Journal of Catalysis **200,** 4–9 (2001)
doi:10.1006/jcat.2001.3179, available online at http://www.idealibrary.com on IDEAL®

Hydrogen–Deuterium Exchange Studies on the Decomposition of Methane over Ni/SiO$_2$

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Received April 7, 2000; revised January 23, 2001; accepted January 24, 2001; published online April 18, 2001

The reaction mechanism of methane decomposition over silica-supported Ni catalyst (Ni(5 wt%)/SiO$_2$) was investigated by performing kinetic studies of the reactions using isotopic methane (CH$_4$, CD$_4$, and ^{13}CH$_4$) and hydrogen (H$_2$ and D$_2$). An isotope effect between CH$_4$ and CD$_4$ was observed in the decomposition of methane over the Ni/SiO$_2$ catalyst. In the decomposition of a gas mixture of CH$_4$ and CD$_4$ over the Ni/SiO$_2$ catalyst, the H–D exchanged methanes were not formed. These results suggested that the first C–H bond cleavage in CH$_4$ was the rate-determining step in the decomposition of CH$_4$ into carbon and H$_2$. The idea well explained the reverse isotopic effect between H$_2$ and D$_2$ in the hydrogenation of the carbons deposited on the catalyst back into methane. Moreover, the rate-determining step was supported by the result that only CD$_4$ was formed in the early part of the exchange reaction between CH$_4$ and D$_2$ (CH$_4$ $\ll$ D$_2$). The mechanism of carbon deposition on the Ni/SiO$_2$ catalyst was examined by performing successive depositions from ^{12}CH$_4$ and ^{13}CH$_4$, followed by hydrogenation of the deposited carbon with H$_2$. The carbon atoms deposited last were found to be hydrogenated to CH$_4$ at first, suggesting that the carbon atoms did not scramble and the amorphous parts in a carbon fiber would be hydrogenated back into CH$_4$ catalyzed by a Ni particle present at the tip of a carbon fiber. © 2001 Academic Press

Key Words: **methane decomposition; H–D exchange; Ni/SiO$_2$; reaction mechanism.**

INTRODUCTION

Hydrogen is a clean fuel in the sense that no CO$_2$ is emitted when it is burned or used in H$_2$–O$_2$ fuel cells. However, the current processes of hydrogen production use natural gas and water or other fossil resources and water, which emit a huge quantity of CO$_2$ to the atmosphere.

The production of hydrogen from water-splitting by using solar or other renewable energy sources, such as wind power, tides, geothermal, atomic, and others, is not competitive with present-day renewable energy costs. Now, we believe that a realistic way to produce hydrogen with less CO$_2$ emission is to utilize methane, the main component of natural gas or of petroleum-associated gas, as the source of hydrogen.

For the production of hydrogen without CO$_2$ emission, the source of hydrogen must be only the methane itself. The thermal catalytic decomposition of methane produces hydrogen and carbon,

$$n\mathrm{CH}_4 \rightarrow n\mathrm{C} + 2n\mathrm{H}_2, \qquad [1]$$

where the hydrogen is used as clean energy and the carbon is buried back into the gas fields or can be used as functional carbon materials such as fibers, carbon blacks, graphite, active carbons, etc. The idea has already been proposed and reviewed (1–3). It has been known that the decomposition of methane takes place over supported nickel catalysts at >673 K (4–7). We have demonstrated that Ni/Cab-O-Sil is one of the most active catalysts for the decomposition of methane (8). In general, silica-supported nickel catalysts are known to be active for this reaction, depositing carbon as carbon fibers on the catalysts (4–7). However, with regard to the reaction mechanism of methane decomposition, detailed studies have not been reported yet. Therefore, the purpose of this work is to get information about the reaction mechanism of methane decomposition over silica-supported nickel catalysts on the bases of hydrogen–deuterium exchange studies using D$_2$ and CD$_4$.

EXPERIMENTAL

Catalysts

Silica-supported Ni (denoted as Ni/SiO$_2$) was prepared by impregnating a silica support with an aqueous solution of Ni(NO$_3$)$_2\cdot$6H$_2$O at 353 K, and drying up the impregnated samples at the same temperature. The samples were dried at 393 K for 5 h, and calcined at 673 K for 3 h in air. The loading amount of Ni was adjusted to 5 wt%. Kieselgel (Merck) was utilized as the silica support. The specific surface area of the silica support was estimated to be 270 m$^2\cdot$g^{-1} by the BET method.

