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Reactivity of Deposited Carbon on Co–Al_2O_3 Catalyst

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Reactivity and characteristics of the carbon deposited on Co–Al_2O_3 by disproportionation of CO (the Boudouard reaction) were studied by pulse experiments using ^{13}C or D isotopes. Three types of deposited carbon were identified by the reaction with hydrogen: highly reactive CH and/or CH_2 species, reactive carbidic carbon, and less reactive graphitic carbon. The existence of CH and CH_2 species was proved by the reaction with D_2 pulse at 80°C, but the predominant species was carbidic carbon when the disproportionation of CO was performed on cobalt catalyst at 230°C. Carbidic carbon was decomposed to graphitic carbon by raising the temperature. However, a certain amount of carbidic carbon was found to remain on the surface even at 430°C. This phenomenon may suggest reversible formation of carbidic carbon from graphitic carbon on the catalyst.

INTRODUCTION

Significant attention has been paid to the carbon species on transition metal surfaces in relation to the intermediates for methanation and Fischer–Tropsch synthesis (*1–9*) and as a source of coaking (*10, 11*) formation or poison of catalyst (*12*). Wentrcek *et al.* (*3*) and Araki and Ponec (*5*) showed that surface carbon deposited on nickel catalyst from CO is the intermediate for methanation reaction.

More recently, characterization of carbonaceous deposit on poly- or single-crystal metals has been performed by XPS, AES, and EELS. Two types of carbon, reactive carbidic carbon and inert graphitic carbon, have been identified on transition metals. Goodman (*13*) showed that carbidic carbon is an intermediate for the methanation reaction on nickel.

On the other hand, CH_2 species have been speculated as a precursor for chain growth in Fischer–Tropsch synthesis (*14, 15*), and CH (*16*) and/or CH_2 (*17*) have been detected on Ru(001) and CH_3 (*18*) on Ni(110).

In this paper, we study the reactivity of carbon species deposited on cobalt catalyst in detail.

EXPERIMENTAL

Deposition of carbon species on cobalt catalyst and its reaction with hydrogen were performed in a circulation system with a volume of 229 cc and/or in a flow system with helium carrier gas. In helium flow, the pulse of hydrogen or deuterium was injected by changing the helium flow line through a pulse doser of 13 cc of volume which was filled with 100 Torr of H_2 or D_2. The products flowing out from the reactor were analyzed by an on-line gas chromatograph combined with a mass spectrometer.

Cobalt catalyst used in the present experiments was prepared by impregnating γ-aluminum with a cobalt nitrate solution. Five grams of the catalyst containing 5.99 wt% of Co was mounted in the reactor and was followed by reduction with hydrogen at 430°C for 3 h. After the evacuation ($2–5 \times 10^{-5}$ Torr) at 430°C for 3 h, carbon was deposited by the Boudouard reaction with an initial pressure of 100 Torr of CO. The deposition of carbon on the catalyst was evaluated from the decrease in the total pressure by the Boudouard reaction ($2CO \rightarrow C + CO_2$).

The analysis of ethane and methane was

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performed by gas chromatography, and the analysis of isotope-labeled (^{13}C or D) products was carried out by a mass spectrometer.

RESULTS

Carbidic Carbon and Graphitic Carbon on Cobalt Catalyst

If a cobalt surface is carburized by performing the disproportionation reaction of CO at about 230°C, carbidic carbon is mainly formed (*19, 20*). Such carbidic carbon converts to graphitic carbon if the temperature is raised up to 400°C (*19, 20*). In agreement with these facts, we can prepare the two types of carbon on $Co-Al_2O_3$ catalyst by changing the deposition temperature, 230 and 430°C.

The reaction of deposited carbon with a pulse of H_2 was plotted against the temperature in Fig. 1. When a H_2 pulse was injected onto the carbidic carbon at the temperature range 80–220°C, CH_4 and C_2H_6 were formed, but the reaction of graphitic carbon with hydrogen at the same temperature range gave only a small amount of CH_4. When the carbidic carbon prepared at 230°C was heated up to 430°C under vacuum, the reactivity of the carbon became equal to that of the carbon deposited at 430°C. That is, the carbidic carbon on cobalt catalyst undergoes decomposition to less reactive graphitic carbon by heating at 430°C.

