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Intermediates and Carbonaceous Deposits in the Hydrogenolysis of Ethane on a Ni–Al_2O_3 Catalyst

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Hydrogenolysis of ethane and hydrogenation of ethylene were performed on a fresh and carburized Ni/Al_2O_3 catalyst. It was deduced that any type of carbon deposits on Ni/Al_2O_3 could retard the hydrogenolysis of C_2H_6 provided they were stable under the reaction conditions, while such carbonaceous deposits did not retard the hydrogenation of C_2H_4. The action of the carbon deposits was quite analogous to that of inert components such as Cu in the Cu–Ni alloy in the two reactions. The results suggested that the rate determining step might be the C–C bond cleavage of highly dehydrogenated precursor species which subsequently yielded highly reactive CH_2 species with H_2.

INTRODUCTION

The hydrogenolysis reaction of ethane is rather sensitive to the particle size and/or the dispersion of supported metals (*1*) and to the surface composition of alloy catalysts (*2*), while the hydrogenation of ethylene is insensitive to these properties of the catalysts (*3*).

Such demanding characteristics for the catalytic hydrogenolysis reaction depend on the rate determining step. The proposed rate determining steps in the past are (i) adsorption of C_2H_6 in highly dehydrogenated forms (*4*), (ii) C–C bond cleavage of precursor species (*5*), and (iii) hydrogenation of C_1 fragments (*6*).

It is still uncertain which one of the three steps is the actual rate controlling step. However, we suspect that one of the three processes may be the rate determining step and may require specific sites, and the demanding characteristics observed in this reaction may be caused by such prerequisites for active sites. On the other hand, it has recently been admitted that the hydrogenation of CO to methane proceeds via carbonaceous intermediates which are formed by the previous dissociation of CO (*7*). With these facts in mind, we discussed the intermediates for the hydrogenolysis reaction in relation to the carbonaceous deposits and the ethyl intermediates for the hydrogenation of ethylene.

EXPERIMENTAL

The reaction was performed in a closed circulation system having a volume of 347 ml. Unless otherwise stated, the hydrogenolysis reaction was carried out in 9 Torr of ethane and 18 Torr of hydrogen. In most experiments, the carbonaceous deposits were made on the catalyst by the Boudouard reaction or by decomposition of CH_4 at the corresponding reaction temperatures. The nickel catalyst used in the present experiments was prepared by impregnating standard alumina (JRC-ALO-1) into nickel nitrate solution. The amount 1.006 g of the catalyst, containing 5.44 wt% of NiO, was placed in a reactor and then reduced with hydrogen at 450°C. The analyses of ethylene, ethane and methane were carried out by an on-line gas chromatography, and those of the ^{13}C containing products were carried out by mass spectrometer.

RESULTS

A large negative order with respect to hydrogen pressure was first explained by the rate determining step of the C–C bond

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breaking of highly dehydrogenated species (*5*). Alternative mechanisms such as the rate determining steps of dissociative adsorption (*4*) or hydrogenation of C_1 species (*6*) have been proposed to explain the kinetics. The adsorbed species during the reaction will depend on the elementary process which is the rate determining step.

In the present experiments, adsorption of hydrocarbons during the hydrogenolysis of ethane under various hydrogen pressures was measured. As shown in Fig. 1, the adsorption decreased as the hydrogen pressures increased. One interesting point to note is that the rate of CH_4 formation decreased more markedly than the decrease of the adsorption caused by the hydrogen pressure increase. It is also interesting that the formation of CH_4 accompanied a certain period of induction time and seemed to grow longer as the hydrogen pressures increased.

To evaluate the contribution of the carbonaceous deposits on the hydrogenolysis reaction of ethane, the reaction was performed on both fresh and carbon deposited catalysts. Figure 2 shows the reactions at 200°C where carbon deposition was carried out by the Boudouard reaction, depositing about 9.9 Torr of CO as the carbon. As will be discussed later, the Boudouard reaction on the nickel catalyst at 200°C prefers the formation of carbidic carbon. Accordingly, the reaction over the carbon deposited catalyst in Fig. 2 may correspond to the reaction over a catalyst covered with carbidic carbon. In this case, a clear induction time appears on the fresh catalyst but not on the carbon deposited catalyst. It is known that the CH_4 formation in the initial stage occurs much faster on the carbon deposited catalyst than on the fresh catalyst. However, such a rapid formation of CH_4 on the carbon deposited catalyst undoubtedly slows down as the reaction proceeds, while the reaction on the fresh catalyst continues without a decrease in rate. This fact indicates that a part of the deposited carbon, which might be a carbidic carbon, undergoes hydrogenation in the initial stage of the hydrogenolysis of C_2H_6, and that the part of the carbon remaining on the catalyst may be a free carbon which inhibits the hydrogenolysis reaction.