The amount of surface Ni evaluated by the adsorption of hydrogen at 273 K was 30.4 μmol per gram of the fresh

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0021-9517/01 $35.00

Ni(5 wt%)/SiO_2. The dispersion of Ni metal on the support was 3.6% for this catalyst.

Reactants

CH_4 (99.99%) and H_2 (>99.99%) were supplied from Taiyo Toyo Sanso Co., Ltd. and Nippon Sanso Co., respectively. These reactants were introduced into the reaction apparatus through molecular sieves 5A cooled at 200 K. CD_4 (99%; Cambridge Isotope Laboratories), D_2 (99%; Cambridge Isotope Laboratories), and $^{13}CH_4$ (99%; Takachiho Chemical Industry) were used without further purification.

Reaction Procedure

All the reactions (decomposition of methane and hydrogenation of the carbon deposited on catalysts) were carried out in a conventional closed gas circulation system. The Ni/SiO_2 catalyst (20 mg) was dispersed on the bottom of a reactor made of quartz. Prior to the reaction, the Ni/SiO_2 catalyst was conditioned in a vacuum (<0.01 Pa) at 823 K for 30 min, treated in a flow of hydrogen gas (40 kPa) at 823 K for 60 min, and degassed at 823 K for 30 min under a vacuum (<0.01 Pa), successively. Reaction was started by adding reactants into the gas circulation line (dead volume, ca. 370 ml) with the reactor. During the reaction, a part of the gases in the gas circulation system was sampled out and analyzed by GC and Q-mass spectrometry.

RESULTS AND DISCUSSION

Kinetic Isotope Effect between CH_4 and CD_4 on the Decomposition of Methane

Our previous studies indicated that the decomposition of CH_4 over Ni(5 wt%)/SiO_2 occurred at temperatures above 623 K, giving only hydrogen as a gaseous product (8, 9). The SEM pictures of the deposited carbon on this catalyst showed a filamentous structure growing out from metal particles (8). The amount of carbon deposited on this catalyst before the complete deactivation of the catalyst was ca. 320 mmol per gram of catalyst. In this case, the number of carbons per Ni atom (denoted as C/Ni, hereafter) was ca. 370. The C/Ni value was evaluated from the total number of deposited carbons divided by the total number of Ni atoms on the catalyst.

The kinetic isotope effect on the decomposition rate of methane over Ni(5 wt%)/SiO_2 catalyst (20 mg) has been examined for CH_4 and CD_4 at 673 K. The initial pressure of CH_4 or CD_4 was 2.67 kPa (393 μmol). The amount of surface Ni atoms on 20 mg of catalyst was 0.61 μmol. Figure 1 shows the turnover number of CH_4 or CD_4 decomposed per surface Ni atom on a fresh catalyst as a function of reaction time. The experiments were performed twice for each methane. As can be seen from these kinetic curves, the decomposition rate of CH_4(r_d(CH_4)) was clearly faster than that of CD_4(r_d(CD_4)). The average steady state decomposition rates after 30 min for CH_4 and CD_4 indicated a kinetic isotope effect ($r_d(CH_4)/r_d(CD_4)$) of 1.6.

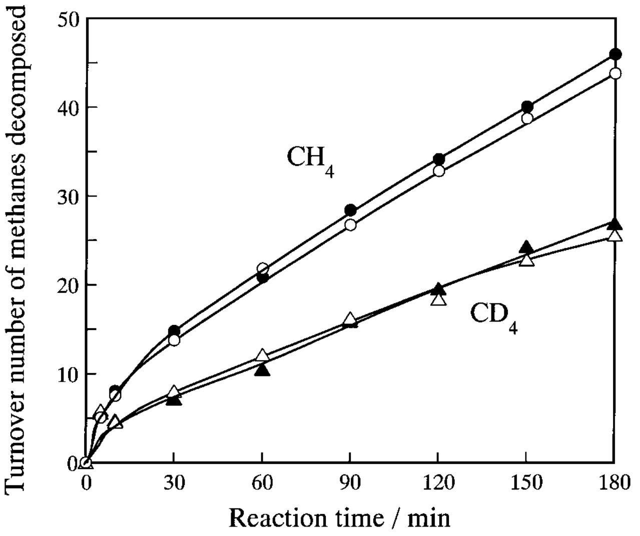

FIG. 1. Kinetic curves of the decomposition of CH_4 and CD_4 on the fresh catalyst.

