

## Hydrogen production by decomposition of ethane-containing methane over carbon black catalysts

Mi So Kim, Sang Yup Lee, Jung Hun Kwak, Gui Young Han, and Ki June Yoon<sup>†</sup>

School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

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**Abstract**—Mixtures of methane and small amounts of ethane were decomposed in the presence of carbon black (CB) catalysts at 1,073-1,223 K for hydrogen production. Although most of the added ethane was first decomposed to ethylene and hydrogen predominantly by non-catalytic reaction, subsequent decomposition of ethylene was effectively facilitated by the CB catalysts. Because some methane was produced from ethane, the net methane conversion decreased as the added ethane increased. The rate of hydrogen production from methane was decreased by the added ethane. A reason for this is that adsorption of methane on the active sites is inhibited by more easily adsorbing ethylene. In spite of this, the hydrogen yield increased with an increase of the added ethane because the contribution of ethane and ethylene decomposition to the hydrogen production was dominant over methane decomposition. A higher hydrogen yield was obtained in the presence of a higher-surface-area CB catalyst.

Key words: Carbon Black Catalyst, Decomposition, Ethane, Hydrogen Production, Methane

### INTRODUCTION

The steam reforming of natural gas is currently the largest and most economical process for the production of  $H_2$ , but this process is accompanied by simultaneous production of  $CO_2$  which is to be reduced due to the greenhouse effect. An attractive alternative for the production of  $H_2$  without  $CO_2$  emission is catalytic decomposition of methane ( $CH_4 \rightarrow C(s) + 2H_2$ ) [1-5]. Transition metals such as Fe, Ni and Co can be used as the catalyst for  $CH_4$  decomposition at low temperatures (450-1,000 K), but the carbon build-up induces rapid catalyst deactivation as well as other problems such as reactor blocking and bothersome catalyst regeneration. Regeneration of those catalysts by combustion or gasification of carbon deposits results in production of a large amount of  $CO_2$  [6-9]. On the contrary, several recent studies have shown that carbon black (CB) is a stable and effective catalyst for  $CH_4$  decomposition [10-16].  $CH_4$  decomposition using CB as a catalyst has several advantages compared with the conventional steam reforming. The produced clean carbon can be commercialized, and additional treatments such as the water gas shift reaction,  $CO$  removal, and catalyst regeneration are not necessary, which simplifies the process significantly [11].

Although natural gas is mostly composed of  $CH_4$ , it contains considerable amounts (5-30%) of higher hydrocarbons such as  $C_2H_6$ ,  $C_3H_8$  and  $C_4H_{10}$ . However, the studies cited above have mostly been confined to the decomposition of pure  $CH_4$ . Because those higher hydrocarbons are less stable than  $CH_4$ , they can decompose more easily than  $CH_4$ , and moreover  $CH_4$  and  $C_2H_4$  can be produced in addition to the solid carbon and  $H_2$ . For example, it has been reported that when pure  $C_2H_6$  is decomposed at 1,123 K over a CB catalyst, the compositions of  $H_2$ ,  $CH_4$  and  $C_2H_4$  in the reactor effluent

gas are 55, 32 and 11 vol%, respectively [17]. Therefore, the  $H_2$  yield and product distribution obtained by the decomposition of mixtures of  $CH_4$  and  $C_2H_6$  will be different from those by the decomposition of pure  $CH_4$ . Nevertheless, studies on decomposition of mixtures of  $CH_4$  and higher hydrocarbons over CB catalysts are rare. A recent study reported that when mixtures of  $CH_4$  and  $C_2H_6$  or  $C_3H_8$  were decomposed in the presence of a CB catalyst, higher  $H_2$  yields could be obtained compared with the decomposition of pure  $CH_4$  [17]. However, the detailed distributions of the products from the mixtures, especially  $CH_4$  and  $C_2H_4$ , were not presented; moreover, the reason for the higher  $H_2$  yield was only superficially proposed by attributing it to the higher content of hydrogen in  $C_2H_6$  and  $C_3H_8$ . Therefore, a more detailed study on the decomposition of mixtures of  $CH_4$  and  $C_2H_6$  or  $C_3H_8$  is required.