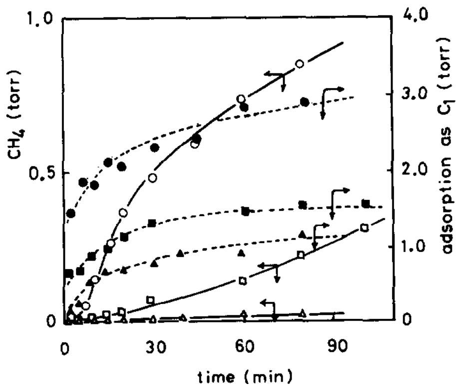


FIG. 1. Adsorption of carbon species (solid marks) during hydrogenolysis of ethane in different hydrogen pressures at 200°C. Initial pressures are C_2H_6: 9.1 Torr; H_2: (○●) 0 Torr, (□■) 18.2 Torr, (△▲) 36.4 Torr.

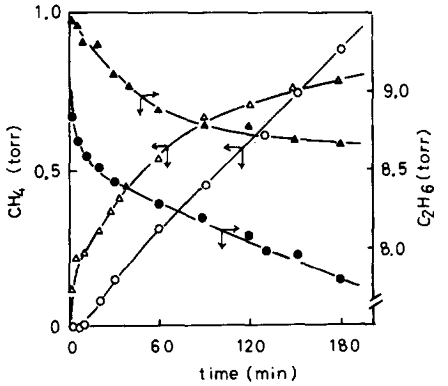


FIG. 2. Hydrogenolysis reaction at 200°C on fresh (○,●) and carburized catalysts (▲,△). Total of 9.9 Torr of CO was deposited at 200°C. Initial pressures are C_2H_6: 9.0 Torr; H_2: 18.0 Torr.

To check this speculation, a ^{13}C tracer study was performed. A 2.1 Torr of ^{13}C was deposited by the Boudouard reaction of ^{13}CO at 200°C, on which the hydrogenolysis of $^{12}C_2H_6$ was performed at the same temperature. The methane obtained in the initial 10 min was composed of about 82% of $^{13}CH_4$ and 18% $^{12}CH_4$, but that which was formed in the subsequent 20 min was mainly $^{12}CH_4$(89%), as shown on runs 1 and 2 in Table 1. Furthermore, it was proved that the hydrogenation of the catalyst after run 2 at 470°C yielded about 76% $^{13}CH_4$, as shown on run 3 in Table 1.

These results are quite consistent with those obtained in Fig. 2; that is, a part of the deposited ^{13}C on the catalyst underwent rapid hydrogenation in the initial 10 min, but some of the ^{13}C remained on the catalyst and retarded the hydrogenolysis of C_2H_6.

It was shown in Fig. 1 that some carbonaceous species are adsorbed on the catalyst during the hydrogenolysis reaction and that the amount depends on hydrogen pressures. Considering the retardation effect of the deposited carbon by the Boudouard reaction, an interesting question arises as to whether the carbonaceous species formed during the hydrogenolysis of C_2H_6 retards the reaction or not. To solve this question, hydrogenolysis of C_2H_6 was repeated on the same catalyst upon which the first run was invariably performed on a fresh catalyst. As shown in Fig. 3, a remarkable deactivation was observed at 200°C, which was slight at 260°C while no deactivation was recognized at 300°C. These results were in sharp contrast to the retardation effect of the carbon which was deposited on the catalyst by the Boudouard reaction. In this case, a carbonaceous species which retards the reaction was accumulated at 200°C during the hydrogenolysis reaction but not during the reaction at higher temperatures.

TABLE 1

Hydrogenolysis of $^{12}C_2H_6$ on ^{13}C-deposited Ni/Al_2O_3 Catalyst at 200°C (2.1 Torr of ^{13}CO was deposited by the Boudouard Reaction at 200°C)

Runs	Reaction time (min)	CH_4 attained (Torr)	Composition (%)	
			$^{13}CH_4$	$^{12}CH_4$
1	10	0.29	82.2	17.8
2[a]	20	0.03	11.3	88.7
	400	0.23	34.1	65.9
3[b]	180	0.35	75.7	24.3

[a] The catalyst used for run 1 was evacuated for 30 min at 200°C.

