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ -AC at different temperatures for 2 hr, except for the uppermost pattern which was obtained in the experiment of temperature rising.

47.9° can be identified as belonging to the rhodium, and the broad peak at $2\theta = 22$ and 43° to the carbon. The X ray patterns for the samples treated below 500°C show no peaks due to metallic rhodium, whereas $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ itself was found to be completely reduced to metal below 200°C. This fact suggests that much of the rhodium reduced below 500°C is so highly dispersed as to be undetectable by X ray diffraction. The apparent mean crystallite size was estimated at about 130 Å when treated at 600°C for 2 hr. A further aggregation of rhodium occurred when the sample was heated up to 860°C at a constant rate of 100°C/hr. Reaction time was not 2 hr in this case.

Microbalance Studies

Figures 3-5 illustrate the amount of methane formed and the weight decrease of metal chloride-AC systems as a function

TABLE I
WEIGHT DECREASE UPON HYDROGEN TREATMENT^a

Temperature (°C)	AC (%)	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ -AC ^b (%)
200	1.0	2.2
300	—	2.4
400	2.2	4.6
500	3.8	10.3
550	—	23.9
600	5.4	50.5

^a Reaction time: 2 hr.

^b Rh content: 4.8%.

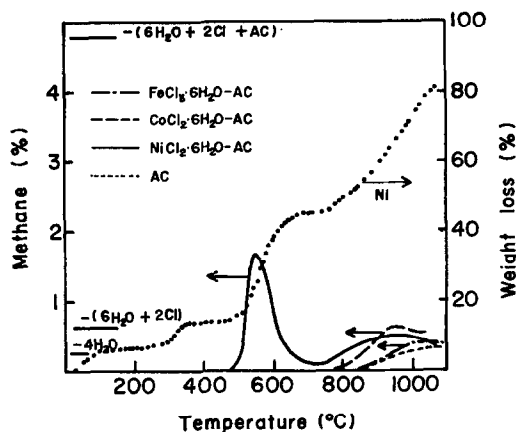


FIG. 3. The amount of methane formed from AC catalyzed by transition metals of the first long period and a thermogram for a nickel catalyst. Heating rate, 100°C/hr.

of temperature which was raised at a constant rate. The amount of methane was represented as the concentration in the exit gas. One percent of methane corresponds to about 24.5 μ mole/min. A thermogram for a $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}-\text{AC}$ system is presented in Fig. 3. Loss of water occurred below 100°C, the weight change corresponding to approximately $4\text{H}_2\text{O}$. This stage was followed by slow liberation of the remaining water of crystallization between 100 and 250°C. Calculated values of weight decrease in each stage was designated in the

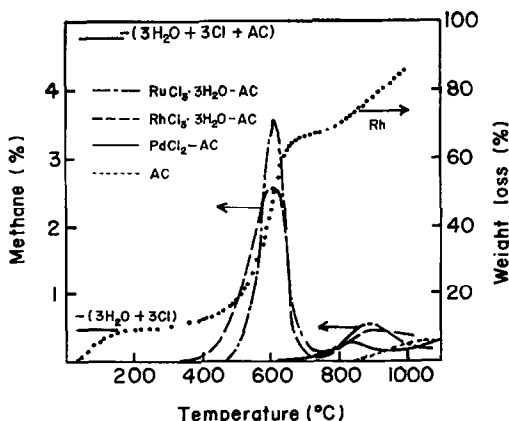


FIG. 4. The amount of methane formed from AC catalyzed by transition metals of the second long period and a thermogram for a rhodium catalyst. Heating rate, 100°C/hr.

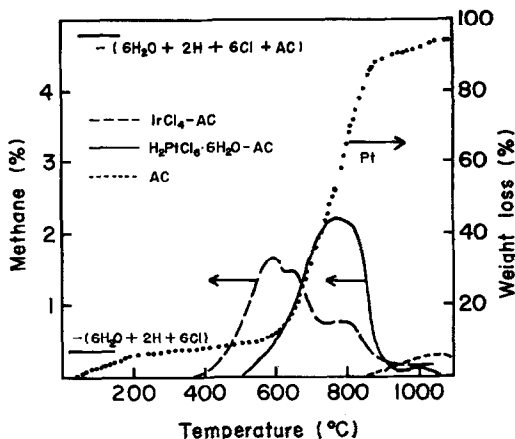


FIG. 5. The amount of methane formed from AC catalyzed by iridium and platinum and a thermogram for a platinum catalyst. Heating rate, 100°C/hr.