A study on decomposition of pure  $C_2H_6$  in the presence of CB catalysts has recently been reported [18].  $C_2H_6$  starts to thermally (in the absence of a catalyst) decompose from 950 K, while  $CH_4$  does from 1,223 K [10]. In the presence of CB catalysts the  $C_2H_6$  conversion and the  $H_2$  yield increase significantly. For example, at 1,173 K the  $C_2H_6$  conversion and the  $H_2$  yield in the absence of a catalyst are 94% and 50%, respectively, while in the presence of a CB catalyst they are 99% and 80%, respectively. The marked increase of the  $H_2$  yield is mainly owing to a considerable decrease of the selectivity of  $C_2H_4$  that has been produced by dehydrogenation of  $C_2H_6$ , which indicates that CB catalysts are efficient for decomposition of  $C_2H_4$  to  $H_2$  and solid carbon. Another study on decomposition of pure  $C_2H_6$  in the presence of a CB catalyst has reported similar results [17]. Studies on decomposition of pure  $C_3H_8$  and  $C_4H_{10}$  in the presence of a CB catalyst have also been reported [17,19], and the trends for the  $C_3H_8$  or  $C_4H_{10}$  conversion, the  $H_2$  yield and the  $C_2H_4$  selectivity are similar to those obtained from the decomposition of pure  $C_2H_6$ .

Because  $C_2H_6$  is the second most abundant component of natural gas, this study investigated the  $H_2$  production by decomposition

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: kijyoon@skku.edu

of  $\text{CH}_4$  mixed with small amounts of  $\text{C}_2\text{H}_6$ , focusing on the effects of added  $\text{C}_2\text{H}_6$  on the  $\text{H}_2$  yield and  $\text{CH}_4$  decomposition. Three representative CB samples were employed as the catalysts, and catalytic effects of the CB catalysts were also examined by comparing with the results of non-catalytic thermal decomposition and by comparing the activities of CB catalysts one another.

## EXPERIMENTAL

Three representative CB catalysts were selected in this study from the previous studies on decomposition of pure  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  [13, 16, 18]: a pelletized rubber CB (N330(P): surface area=70  $\text{m}^2/\text{g}$ , from OCI, Korea), a fluffy rubber CB (N330(F): surface area=77  $\text{m}^2/\text{g}$ , from OCI, Korea), and a color CB (HI-900L: surface area=256  $\text{m}^2/\text{g}$ , from Degussa, Germany). In the decomposition of pure  $\text{CH}_4$  and pure  $\text{C}_2\text{H}_6$ , the catalytic activities of N330(F) and HI-900L were comparable to each other but higher than the activity of N330(P).

The experimental procedure was essentially the same as in the previous studies [13, 16, 18]. All the CB catalysts were dried at 373 K for 24 h in air before the reaction test. The decomposition reaction was carried out in a vertical, fixed-bed, 8 mm I.D. quartz-tube flow reactor heated by an electric tube furnace (Lindberg Blue M, US). The tube was narrowed somewhat in the middle and rock wool was placed there to support the CB particles.  $\text{CH}_4$  (99.99%, Dong-a Gas, Korea),  $\text{C}_2\text{H}_6$  (99.95%, Duckyang Energen, Korea) and Ar (MS Dongmin Specialty Gas, Korea) were used without further purification. The standard reaction conditions were a catalyst charge of 0.1 g, a fixed  $\text{CH}_4$  flow rate of 30  $\text{cm}^3$  (STP)/min (a volumetric hourly space velocity (VHSV) of 18,000  $\text{cm}^3 \text{CH}_4/\text{h} \cdot \text{g}_{\text{CB}}$ ;  $\text{g}_{\text{CB}}$  denotes the mass in grams of before-reaction dried CB), and  $\text{C}_2\text{H}_6$  flow rates of 1.58–5.29  $\text{cm}^3$  (STP)/min ( $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratios=5/95, 10/90, and 15/85). The reaction temperature ranged from 1,073 to 1,223 K in 50 K intervals. Non-catalytic thermal decomposition was also performed for comparison purpose. Because the stainless steel sheath of the thermocouple is a good catalyst for hydrocarbon decomposition [10], the thermocouple was removed before the reaction experiments after the desired temperature was reached under Ar flow. The first sampling and analysis was usually done 5 min after the feed gas flowed, because it took time to flush the Ar gas initially present and for the reaction system to reach steady state. Afterwards, the sampling and analysis was done every 15 min for 2 h. The product gas was analyzed by gas chromatography (Younglin M600D, Korea), using a HayeSep Q column (Supelco, US) with Ar carrier and a thermal conductivity detector. The oven temperature of the gas chromatograph was maintained at 323 K for 0.7 min and then raised to 473 K with 45 K/min. The amounts of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  in the product gas were determined using calibrated data.