[b] Methane obtained by the hydrogenation of the catalyst used for run 2 at 470°C.

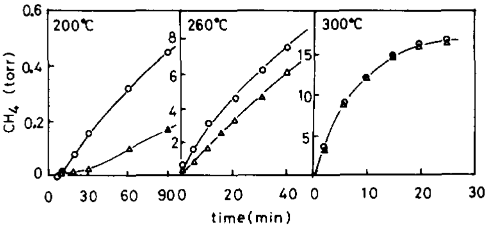


FIG. 3. Deactivation of Ni/Al_2O_3 catalyst for the hydrogenolysis of ethane by repeated experiments at various temperatures. (○) First run. Reaction time for the first run was 395 min (200°C), 40 min (260°C), and 30 min (300°C). (▲) Second run. Initial pressures are H_2: 18.2 Torr; C_2H_6: 9.1 Torr.

To obtain a better understanding of the reactivity of the carbon containing species formed from C_2H_6, self-dehydrogenolysis of C_2H_6 was carried out on both fresh and carbon deposited catalysts. In these experiments, if 9.1 Torr of C_2H_6 was added solely onto a fresh catalyst at 200°C, self-hydrogenolysis reaction occurred after a certain induction time as shown in Fig. 4. And if H_2 was added in the middle of the reaction, a very rapid evolution of CH_4 took place at about 0.15 Torr; however, the subsequent reaction proceeded at a rate which was approximately equal to that observed immediately prior to the addition of H_2.

If the same experiments were conducted on a carbon deposited catalyst (i.e., 0.8 Torr of CO was deposited as the carbonaceous species at 200°C), an induction time would appear also, but it was shorter than that which occurred on the fresh catalyst. The addition of H_2 in the course of the reaction brought about an abrupt evolution of CH_4 as observed on the fresh catalyst. The subsequent formation of CH_4 which followed the rapid evolution of CH_4, however, was apparently faster than the rate of CH_4 formation immediately prior to the hydrogen addition; however, it decreased quickly, as shown in Fig. 4. Such a rapid

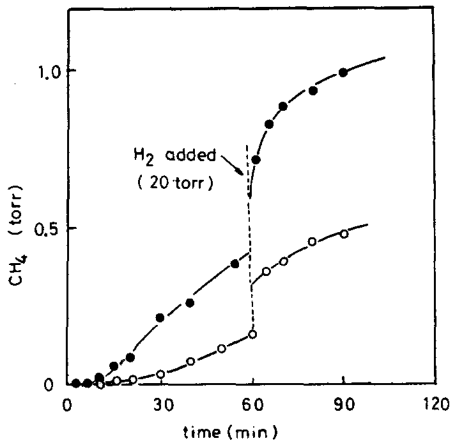


FIG. 4. Self-hydrogenolysis of ethane at 200°C on fresh and carburized Ni/Al_2O_3 catalysts; (○) fresh surface, (●) carburized surface (0.8 Torr of CO deposit).

subsequent reaction may correspond to the hydrogenation of carbidic carbon with H_2 as that observed in the initial stage of the hydrogenolysis over the carbon deposited catalyst in Fig. 2.

It should be noted that the self-hydrogenolysis of ethane over the carbon deposited catalyst has an apparent induction time while the hydrogenolysis of C_2H_6 with H_2 over a similar catalyst has no induction time (Fig. 2). This result may suggest that the induction time observed in the self-hydrogenolysis on the carbon deposited catalyst in Fig. 4 might correspond to the dehydrogenation process of C_2H_6.

It has been admitted that the hydrogenation of ethylene is a facile reaction, while the hydrogenolysis of ethane is demanding to the structure and the composition of the catalyst surface. Taking into account these characteristics of the two reactions, the effects of deposited carbon were systematically studied, that is, the hydrogenation of ethylene (C_2H_4, 18 Torr; H_2, 18 Torr) at 0°C and the hydrogenolysis of ethane (C_2H_6, 9 Torr; H_2, 18 Torr) at 295°C were compared by changing the amount of carbon deposited on the catalyst. The results were summarized in Fig. 5. Run 1 shows the hydrogenation of ethylene on a fresh catalyst at 0°C, and run 2 indicates the reaction on a carbon deposited surface (2.6 Torr of CO was deposited at 300°C). Here it is obvious that the deposit of carbon brought about inhibition on the hydrogenation of ethylene to some extent. After the experiment on run 2, the catalyst was reduced with H_2 at 190°C for 50 min, by which 0.23 Torr of carbon was removed as CH_4. By this reduction, the catalytic activity for the hydrogenation of ethylene was entirely recovered as shown on run 3. However, the hydrogenolysis reaction at 295°C was undoubtedly suppressed on this catalyst, as shown on run 4. Complete recovery of the catalytic activity for the hydrogenation reaction of ethylene was assured again after run 4 as shown on run 5. This fact proves that the adsorption of hydrocarbons during hydrogenolysis at 295°C may not inhibit the hydrogenation reaction. After run 5, about one half of the deposited carbon (1.6 Torr as CH_4) was removed by hydrogenation at 470°C, and the hydrogenolysis of C_2H_6 was subsequently performed at 295°C. This high temperature reduction with H_2 recovered the activity for