left-hand side of the figure. A complete decomposition of the salt occurred between 300 and 350°C. Chloride ion were liberated as hydrogen chloride. Decomposition of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ alone under the same condition was also studied; rapid loss of $4\text{H}_2\text{O}$ at 60°C, slow liberation of $2\text{H}_2\text{O}$ at 150–230°C, and of 2Cl at 310–430°C were observed. A trace amount of methane was detected at 290°C, and the maximal content of methane (2.6%) was observed at 550°C. The thermogram also showed a maximal weight decrease at about this temperature. Heavier hydrocarbons were not detected. A plateau at around 700°C was followed by further hydrogenation of the remaining carbon. The second maximal concentration was observed at 950°C. An integrated value of the methane produced from the gas chromatographic data was in good agreement with the thermogram. In this figure the curves for $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}-\text{AC}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}-\text{AC}$, and AC are also shown. Their reactivities are much smaller than that of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}-\text{AC}$. Only 8–25% of the carbon was gasified at the higher temperature region which corresponds to the second-stage hydrogenation of the nickel-catalyzed reaction.

Figure 4 shows the methane formation catalyzed by metals of the second long period. A thermogram is presented only

for a $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}-\text{AC}$ system. The pattern of methane formation by rhodium and ruthenium was quite similar to the pattern described in the case of nickel. Methane concentration vs temperature plots have two maxima: 610 and 890°C for ruthenium, and 605 and 880°C for rhodium. The low activity of palladium is strange in view of its high activity in various hydrogenation reactions. It was less active than cobalt, although the temperature of maximal methane concentration (830°C) was lower by about 120°C.

Figure 5 shows the thermogram for $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}-\text{AC}$ and the methane formation curves for iridium and platinum which show unique patterns. Three maxima at 590, 650, and 780°C were observed for iridium. For platinum, no maximum around 600°C was observed and a broad peak and a very small peak were observed at higher temperatures. Table 2 summarizes the fraction of carbon decomposed below 750 and below 1050°C. In most cases 750°C was the temperature where the methane formation at the first stage finished and the second-stage formation began.

Figure 6 represents the different reactivity attributable to the type of carbon. The order of reactivity is $\text{AC} > \text{HAFn2} > \text{GS}$, as was expected. The reactivity of the least active GS is, however, much larger

TABLE 2
THE TEMPERATURE OF MAXIMAL METHANE FORMATION AND THE FRACTION OF AC GASIFIED

Metal	Peak Temperature (°C)	AC gasified (%)	
		30-750°C ^a	30-1050°C ^a
Rh	605, 880	73	100
Ru	610, 890	72	96
Ir	600, 650, 780	70	94
Pt	770, 1000	48	100
Ni	550, 950	36	62
Pd	830	0.4	12
Co	950	0.1	25
Fe	1020	0	9
None	1050	0	8

^a The temperature was raised at a rate of 100°C/hr.

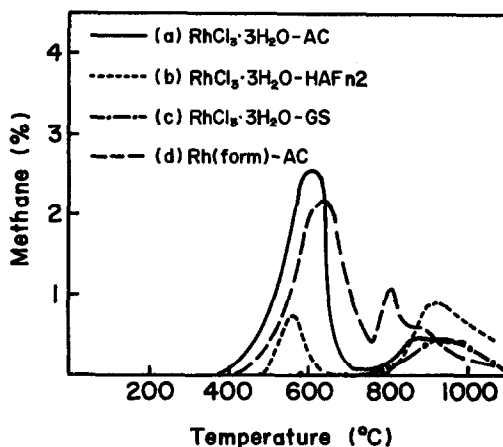


FIG. 6. The effect of the kind of carbon and the preparative method of the Rh-carbon on the methane formation.

than the graphite without catalysts. The rate for methane production from graphite at 800°C was about 6.7×10^{-7} mole/g sec, while Breisacher and Marx (4) reported the value of 3.3×10^{-12} mole/g sec in the uncatalyzed reaction. Direct observations of the graphite surface were made with an optical microscope. Figures 7(a) and 7(b) show the surface of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}-\text{GS}$ before and after the hydrogen treatment up to 1050°C, where the conversion of GS to methane was about 26%. The latter photograph shows the formation of many steps on the basal plane of the graphite. The etch pattern shows no preferred orientation. Rhodium metal particles seem to locate mainly at the edges of the flakes and at the steps. The hydrogenation reaction may proceed around them. In some special cases, a perpendicular etch pit and a catalytic channeling were also observed. These observations are quite similar to those reported in the case of catalytic oxidation of graphite (12).