When a mixture of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  is decomposed, some  $\text{CH}_4$  is produced from  $\text{C}_2\text{H}_6$  [17, 18] while a part of the  $\text{CH}_4$  fed is concurrently decomposed. Because the produced  $\text{CH}_4$  is not distinguishable from the unreacted feed  $\text{CH}_4$ , the conversion of the feed  $\text{CH}_4$  cannot be determined separately. Therefore, only the net  $\text{CH}_4$  conversion, accounting for the sum of the produced  $\text{CH}_4$  and the unreacted feed  $\text{CH}_4$ , is presented in this study.

$$\text{Net } \text{CH}_4 \text{ conversion (\%)} = 100 \times (\text{moles of } \text{CH}_4 \text{ fed} - \text{moles of } \text{CH}_4 \text{ coming out of the reactor}) / (\text{moles of } \text{CH}_4 \text{ fed})$$

$\text{C}_2\text{H}_6$  conversion is defined as follows:

$$\text{C}_2\text{H}_6 \text{ conversion (\%)} = 100 \times (\text{moles of } \text{C}_2\text{H}_6 \text{ converted}) / (\text{moles of } \text{C}_2\text{H}_6 \text{ fed})$$

$\text{C}_2\text{H}_4$  selectivity and  $\text{H}_2$  yield are defined as follows:

$$\text{C}_2\text{H}_4 \text{ selectivity (\%)} = 100 \times (\text{moles of } \text{C}_2\text{H}_4 \text{ produced}) / (\text{moles of } \text{C}_2\text{H}_6 \text{ fed})$$

$$\text{H}_2 \text{ yield (\%)} = 100 \times (\text{moles of } \text{H}_2 \text{ produced}) / [2 \times (\text{moles of } \text{CH}_4 \text{ fed}) + 3 \times (\text{moles of } \text{C}_2\text{H}_6 \text{ fed})]$$

## RESULTS AND DISCUSSION

### 1. $\text{C}_2\text{H}_6$ Conversion and $\text{C}_2\text{H}_4$ Selectivity

The conversions of  $\text{C}_2\text{H}_6$  with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratios of 5/95 and 15/85 are presented in Fig. 1. Since the conversions with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio of 10/90 were between those with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratios of 5/95 and 15/85 [20], they are not shown here for brevity. At 1,073 K, the  $\text{C}_2\text{H}_6$  conversion by the non-catalytic reaction with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio of 5/95 was 66% and those in the presence of the catalysts were 70–76%. The  $\text{C}_2\text{H}_6$  conversion by the non-catalytic reaction with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio of 15/85 was 81% and those in the presence of the catalysts were 75–78%. The higher  $\text{C}_2\text{H}_6$  conversion by the non-catalytic reaction at 1,073 K with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio of 15/85 than that with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio of 5/95 is considered due to the higher  $\text{C}_2\text{H}_6$  partial pressure, or generation of a higher concentration of ethyl radicals that propagate the homogeneous gas-phase dehydrogenation of  $\text{C}_2\text{H}_6$ . However, in the presence of the catalysts the differences in the  $\text{C}_2\text{H}_6$  conversion were small. At higher temperatures from 1,123 to 1,223 K the conversions were very high (93–99%) and nearly the same regardless of the presence of the catalysts and the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio. These results indicate that conversion of  $\text{C}_2\text{H}_6$ , more precisely de-