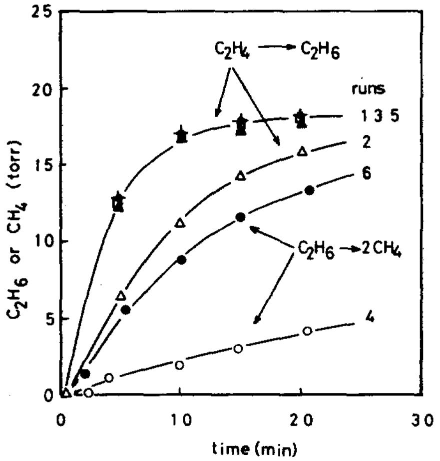


FIG. 5. Influence of carbon deposit on the hydrogenation of ethylene at 0°C and on the hydrogenolysis of ethane at 295°C. Initial pressures are C_2H_4: 18 Torr and H_2: 18 Torr; C_2H_6: 9.1 Torr and H_2: 18.2 Torr. Run 1: fresh surface. Run 2: carburized surface by 2.6 Torr of CO deposit at 300°C. Run 3: 0.23 Torr of carbon removed surface by hydrogenation at 190°C. Runs 4 and 5: the same surface used for run 3. Run 6: 1.16 Torr of carbon removed surface by hydrogenation at 470°C.

the hydrogenolysis of ethane, as shown in Fig. 5, and the activity was almost equal to that observed on the fresh catalyst.

DISCUSSION

It has been recognized that various types of carbon are deposited on nickel catalyst by exposure to CO or hydrocarbons, and that these carbonaceous species have a different reactivity with H_2.

In spite of remarkable progress of electron spectroscopic techniques such as UPS, AES, and XPS, the characterization of these species is a difficult subject, especially for supported catalyst. McCarty and Wise (*8*) reported the formation of two types of carbon designated as α-carbon and β-carbon, on exposure of Ni/Al_2O_3 in CO at 277°C. By raising the temperature of the carburized catalyst in a H_2 stream, α-carbon gave a maximum CH_4 evolution at about 197°C, while the β-carbon gave a maximum at about 407°C. On the other hand, by exposing the catalyst to ethylene at 300°C, α- and β-carbons, plus a new species designated γ-carbon, were obtained. The maximum temperatures for CH_4 evolution were approximately 222°, 277°, and 427°C for α, γ, and β states, which were identified as dispersed carbidic carbon, bulk Ni_3C, and amorphous carbon, respectively. The carburization temperature determined whether Ni_3C or free carbon was preferentially attained by exposure to CO; that is, Ni_3C formation preferred a lower temperature, such as below 270°C, as has been reported in the literatures (*9*), and between 300° to 340°C (*10*). In contrast to this, the decomposition of Ni_3C to free carbon and Ni is caused at 360°C (*10*) or 428°C (*11*).

Taking into account these characteristic temperatures reported in the literatures, carburization was performed at about 200°C in most of the cases (Figs. 1, 2, and 4) in which carbidic carbon was expected to be the dominant carbon deposit. Carburization at 300°C, shown in Fig. 5, however, may include the formation of both carbidic carbon and free carbon, because carburization at 277°C, as reported by McCarty and Wise (*8*), resulted in the formation of two types of carbon, α- and β-carbons.

It should be mentioned here that the amount of CH_4 evolved (0.15 Torr) by the addition of H_2 in Fig. 4 is merely several percent of the total adsorption observed during the self-hydrogenolysis in Fig. 1. This fact implies that the amount of adsorbed carbon species depending on hydrogen pressures in Fig. 1 cannot correspond to such an active species observed in Fig. 4. We found a similar highly reactive species on the Co/Al_2O_3 catalyst, and also found that the reaction with D_2 yielded dominant CH_2D_2 (*12*). Demuth and Ibach (*13*) proved that the adsorption of acetylene on the Ni(111) surface underwent the formation of CH species at a lower temperature but that CH_2 species appeared at a temperature above 177°C.