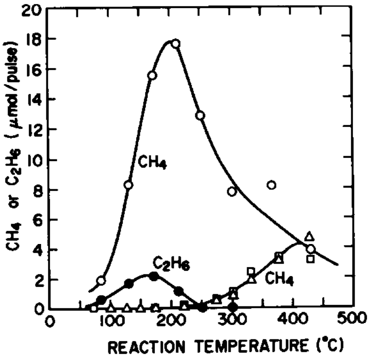


FIG. 1. Reaction of deposited carbon on $Co-Al_2O_3$ with a successive H_2 pulse. Carbon was deposited at 230°C (○, ●) and 430°C (△). Carbon was deposited at 230°C and heated at 430°C (□). The atomic ratio of C/Co is 0.024.

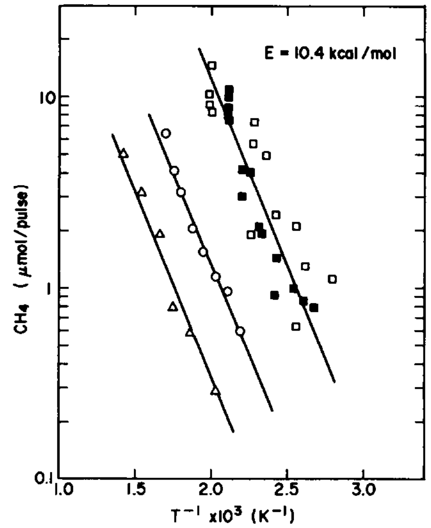


FIG. 2. Plot of CH_4 versus $1/T$ with various deposition temperatures. Deposition temperature (□, ■) 230°C, (○) 280°C, and (△) 430°C. C/Co, 0.024.

In order to clarify the reactivity of the deposited carbon on cobalt catalyst, the apparent activation energy for the methane formation reaction was evaluated by a graphical plot as shown in Fig. 2. It was found that the activation energy for CH_4 formation (about 10.4 kcal/mol) was almost the same although the activity was widely changed depending on the deposition temperature. This fact implies that CH_4 is formed by the hydrogenation of an identical precursor carbon, which may be carbidic carbon. The apparent reactivity of the deposited carbon is responsible for the amount of carbidic carbon on a cobalt surface.

If this is the case, the decrease in the reactivity of the carbon deposited at 230°C by heating to 430°C is attributed to the decrease in carbidic carbon by decomposition to graphitic carbon. Decomposition of carbidic carbon occurred rather rapidly at temperatures higher than 230°C, but a limited amount of carbidic carbon always remained on the surface. This fact suggests that the carbidic carbon and graphitic carbon are in equilibrium on a cobalt surface. The apparent decomposition temperature of carbidic carbon shifts to higher temperatures for the carbidic carbon deposited at higher temperatures, such as that shown in Fig. 3. This is well explained if the equilibration is established at each deposition temperature.

Evidence for CH and CH_2 Species

When a H_2 pulse was injected onto the carbon deposited at 230°C, a small amount of the highly reactive species was detected at temperatures lower than 100°C as shown in Fig. 4. That is, the highly reactive species is hydrogenated before the major carbidic carbon. As a result, we can selectively remove this highly reactive carbon species from the catalyst surface by the reaction with hydrogen below 200°C. The existence of this highly reactive carbon species becomes more clear when the deposition of carbon is lowered.

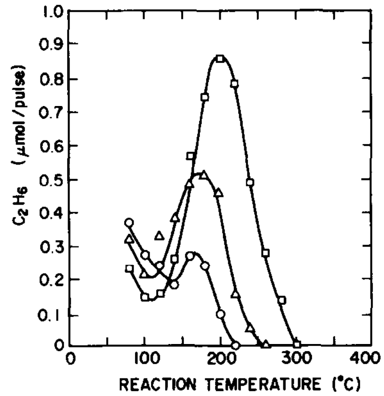


FIG. 4. Ethane formation by reaction of carbon deposited at 230°C with successive H_2 pulses. C/Co: (○) 0.005, (△) 0.012, and (□) 0.036.