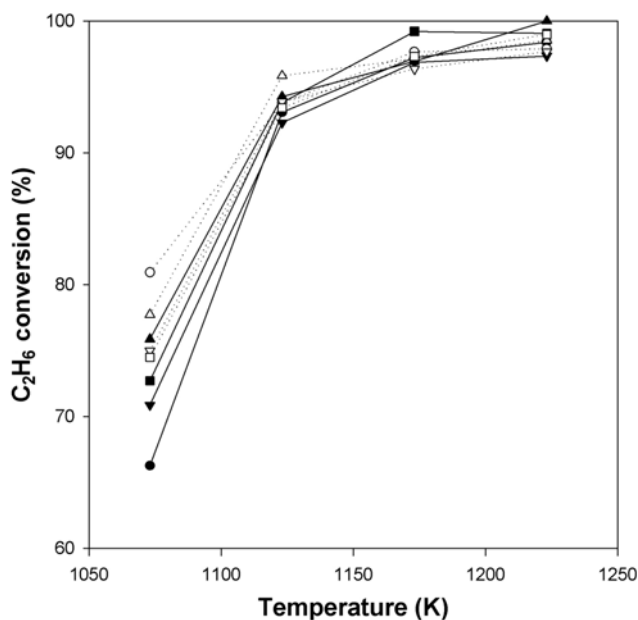


Fig. 1.  $\text{C}_2\text{H}_6$  conversion in non-catalytic reaction and in the presence of catalysts at different temperatures (VHSV=18,000  $\text{cm}^3 \text{CH}_4/\text{h} \cdot \text{g}_{\text{CB}}$ ;  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio=5/95 (solid symbols): non-catalytic (●), N330(P) (▼), N330(F) (▲), HI-900L (■);  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio=15/85 (open symbols): non-catalytic (○), N330(P) (▽), N330(F) (△), HI-900L (□)).

hydrogenation of  $C_2H_6$ , proceeds dominantly by the non-catalytic reaction. In decomposition of pure  $C_2H_6$ , it has been observed that the  $C_2H_6$  conversions over the CB catalysts are considerably higher than the non-catalytic  $C_2H_6$  conversion [18]. However, the results in Fig. 1 show that the contribution of the CB catalysts to the  $C_2H_6$  conversion is not significant. This is attributable to the much lower partial pressures of  $C_2H_6$  in this study compared with the case of feeding pure  $C_2H_6$ .

On the other hand, with the  $C_2H_6/CH_4$  feed ratio of 15/85, the non-catalytic  $C_2H_6$  conversion at 1,073 K was higher than the catalytic conversion. This is an unexpected result when considering the result in the previous study [18]. One possible explanation for this may be given as follows by taking into account the low partial pressure of  $C_2H_6$  and the action of the CB catalyst. By the free-radical chain reaction mechanism for the non-catalytic reaction, ethyl radicals generated in the gas phase in the initiation and propagation steps are transformed to ethylene and hydrogen [18]. However, in the presence of a CB catalyst, an ethyl radical can be transformed to an ethylene molecule and an adsorbed hydrogen atom with the aid of the catalyst [18],



where S denotes the active site on CB. This reaction (1) accelerates the  $C_2H_6$  dehydrogenation rate, as observed in the case with the  $C_2H_6/CH_4$  feed ratio of 5/95 at 1,073 K in the presence of the catalyst. On the other hand, an ethyl radical can react with the adsorbed hydrogen atom to produce an ethane molecule.