Figure 2 shows the kinetic curves observed for the catalyst with 1.28 to 1.37 mmol of carbon (C/Ni = 75–81) predeposited from methane. Before the experiment for the kinetic curve 1, 1.28 mmol of CH_4 was decomposed on a fresh catalyst (20 mg) at 773 K. After the residual gases (CH_4 and H_2) were evacuated at 673 K, the decomposition of CH_4 was started by introducing and circulating

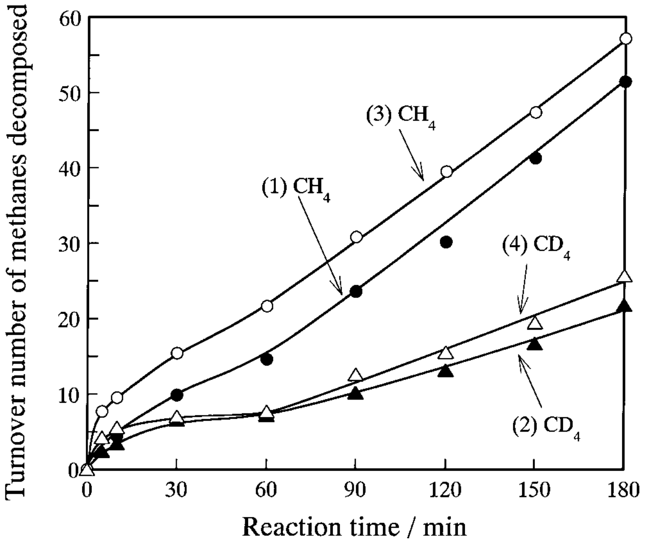

FIG. 2. Decomposition of CH_4 and CD_4 on the catalyst with a predeposited carbon amount of 1.28 (C/Ni = 75)–1.37 (C/Ni = 81) mmol per 20 mg of catalyst. Average turnover frequencies of decompositions in the range of 90 to 180 min: ●, 5.3×10^{-3}; ○, 5.1×10^{-3}; ▲, 2.1×10^{-3}; △, $2.4 \times 10^{-3}\ s^{-1}$.

CH_4 (2.67 kPa, 393 μmol) through the catalyst bed. The kinetic experiments for the decomposition of CD_4 (curve 2) were performed subsequently on the same catalyst after evacuating the residual gases and introducing CD_4. The experiments for the curves 3 and 4 were carried out consecutively by the same procedure. All the kinetic curves indicated a fast initial decomposition followed by an induction period of about 50 min. The reaction proceeded steadily after 60 min. The average kinetic isotope effect for the steady state decomposition observed on this carbon-deposited catalyst was ca. 2.3 which was greater than that on the fresh catalyst (Fig. 1). We speculate that the induction periods in Fig. 2 could be caused by the predeposited carbons which cover the active sites of Ni catalyst during the degassing pretreatment of the catalyst at 673 K. The removal of the carbons formed from CH_4 or CD_4 on the active sites by H_2 and D_2 might require some induction period. This explains the different kinetic curves and the different isotope effects between fresh and predeposited catalysts (Figs. 1 and 2).

The clear kinetic isotope effect between CH_4 and CD_4 in Figs. 1 and 2 strongly suggests that the rate-determining step in the decomposition of methane is the C–H bond breaking of either of CH_4, CH_3, CH_2, or CH species.