It is interesting to speculate whether or not the highly reactive carbon species discussed above involves hydrogen atoms. It may be possible to identify the species by the reaction with D_2 if the hydrogen scrambling is slow. Table 1 shows the deuterium distribution of the methane obtained by the first D_2 pulse at the temperatures between 150 and 400°C. Contrary to expectation, methane showed random deuterium distribution. The hydrogen atom (H) in the methane seems to be furnished by the residual hydrogen H(a) on the catalyst. If this is the case, the identification of CH_x species is difficult. When the reaction temperature was lowered to 80°C, the deuterium distribution in methane was found to be changed as shown in Fig. 5. From these results, the highly reactive species were identified as CH and CH_2, because of the significant amount of CHD_3 and CH_2D_2 formed in the first D_2 pulse. The formation of CD_4 may be responsible for the reaction of carbidic carbon with D_2 pulse, and the amount of CD_4

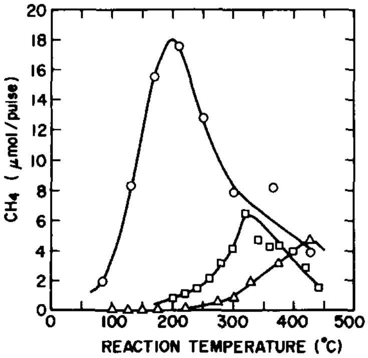


FIG. 3. Different decomposition temperature of carbidic carbon. Deposition temperature (○) 230°C, (□) 280°C, and (△) 430°C. C/Co, 0.024.

TABLE 1

Deuterium Distribution in the Methane Obtained by Reaction of Carbon with Deuterium at Various Temperatures

Reaction temperature (°C)	Deutromethane distribution (%)				
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
150	11	31	36	17	5
	(10)	(31)	(36)	(19)	(4)
230	47	38	13	3	0
	(45)	(40)	(13)	(2)	(0)
300	80	18	2	0	0
	(80)	(19)	(1)	(0)	(0)
400	87	13	0	0	0
	(88)	(12)	(0)	(0)	(0)

Note. Parentheses show the random distribution calculated from D content in produced deutromethane. Carbon was deposited at 230°C.

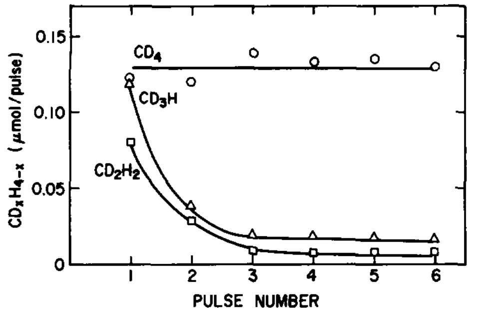


FIG. 5. Deutromethane formation by reaction of deposited carbon with a successive D_2 pulse at 80°C. Carbon was deposited at 230°C. C/Co, 0.008.

TABLE 2

^{13}C or ^{12}C Distribution in Methane and Ethane

Pulse number	$^{12}CH_4$ (%)	$^{13}CH_4$ (%)	$^{12}C_2H_6$ (%)	$^{12}C^{13}CH_6$ (%)	$^{13}C_2H_6$ (%)
4	68	32	55	38	8
			(55)	(38)	(8)
5	52	48	38	44	18
			(36)	(48)	(16)
6	47	53	26	55	19
			(28)	(50)	(22)

Note. ^{13}C and ^{12}C were deposited at 230°C. The amounts of methane and ethane are shown in Fig. 6.

formed does not change appreciably by the repeated pulse dose.