If reaction (2) is significant, the net  $C_2H_6$  conversion decreases. Between reactions (1) and (2), which one is more significant may depend on the conditions such as the concentrations of  $C_2H_5$  and H-S and temperature. Because reaction (2) can be more significant than reaction (1) with the  $C_2H_6/CH_4$  feed ratio of 15/85 at 1,073 K in the presence of the catalyst, where the concentrations of  $C_2H_5$  and H-S are higher than those with the  $C_2H_6/CH_4$  feed ratio of 5/95, the lower catalytic  $C_2H_6$  conversion than the non-catalytic conversion may be explained. When the partial pressure of  $C_2H_6$  is much higher or the reaction temperature is higher, reaction (2) proceeds much faster and will be almost equilibrated, and thus the net effect of reaction (2) on the  $C_2H_6$  conversion makes negligible difference regardless of the presence of the catalyst. Under these conditions, however, other reaction steps - non-catalytic reactions, reaction (1),  $2H-S \leftrightarrow H_2 + 2S$ , and catalytic decomposition of  $C_2H_4$  - can proceed faster, resulting in a higher rate of  $C_2H_6$  conversion. All in all, the differences between the non-catalytic and catalytic  $C_2H_6$  conversions were observed to be small in this study.

The selectivities of  $C_2H_4$  with different  $C_2H_6/CH_4$  feed ratios are shown in Fig. 2. The selectivities of  $C_2H_4$  in the presence of the catalysts were considerably lower than those for the non-catalytic decomposition, indicating that CB catalysts are effective for decomposition of  $C_2H_4$  to  $H_2$  and solid carbon. The effectiveness of the CB catalysts for the decomposition of  $C_2H_4$  was in the order HI-900L > N330(F) > N330(P). This trend is in agreement with the results of the previous study on the decomposition of pure  $C_2H_6$  over the CB catalysts [18]. When the selectivities of  $C_2H_4$  in the non-catalytic reaction with the  $C_2H_6/CH_4$  feed ratio of 5/95 were compared with

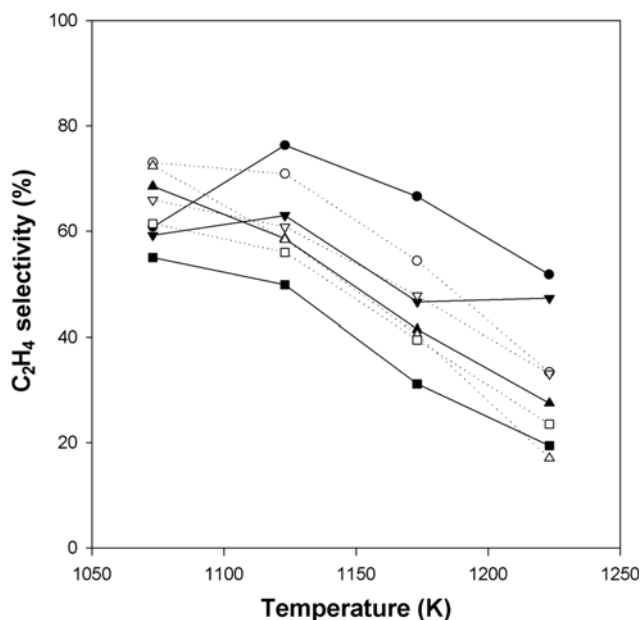


Fig. 2.  $C_2H_4$  selectivity in non-catalytic reaction and in the presence of catalysts at different temperatures (VHSV=18,000  $cm^3 CH_4/h \cdot g_{CB}$ ;  $C_2H_6/CH_4$  feed ratio=5/95 (solid symbols): non-catalytic (●), N330(P) (▼), N330(F) (▲), HI-900L (■);  $C_2H_6/CH_4$  feed ratio=15/85 (open symbols): non-catalytic (○), N330(P) (▽), N330(F) (△), HI-900L (□)).

those with the  $C_2H_6/CH_4$  feed ratio of 15/85, the former were considerably higher than the latter at the temperatures 1,123-1,223 K. The higher decomposition rate of  $C_2H_4$  with the  $C_2H_6/CH_4$  feed ratio of 15/85 is again considered due to the higher partial pressure of  $C_2H_4$ . However, in the presence of the catalysts, the differences in the selectivity of  $C_2H_4$  with different  $C_2H_6/CH_4$  feed ratios were relatively small, which indicates that in the presence of the catalysts the effect of the partial pressure of  $C_2H_4$  on the selectivity of  $C_2H_4$  is small. Nevertheless, this in turn indicates that the rate of  $C_2H_4$  decomposition is almost proportional to the partial pressure of  $C_2H_4$  over a specified catalyst.