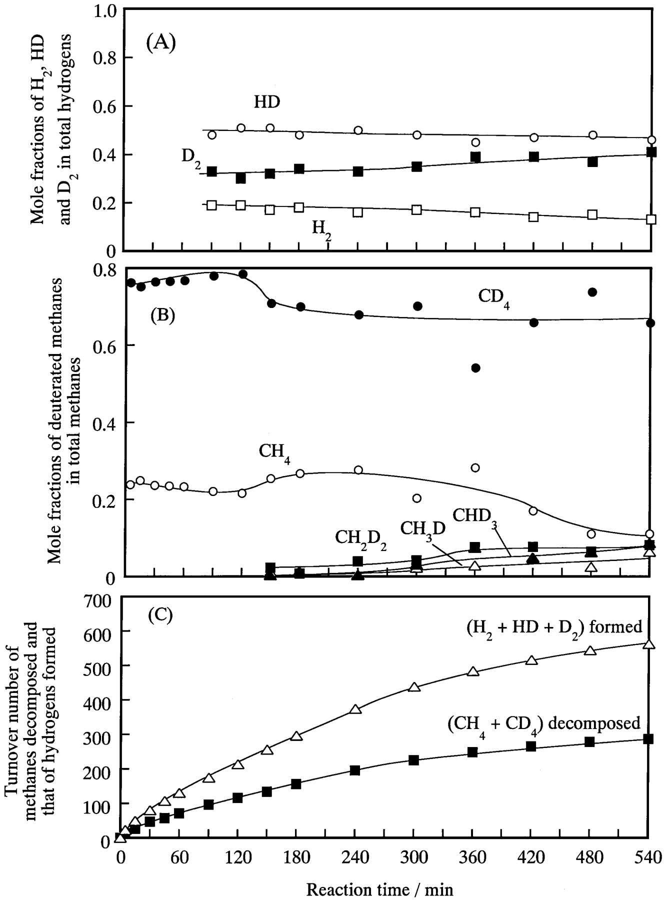

FIG. 3. Decomposition of a mixture of CH_4 and CD_4 and H–D exchange reactions at 773 K.

H–D Exchange between CH_4 and CD_4 during Methane Decomposition

The experiments over a fresh Ni/SiO_2 catalyst at 673 K using a CH_4–CD_4 mixture ($[CH_4]/[CD_4] = 1.1$, total initial pressure 2.67 kPa) showed a preferential decomposition of CH_4 due to the kinetic isotope effect described in the previous section. The increase in temperature to 723 K clearly accelerated the decompositions of both CH_4 and CD_4. However, the H–D exchange between CH_4 and CD_4, which should be verified by the formations of CH_3D, CH_2D_2, or CHD_3, did not occur at all at temperatures below 773 K during the decomposition of methanes. The results for the decomposition of a CH_4–CD_4 mixture ($[CH_4]/[CD_4] = 1/3$, total initial pressure 2.67 kPa) at 773 K are demonstrated in Fig. 3. The molar fractions of H_2, HD, and D_2 and those of CH_4, CD_4, CH_2D_2, CH_3D, and CHD_3 in methanes are plotted versus reaction time in Figs. 3A and 3B, respectively. The turnover number of methanes ($CH_4 + CD_4$) decomposed and that of hydrogens ($H_2 + HD + D_2$) formed per surface Ni atom are plotted in Fig. 3C. The amounts of methanes and hydrogens were evaluated from the gas chromatographic analyses of total methanes and the volumetric measurement of total gaseous compounds in the closed gas circulation system. The mass spectroscopic analyses of the H_2, D_2, and HD showed a large experimental error in these mole fractions at the early stage of the reaction due to the small amount of these products. Therefore, the mole fractions of hydrogen isotopes are indicated only after 80 min in Fig. 3A. The results in Fig. 3 indicate a smooth decomposition of CH_4 and CD_4 as well as the equilibrium compositions of HD, D_2, and H_2 but a very slow H–D exchange reaction between CH_4 and CD_4. The very fast H_2–D_2 exchange reaction,

$$H_2 + D_2 \rightleftarrows 2HD, \qquad [2]$$

over both fresh and carbon-deposited Ni(5 wt%)/SiO_2 catalyst was confirmed separately at temperatures <773 K. The reaction completely equilibrated within 90 min even at room temperature. The very slow H–D exchange between CH_4 and CD_4 during the decomposition of these methanes strongly suggests that the C–H bond breaking of CH_4 must be the rate-determining step in the overall reactions, because if one of the C–H bond splits of CH_3, CH_2, or CH (Eq. 4) is the rate-determining step, we should observe a faster H–D exchange between CH_4 and CD_4 than the decomposition of methane due to the recombination of CH_{4-n} and D or of CD_{4-n} and H (backward reactions of Eqs. [3] and [3′]), where n should be 2 or 3:

$$CH_4 \rightleftarrows CH_{4-n} + nH \qquad [3]$$

$$CD_4 \rightleftarrows CD_{4-n} + nD \qquad [3']$$

$$CH_{4-n} \rightarrow CH_{3-n} + H \qquad [4]$$

$$CD_{4-n} \rightarrow CD_{3-n} + D. \qquad [4']$$

The gaseous compositions of H_2, HD, and D_2 were always in equilibrium during the decompositions of CH_4 and CD_4, indicating a very fast desorption and migration of H and D on the catalyst.