The effect of the preparative method can be seen in curves (a) and (d) in Fig. 6. In contrast to two maxima for $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}-\text{AC}$, three maxima at 635, 810, and 880°C were observed in the case of $\text{Rh}(\text{form})-\text{AC}$, which was prepared by the reduction with formaldehyde. This discrepancy is surprising in view of the fact that the metal catalyst and the kind of

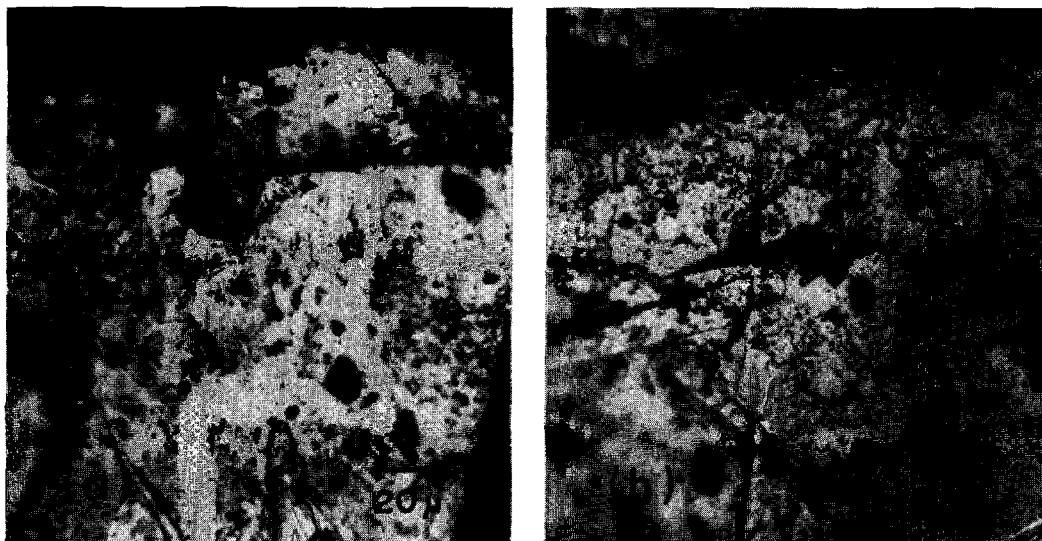


Fig. 7. Optical micrograph of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ -GS before (a), and after (b) the hydrogenation.

carbon were the same for both cases. Trace amount of remaining alkali would play an important role for Rh(form)-AC. The reactivity of a $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ -AC system was nearly identical with that of a $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -AC presented in Fig. 3. The kind of anions found in a metal salt have little effect on this reaction. The activity of a Ni(powd)-AC system was so small that the amount of methane formed was nearly equal to the blank run. This result can be ascribed to the large particle size, and therefore the small specific surface area, of the nickel metal.

Figure 8 shows the effect of heating rate

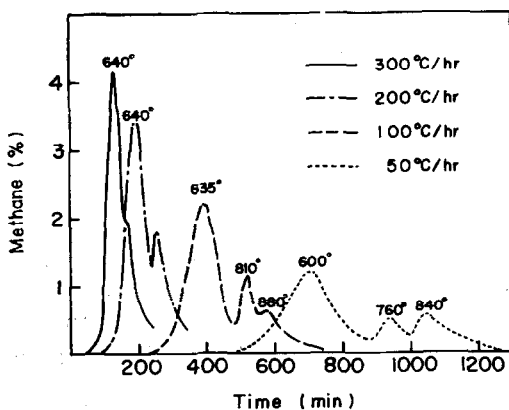


Fig. 8. The effect of heating rate on the hydrogenation of Rh(form)-AC.