The results in Figs. 1 and 2 are summarized as follows: 1) in the first stage dehydrogenation of  $C_2H_6$  to  $C_2H_4$  and  $H_2$  proceeds dominantly by the non-catalytic reaction and the effect of the catalyst on dehydrogenation of  $C_2H_6$  is not significant; 2) the conversions of  $C_2H_6$  are nearly the same regardless of the  $C_2H_6/CH_4$  feed ratio and the presence of the catalysts especially at temperatures from 1,123 to 1,223 K; 3) however, subsequent decomposition of  $C_2H_4$  to  $H_2$  and solid carbon is considerably facilitated by the CB catalysts, which is in agreement with the previous study [18].

## 2. Net $CH_4$ Conversion and $H_2$ Yield

Fig. 3 presents the net  $CH_4$  conversions with the  $C_2H_6/CH_4$  feed ratio of 5/95. The net  $CH_4$  conversions in the presence of the catalysts were higher than those for the non-catalytic decomposition. Although a part of  $C_2H_6$  is converted to  $CH_4$  and the amount of  $CH_4$  produced from  $C_2H_6$  is larger in the presence of the catalysts than in the absence of the catalyst [18], the higher net  $CH_4$  conversions in the presence of the catalysts manifest the effectiveness of the CB catalysts for decomposition of  $CH_4$ . On the other hand, because of the production of some  $CH_4$  from  $C_2H_6$ , the net  $CH_4$  conversions in

the presence of the catalysts for the feed containing a small amount of  $C_2H_6$  are lower than the  $CH_4$  conversions obtained in decomposition of pure  $CH_4$ . For example, in the presence of N330(F), the net  $CH_4$

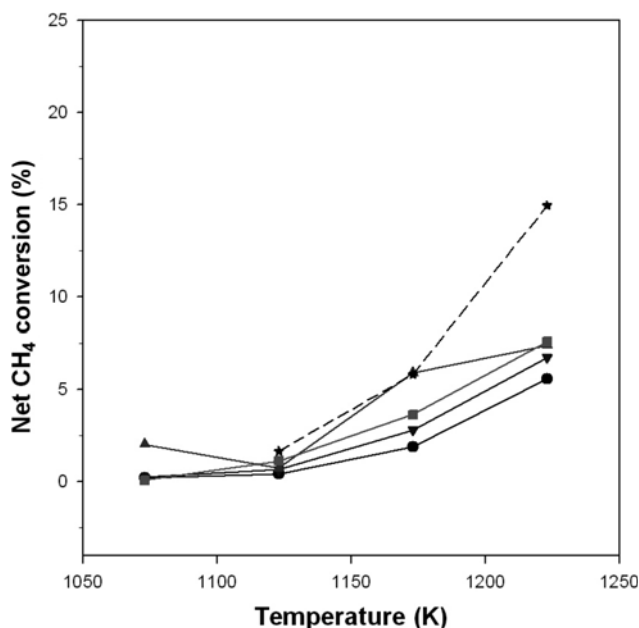


Fig. 3. Net  $CH_4$  conversion in non-catalytic reaction and in the presence of catalysts at different temperatures (VHSV=18,000  $cm^3 CH_4/h \cdot g_{CB}$ ;  $C_2H_6/CH_4$  feed ratio=5/95: non-catalytic (●), N330(P) (▼), N330(F) (▲), HI-900L (■);  $C_2H_6/CH_4$  feed ratio=0/100 over N330(F) (★), adopted from [21] and corrected for the given VHSV).