Kinetic Isotope Effect between H_2 and D_2 on the Hydrogenation of Carbon into Methane

The hydrogenation of the deposited carbon on Ni(5 wt%)/SiO_2 catalyst regenerated only methane at >623 K according to the backward reaction of Eq. [1] (9). We can expect to get useful information on the decomposition mechanism from the studies on the hydrogenation of the carbons deposited.

Figure 4 shows the kinetic curves of methanes (CH_4 and CD_4) formed from the reaction of carbon on Ni(5 wt%)/SiO_2 with H_2 and D_2 at 773 K. Carbons amounts of 544–567 μmol (corresponding to C/Ni = 32–34) were predeposited on the catalyst (20 mg) at 773 K from decomposition of CH_4. After degassing H_2 and the residual CH_4, pure H_2 or D_2 (2.67 kPa, 390 μmol) was added and reacted at 773 K with carbons deposited on the catalyst. The kinetic curves in Fig. 4 indicate that the rate of CD_4 formation from the carbon and D_2 was considerably faster than that of CH_4 from the hydrogenation of carbon with H_2. The amount of CD_4 formed at 180 min was ca. 1.6 times larger than that of CH_4. The converse isotope effect observed here can be explained by the idea that the hydrogenation (or deuteration) of methyl group (or CD_3) into methane,

$$CH_3 + H \rightarrow CH_4 \qquad [5]$$

$$CD_3 + D \rightarrow CD_4, \qquad [6]$$

must be the slowest step in the regeneration of methane (CH_4 and CD_4). The converse isotope effect may be caused by the concentration of the surface deuterium atoms being higher than that of hydrogen atoms at the same partial pressures of D_2 and H_2 because of the following consideration.

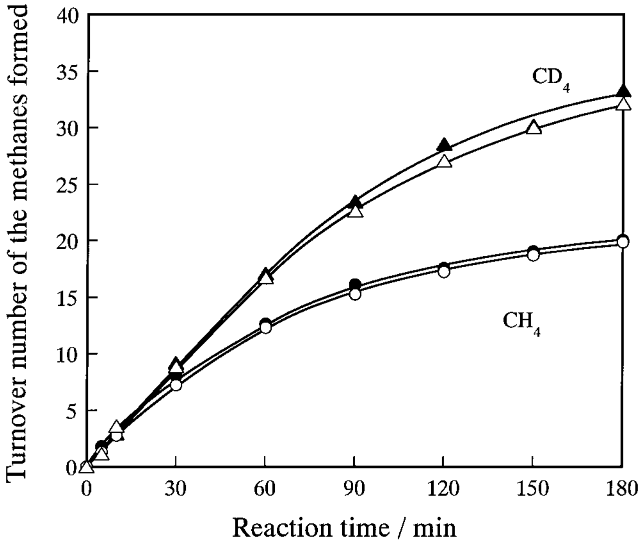

FIG. 4. Kinetic curves of the formation of methanes from deposited carbons with H_2 and D_2 at 773 K: ● and ○, with H_2; ▲ and △, with D_2.

Adsorption energies of H_2 and D_2, $Q(H_2)$ and $Q(D_2)$, can be evaluated

$$2Ni + H_2 \rightarrow 2Ni\text{–}H \qquad Q(H_2)$$

$$2Ni + D_2 \rightarrow 2Ni\text{–}D \qquad Q(D_2)$$

$$Q(H_2) = 2E_{dis}(Ni\text{–}H) - E_{dis}(H\text{–}H)$$

$$Q(D_2) = 2E_{dis}(Ni\text{–}D) - E_{dis}(D\text{–}D),$$

where E_{dis} means dissociation energies.

$$Q(D_2) - Q(H_2) = (2E_{dis}(Ni\text{–}D) - 2E_{dis}(Ni\text{–}H)) - (E_{dis}(D\text{–}D) - E_{dis}(H\text{–}H)),$$

where $E_{dis}(Ni\text{–}D) > E_{dis}(Ni\text{–}H)$ and $E_{dis}(D\text{–}D) - E_{dis}(H\text{–}H) \cong 7.5\ kJ \cdot mol^{-1}$.