Figure 6 and Table 2 show the results of ^{13}C-labeled experiments, where the ^{13}C and ^{12}C were sequentially deposited as follows. (i) ^{13}C was first deposited from ^{13}CO at 230°C and this was followed by exposing it to the H_2 pulse three times at 230°C. After that, (ii) ^{12}C was additionally deposited from ^{12}CO at 230°C and was again treated with the H_2 pulse three times at 230°C. Reactive CH and CH_2 species may be removed by the treatment with H_2 pulses, which is reflected by the decrease in methane and ethane with pulses as shown in Fig. 6. The fact that the ^{12}C content in methane and ethane decreased step by step from pulse 4 to 6 in Table 2 implies regeneration of CH and CH_2 by the additional carbon deposition. That is, even if CH and CH_2 are removed by the reaction with hydrogen, new deposition of carbon regenerates CH and CH_2 even in the absence of gas-phase hydrogen.

The random distribution of ^{12}C and ^{13}C in ethane (Table 2) indicates random recombination of $^{12}CH_x$ and $^{13}CH_x$ on the catalyst.

Hydrogenation of Graphitic Carbon

Evidence for a reversible formation and decomposition of carbidic carbon on cobalt catalyst at 430°C is shown in Fig. 7. In this experiment, carbon was deposited at 430°C by the Boudouard reaction, where the

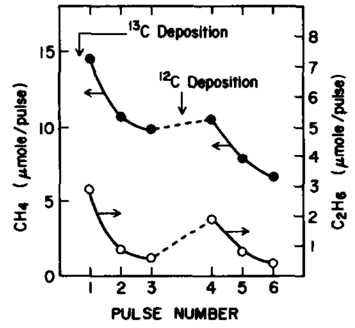


FIG. 6. ^{13}C tracer experiment. The following procedures were carried out at 230°C. (i) ^{13}C deposition (^{13}C/Co, 0.024) and three H_2 pulses. (ii) ^{12}C deposition (^{12}C/Co, 0.008) and three H_2 pulses.

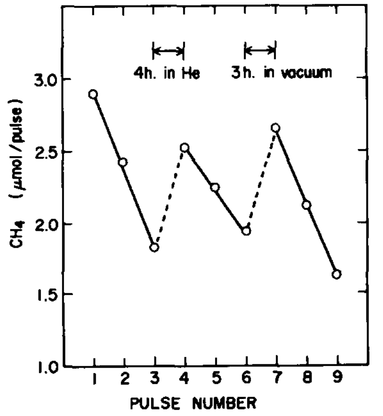


FIG. 7. Regeneration of carbidic carbon from graphitic carbon at 430°C. Carbon was deposited at 430°C and an H_2 pulse was passed successively at 430°C with intervals of 3 and 4 h. C/Co, 0.072.

graphitic carbon was a major component and the carbidic carbon was a minor one on the catalyst. In order to confirm the reversible formation of carbidic carbon from graphitic carbon on cobalt catalyst, carbidic carbon was partly removed by the hydrogenation with three H_2 pulses at 430°C. After this, it was maintained in He or under vacuum at 430°C for a certain period. As shown in Fig. 7, carbidic carbon was evidently regenerated from the graphitic carbon at this temperature. This fact proves that the hydrogenation of carbon or carbonaceous deposit on the catalyst is caused by the formation of carbidic carbon on the catalyst and its hydrogenation.

Such reversibility between carbidic and graphitic carbons on a cobalt surface is better demonstrated in Fig. 8, where ^{13}C was first deposited from ^{13}CO at 430°C, and then ^{12}C was additionally deposited from ^{12}CO at 280°C. By this procedure, a cobalt surface was covered with ^{12}C carbidic carbon and ^{13}C graphitic carbon involving a small amount of ^{13}C carbidic carbon as is shown in Fig. 1. The ratio of the deposited ^{13}C to ^{12}C was 80 : 20. When H_2 pulses were successively passed on the catalyst in the temperature range from 180 to 430°C, the fraction of ^{12}C in methane decreased from one pulse to another at temperatures higher than 280°C as shown in Fig. 8. Furthermore, the ^{12}C content in the methane produced at 430°C approaches the level of the ^{12}C content in the deposited carbon (~20%), if the catalyst was kept at 430°C for a sufficient interval of time. This result evidently shows that ^{13}C and ^{12}C are mixed via reversible formation and decomposition of the carbidic carbon and graphitic carbon convert reversibly on the cobalt surface.