on the pattern and the amount of methane formation. The catalyst used was rhodium, prepared by reduction with formaldehyde. At the slowest heating rate, the curve was clearly resolved into three symmetrical peaks. The slower the heating rate, the lower the temperature of maximum. The temperature of the first maximum was 640, 640, 635, and 600°C for the heating rate of 300, 200, 100, and 50°C/hr, respectively. The thermograms in the first decomposition stage were analyzed according to the method of Ozawa (13). The overall activation energy for the first stage in the hydrogenation of AC catalyzed by Rh(form) was estimated at approximately 34 kcal/mole. The method of Horowitz and Metzger (14) gave about 32 kcal/mole for the same system, 30 kcal/mole for $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ -AC system, and 36 kcal/mole for the $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ -AC system. The higher activation energy for the last system corresponds to the higher temperature of maximal methane formation.

DISCUSSION

Figures 3-6, and 8, show the existence of several stages in the hydrogenation of carbon. A similar phenomenon was also reported in the interaction of carbons with hydrogen by Redmond and Walker (15),

Breisacher and Marx (4), and Bansal *et al.* (16). They suggested that it may be due to surface heterogeneity, which was attributed to the presence of several sites having differing carbon-carbon spacings at the edges of crystallites. Blackwood and McCarthy (8) proposed a slightly different mechanism to account for the stages in the hydrogenation of coal char. This mechanism was also based on the surface heterogeneity of carbon. The existence of two or three stages in the present thermograms may have some relationship to the above mechanism. The actual mechanism, however, is not so simple in the present case, because here a metal catalyst has an important role. The pattern of methane formation, in fact, was dependent on the kind of metal catalyst, even if the same kind of carbon was used. Furthermore, the pattern was strongly dependent on the preparative method of the metal-carbon system. The degree of metal dispersion and the metal-carbon contact must be another important factor in this reaction. The reaction kinetics at a constant temperature will offer a powerful clue to explain the mechanism of this reaction. Further studies along this line are now in progress.

It is well recognized that hydrogen chemisorbed on a metal, say platinum, can migrate to other materials such as alumina (17) and carbon (18). In the present case, it seems reasonable to assume that the hydrogen atoms activated on a metal migrate across the interface and react with the carbon, giving methane. The reactivity of the carbon towards atomic hydrogen is much larger than towards hydrogen molecules (19). Boudart *et al.* (18) proposed the importance of some bridges to transport hydrogen atoms from metal to carbon. The low activity of the Ni(powd)-AC system can be partly attributable to the absence of such bridges. They would not be formed by a mechanical mixing.

The order of activity in Table 2 was compared with the order of catalytic activity for the oxidation of carbon. McKee (12) found the following sequence of activities of transition metal oxides in the oxidation of graphite with dry oxygen:

Co > Fe > Pt > Ni > Ir > Rh > Ru > Pd. This order is almost the reverse of the present case, with the exception of the position of palladium. Although the oxidation is not the reverse reaction of the hydrogenation, it is noteworthy that the order for these reactions is nearly in reverse.

Another comparison was made with the sequence in the hydrogenolysis of hydrocarbons in which the cleavage of a carbon-carbon bond was also an important step. Sinfelt (19) reported that the sequence in the hydrogenolysis of ethane at 205°C was Ru > Ni > Rh > Ir > Co > Fe > Pt ~ Pd. Kikuchi *et al.* (21) reported the order for *n*-pentane: Ru > Rh > Pt > Ni > Co > Ir > Pd ~ Fe. The present result is in reasonable agreement with these data. The active metals in the hydrogenolysis of hydrocarbons of low molecular weight are active in the hydrogenation of carbon, which is a kind of hydrocarbon with very high molecular weight. As suggested by Sinfelt (20), the activity in the present study increases with increasing percentage of *d*-character within a given triad in group VIII, i.e., Fe < Co < Ni, Pd < Rh ~ Ru, and Pt < Ir. The correlation, however, does not hold for the system including all metals examined. This fact suggests that the electronic property of the metal catalyst is one of the important factors, but an additional factor is involved in determining the activity of all catalysts.

Although further work would be required to clarify the mechanism of this reaction, the salient findings of this study may be summarized as follows: (1) Some noble metals have a high catalytic activity in the hydrogenation of carbons; (2) Methane is produced in several stages; (3) The pattern of methane formation depends on the kind of catalyst, carbon, and the method of metal-carbon mixtures preparation.

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