Since the zero-point energy difference for hydrogen and deuterium compounds is more pronounced for heavier ones (10), $2[E_{dis}(Ni\text{–}D) - E_{dis}(Ni\text{–}H)] > [E_{dis}(D\text{–}D) - E_{dis}(H\text{–}H)]$. Thus, $Q(D_2)$ must be greater than $Q(H_2)$. In fact, the stronger adsorption of D_2 on Ni catalysts was confirmed by many researchers (11). Therefore, the surface D atom concentration must be greater than the H atom concentration at same partial pressures and temperatures. These considerations are consistent with the idea that the rate-determining step in the decomposition of methane is the C–H bond breaking of CH_4 as suggested earlier.

Hydrogenation of the Carbon Deposited from $^{13}CH_4$

The study on the reactivity of carbons deposited on the catalysts initially or later may provide information about the deposit mechanism of carbon. This can be investigated by analyzing the regenerated $^{13}CH_4$ from the carbons deposited from $^{12}CH_4$ and $^{13}CH_4$ in order.

^{12}C(400 μmol) was predeposited first on Ni(5 wt%)/SiO_2 (20 mg) from $^{12}CH_4$ at 773 K. After evacuating the gas phase, ^{13}C in an amount of 60 μmol was deposited on the same sample from $^{13}CH_4$ at the same temperature. The hydrogenation of the carbons thus predeposited was started by introducing hydrogen (6.67 kPa, 975 μmol) at 773 K after evacuating the gas phase. The amounts of $^{13}CH_4$ and $^{12}CH_4$ produced are plotted as functions of the reaction time in Fig. 5. The reaction was continued by adding new H_2 (6.67 kPa) after degassing the gas phase at 300 min.

The results in Fig. 5 at the early stage of the reaction indicate only the formation of $^{13}CH_4$, suggesting that the carbon deposited later on the catalyst preferentially reacts with H_2. However, the formation of $^{12}CH_4$ clearly occurred after

50 min. The formation rate of $^{12}CH_4$ exceeded that of $^{13}CH_4$ after 330 min, probably due to the consumption of the reactive ^{13}C deposit. The observations in Fig. 5 suggest that there is no carbon scrambling among the deposited carbons. The amorphous carbons accumulated last from methane, which had been catalyzed by Ni particles at the tips of the fibers, must be hydrogenated successively. XRD studies and TEM images of the carbon fibers formed at $\leq$823 K indicated a very disordered structure of the carbons, i.e., partially graphitized but mostly amorphous (12).

H–D Exchange between D_2 and CH_4

The H–D exchange between CH_4 and CD_4 during decomposition of methane was quite slow at temperatures $\leq$773 K as described earlier. However, the exchange occurred even at 623 K when the partial pressures of H_2, HD, and D_2 formed from the methanes are increased because of the increase in the rate of the backward reaction, i.e., the hydrogenation (or deuteration) of the deposited carbons. This situation can be well demonstrated by the H–D exchange reaction between D_2 and CH_4 in Fig. 6. The gas mixture of CH_4 (29 μmol) and D_2 (557 μmol) was introduced and circulated through a fresh Ni(5 wt%)/SiO_2 catalyst (20 mg) at 623 K. The molar ratios of D_2, HD, and H_2 and those of methanes are plotted versus reaction time. As can be seen from this figure, H–D exchange between D_2 and CH_4 occurred quickly from the early stage of the reaction. It should be noted that the main deuterated methane observed very early in the reaction was CD_4. In contrast, the CH_3D was not formed at all at <20 min. These observations indicate that, once the C–H bond breaking of CH_4 occurs (Eq. [7]), the consecutive C–H bond breakings of CH_3 (Eq. [8]), CH_2 (Eq. [9]), and CH finally to carbon must be very fast:

$$CH_4 \not\rightleftarrows CH_3 + H \qquad [7]$$

$$CH_3 \rightleftarrows CH_2 + H \qquad [8]$$

$$CH_2 \rightleftarrows CH + H \qquad [9]$$

$$CH \rightleftarrows C + H. \qquad [10]$$

This means that the breaking of the C–H bond of CH_4 (Eq. [7]) is the slowest step in the overall decomposition of CH_4 into carbon and hydrogen. The H atoms formed in reactions [7] to [10] should be quickly substituted with D atoms because of greater fractions of D_2 and HD than H_2 in the gas phase. The Ni–D bond, being stronger than Ni–H, must accelerate this tendency. Under these circumstances, the backward reactions of Eqs. [10], [9], [8], and [7] would inevitably produce CD_4 and CHD_3 as observed in Fig. 6. The formations of other deuterated methanes (CH_2D_2 and CH_3D) observed clearly after 30 min must be ascribed to the H atoms in HD released by the decomposition of CH_4.