DISCUSSION

Our pulse experiments using ^{13}C or D isotopic tracers enabled us to distinguish the reactivity of the carbonaceous species on the cobalt catalyst, and the carbonaceous species were classified into three types, highly reactive CH_x (CH and/or CH_2), reactive carbidic carbon, and less reactive graphitic carbon.

Carbidic and graphitic carbon have been distinguished by the chemical shift in XPS or by the fine structures of AES on metals such as Fe (*21, 22*), Ni (*23, 24*), Ru (*24–26*), and Co (*20, 27*). The carbidic carbon on these metals is known to be far more reactive with hydrogen than the graphitic carbon. In the case of Co surface, the carbidic carbon is predominantly formed at low temperatures but the formation of graphitic carbon prefers temperatures higher than 300°C, so that the fraction of graphitic carbon increases with the deposition temperature. We have studied the carbon deposition on cobalt polycrystalline foil by

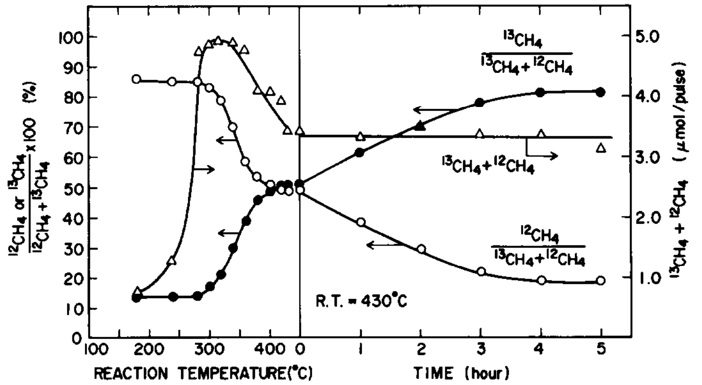


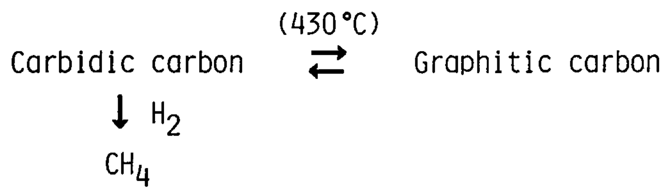
FIG. 8. Reversibility between carbidic carbon and graphitic carbon. ^{12}C and ^{13}C were deposited at 280 and 430°C, respectively. $^{12}C/Co : ^{13}C/Co = 0.012 : 0.048$.

XPS (*20*). The carbidic carbon prepared on the surface at 227°C was found to decompose almost into graphitic carbon by heating up to 427°C. However, a detectable amount of carbidic carbon always remained on the surface at such a high temperature as 427°C, which is quite consistent with the results obtained in this paper. As shown in Fig. 1, the amount of CH_4 formed by one H_2 pulse dose depends on the deposition temperature of carbon, whereas the activation energy for the CH_4 formation changes little as shown in Fig. 2. These results are well explained by the hydrogenation of carbidic carbon, the amount of which depends on the deposition temperature. If the carbidic carbon prepared at 230°C is heated to 430°C, a large part of it undergoes decomposition to graphitic carbon. As a result, apparent activity for the formation of methane decreases steeply as shown in Fig. 1. The activation energy of hydrogenation (10.4 kcal/mol) obtained in the present study is comparable to that on nickel catalyst [9.5–10.4 (*28*), 9.1–14.8 (*29*), and 16.9 kcal/mol (*1*)].