Based on these facts, the highly reactive species attained by exposing Ni/Al_2O_3 to C_2H_6 may be assignable to CH_2 species. It should not be overlooked that the subsequent reaction, after the abrupt evolution of CH_4 by the addition of hydrogen, proceeds at a rate which is almost equal to that attained prior to the hydrogen addition as shown in Fig. 4. This is a very important observation, because if the hydrogen molecule would contribute at the rate determining step of the hydrogenolysis reaction, which is either the C–C bond cleavage (*5*) or the hydrogenation of C_1 fragments (*6*), then the reaction would be accelerated by the addition of hydrogen, provided the concentration of the intermediates does not change. The hydrogenation of carbidic carbon to CH_4 is obviously faster than the hydrogenolysis of C_2H_6, as proved in Figs. 2 and 4. The adsorption of C_2H_6 also occurs rapidly either in the presence or the absence of hydrogen at 200°C as shown in Fig. 1, although hydrogen suppresses the amount of the adsorption.

Considering these facts, it appears that the C–C bond cleavage of highly dehydrogenated precursor species might be a plausible rate determining step of the hydrogenolysis reaction, and that the formation of the highly dehydrogenated precursor species is probably irreversible and requires ensemble sites as suggested by Martin (*4*).

As was described above, carbidic carbon undergoes rapid hydrogenation with H_2 at 200°C. If the carburization at 200°C forms rather pure carbidic carbon on Ni/Al_2O_3, the hydrogenolysis reaction on it will not suffer any retardation. In fact, if the amount of carbon deposit is small, the hydrogenolysis reaction on the carburized surface would be almost the same as that on the fresh catalyst, as shown in Fig. 4. However, it was found that if a rather large amount of carbon was deposited at 200°C, such as that shown in Fig. 2 (about 10 times larger than that in Fig. 4) a remarkable retardation took place. This fact suggests that carbidic carbon may be dominant at 200°C, but free carbon, which inhibits the hydrogenolysis reaction, is also formed, especially in the heavier depositions.

This speculation was proved by the experiments using a ^{13}C tracer shown in Table 1. That is, the carburization at 200°C forms an undoubtedly less reactive carbon deposit on the Ni/Al_2O_3 catalyst which can be removed by hydrogenation at 470°C.

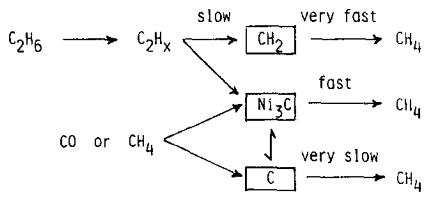
As described in the introduction, the hydrogenolysis reaction on alloy catalysts is sensitive to surface composition (*2*), while the hydrogenation of ethylene on alloy catalysts is insensitive to the surface constitution.

Considering these contrasting characteristics, the influence of carbon deposit on these two reactions was compared. From the results shown in Fig. 5, it may be deduced that carbidic carbon slightly retards the hydrogenation of ethylene at 0°C, but does not influence the hydrogenolysis of ethane at 200°C, because the carbidic carbon is stable at 0°C but entirely unstable at 200°C in the presence of H_2.

In contrast to this, free carbon, which is less reactive with H_2, undergoes remarkable retardation in the hydrogenolysis reaction of C_2H_6 while it brings about no inhibition of the hydrogenation of ethylene. The roles of the carbon deposit observed in this experiment are analogous to these of inert components such as Cu in the Cu–Ni alloy, that is, hydrogenolysis is sensitive to carbon deposits but the hydrogenation of ethylene is insensitive to them.

McCarty and Wise (*8*) found the formation of a new type of carbon on the Ni/Al_2O_3 catalyst upon its exposure to ethylene, and they designated it γ-carbon. This type of carbon reacts with H_2 at slightly higher temperatures than their α-carbon, which may correspond to the carbidic carbon described in this paper, and moreover, it is entirely removed by hydrogenation at 277°C. In conformity with this fact, the deactivation observed in Fig. 3 may be caused by the deposit of a similar type of carbon from C_2H_6 during hydrogenolysis at temperatures below 300°C.

Accordingly, we may conclude that any type of carbon deposit will retard the hydrogenolysis reaction of C_2H_6 providing it is stable under the reaction conditions. In contrast to this, the hydrogenation reaction of ethylene is entirely facile to any kind of carbon deposit. These results and their interpretation may be summarized in the following reaction scheme.



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