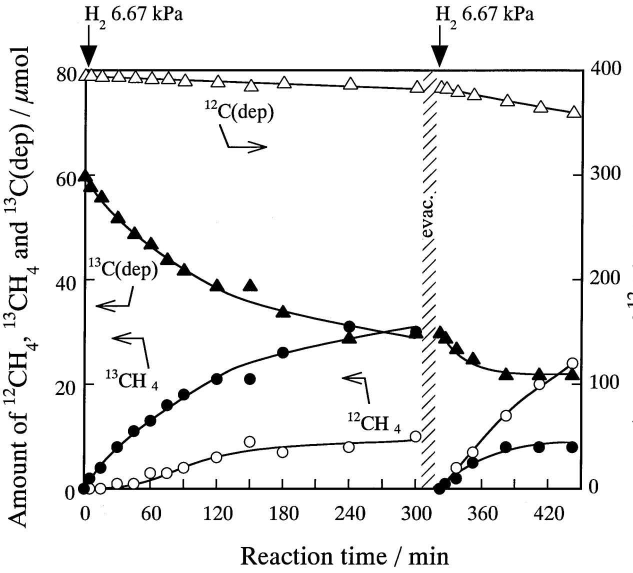

FIG. 5. Regeneration of $^{13}CH_4$ and $^{12}CH_4$ from the carbons deposited from $^{12}CH_4$ and $^{13}CH_4$.

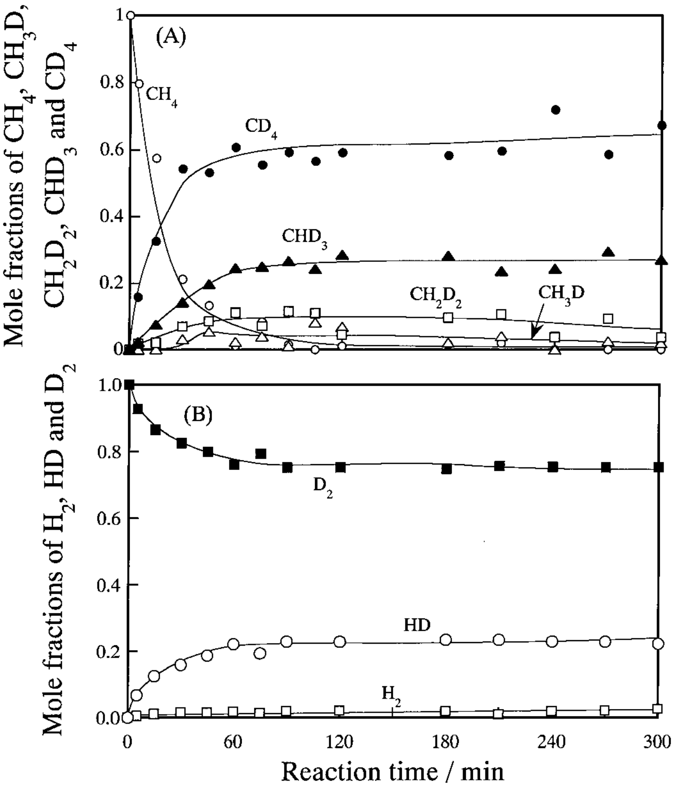

FIG. 6. H–D exchange between D_2 and CH_4 at 723 K over a fresh catalyst.

CONCLUSION

The isotope effects obtained between the decompositions of CH_4 and CD_4 and between the hydrogenation of deposited carbons with H_2 and D_2 were well explained by assuming that the first C–H bond scission of CH_4 was the rate-determining step in the decomposition of CH_4 into carbon and H_2. This idea also explains the observation that only CD_4 was formed early in the H–D exchange between D_2 and CH_4 when the D_2 concentration was much greater than that of CH_4. The experiments using $^{13}CH_4$ suggested that the carbon atoms would not intermingle with the previously deposited carbons. The carbons form and grow a carbon fiber, which is catalyzed by a Ni particle present at the tip of the fiber.

ACKNOWLEDGMENTS

This work was supported by NEDO (International Joint Research Grant) and SANKAKEN (Hiroshima Prefectural Institute of Industrial Science and Technology).

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