It should be emphasized that a certain amount of carbidic carbon always coexists with graphitic carbon on a cobalt surface, and the methane formation in Fig. 3 is responsible for the hydrogenation of the coexisting carbidic carbon; that is, graphitic carbon converts to carbidic carbon on a cobalt catalyst by thermodynamical equilibration at high temperatures. As shown in Fig. 8, an increase in ^{13}C content in carbidic carbon with an increasing temperature higher than 280°C is caused by the decomposition of excess carbidic carbon (^{12}C). As a result, the ^{13}C content in CH_4 shifts gradually to the fraction of ^{13}C in total carbon at above 400°C. This fact undoubtedly indicates the formation of carbidic carbon from graphitic carbon (^{13}C). If the rate of CH_4 formation is proportional to the amount of carbidic carbon, we can estimate the amount of carbidic carbon in equilibrium at 230, 280, and 430°C to be 100 : 20 : 3. As discussed above, graphitic carbon is entirely inactive in the reaction with H_2 in the temperature range 80–430°C. However, the hydrogenation of graphitic carbon on a cobalt surface will be promoted by converting it to carbidic carbon, and the conversion from graphitic carbon is demonstrated in Fig. 7. The tracer experiment shown in Fig. 8 also proves the reversible conversion between carbidic carbon and graphitic carbon as described by Scheme 1.

It is known that the reaction of graphite with atomic hydrogen at 340°C gives hydrocarbons such as cyclopentane, cyclohexane, and cyclohexene and benzene, in addition to methane and ethane (*30*). Contrary to this, the hydrogenation of the graphitic carbon deposited on cobalt catalyst and the hydrogenation of solid carbon on which cobalt is impregnated yielded only methane at 430°C (*31*). This fact may suggest that the hydrogenation of solid carbon by metallic catalyst is caused by the formation of carbidic carbon at the interface between carbon and metals. More recently, we obtained evidence that a carbidic carbon with P_{4g} structure exists at the interface between a Ni(100) and graphitic carbon overlayer (*32*).

So far, the existence of extremely reac-



SCHEME 1

tive carbonaceous species on catalysts is often reported. McCarty and Wise (*1*) named such carbon on the nickel catalyst, which reacts with H_2 at 80°C, α'-carbon. On the other hand, CH_2 species have been presumed to be a precursor for hydrocarbon formation by many investigators (*14*, *15*). In fact, Brady and Pettit (*14*) demonstrated that the CH_2 species furnished metal catalysts in the transition by decomposing CH_2N_2 in the presence of hydrogen, yielded hydrocarbons having compositions similar to that of the Fischer–Tropsch reaction.

In the present study, we identified the highly reactive species on Co–Al_2O_3 to be CH and CH_2 species which give methane and ethane in the reaction with H_2 as shown in Fig. 5. In order to reduce the scrambling of hydrogen during hydrogenation reaction, the deuteriation of CH_x with D_2 was performed at temperatures lower than 80°C, and it was found that the deuteriation of carbidic carbon gives CD_4 while the deuteriation of CH and CH_2 species yielded CHD_3 and CH_2D_2 selectively. From these results, we may derive the following conclusion: (i) a constant amount of CH and CH_2 species is formed on the catalyst independent of the amount of deposited carbon (Fig. 4). (ii) Rapid hdyrogen mixing occurs among CH, CH_2, and the carbidic carbon during hydrogenation of these species at high temperatures (Table 1). (iii) CH and CH_2 species seem to be furnished in accordance with the deposition of carbon from CO (Fig. 6, Table 2). This fact perhaps indicates the formation of CH and CH_2 species on some specific sites during the deposition of carbon at 230°C. The concentration of CH_x species during the hydrogenation of carbidic carbon should be very low, because the hydrogenation of CH_x is much faster than that of carbidic carbon. However, the CH_x species are produced from carbidic carbon (carbidic carbon + $x/2$ $H_2 \rightarrow CH_x$) as shown in Table 2. Accordingly, the reaction intermediates for the Fischer–Tropsch type reaction might involve CH and CH_2 species, which are furnished from either the carbidic carbon or the hydrogenation of dissociatively adsorbed CO.

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