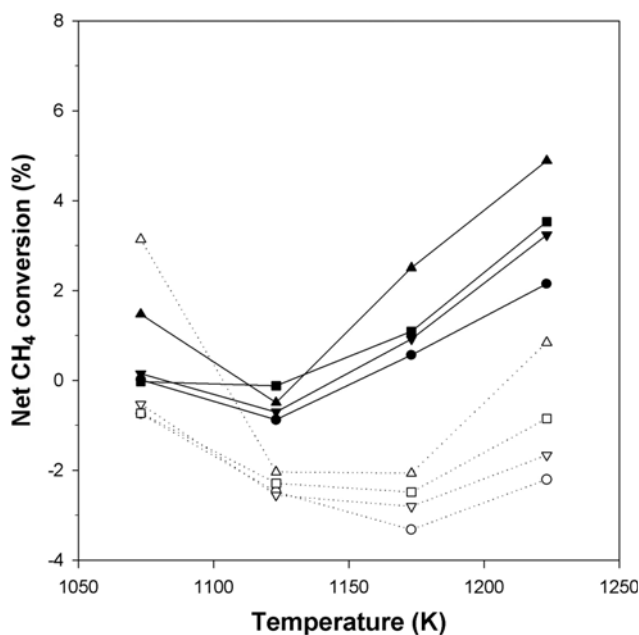


Fig. 4. Net  $CH_4$  conversion in non-catalytic reaction and in the presence of catalysts at different temperatures (VHSV=18,000  $cm^3 CH_4/h \cdot g_{CB}$ ;  $C_2H_6/CH_4$  feed ratio=10/90 (solid symbols): non-catalytic (●), N330(P) (▼), N330(F) (▲), HI-900L (■);  $C_2H_6/CH_4$  feed ratio=15/85 (open symbols): non-catalytic (○), N330(P) (▽), N330(F) (△), HI-900L (□)).

conversion at 1,223 K with the  $C_2H_6/CH_4$  feed ratio of 5/95 is 7%, while the corresponding  $CH_4$  conversions in decomposition of pure  $CH_4$  is 15% [10]; in the presence of HI-900L, the net  $CH_4$  conversion at 1,173 K with the  $C_2H_6/CH_4$  feed ratio of 5/95 is 3.5%, while the corresponding  $CH_4$  conversion in decomposition of pure  $CH_4$  is 6% [16]. For the purpose of comparison, the  $CH_4$  conversions obtained in decomposition of pure  $CH_4$  over N330(F), which are adopted from [21] and corrected for the same VHSV, are also presented in Fig. 3.

The net  $CH_4$  conversions with higher  $C_2H_6/CH_4$  feed ratios are presented in Fig. 4. As the  $C_2H_6/CH_4$  feed ratio increased, the net  $CH_4$  conversion decreased considerably, and moreover negative values of the net  $CH_4$  conversion were obtained. This is certainly due to the higher  $CH_4$  production with a higher amount of  $C_2H_6$  fed since the  $CH_4$  production from  $C_2H_6$  is (moles of  $C_2H_6$  fed)  $\times$  ( $C_2H_6$  conversion)  $\times$  ( $CH_4$  selectivity from  $C_2H_6$ ). With the feed ratio  $C_2H_6/CH_4$  of 10/90, the net  $CH_4$  conversions at 1,123 K were lower than those at 1,073 K even though the former temperature was higher. This is because the  $CH_4$  selectivity from  $C_2H_6$  and the  $C_2H_6$  conversion vary depending on the temperature and the catalyst. In decomposition of pure  $C_2H_6$ , the following results were reported [18]: 1) in the absence of the catalyst and in the presence of N330(P), the  $CH_4$  selectivity increased gradually with temperature from 1,073 to 1,173 K (from 4-5 to 10% of the  $CH_4$  selectivity), but 2) in the presence of N330(F) and HI-900L, the  $CH_4$  selectivity reached the highest value (~15%) at 1,073 K and then decreased slightly with temperature. Therefore, the lower net  $CH_4$  conversion at 1,123 K than that at 1,073 K is due to the higher  $CH_4$  production at 1,123 K be-

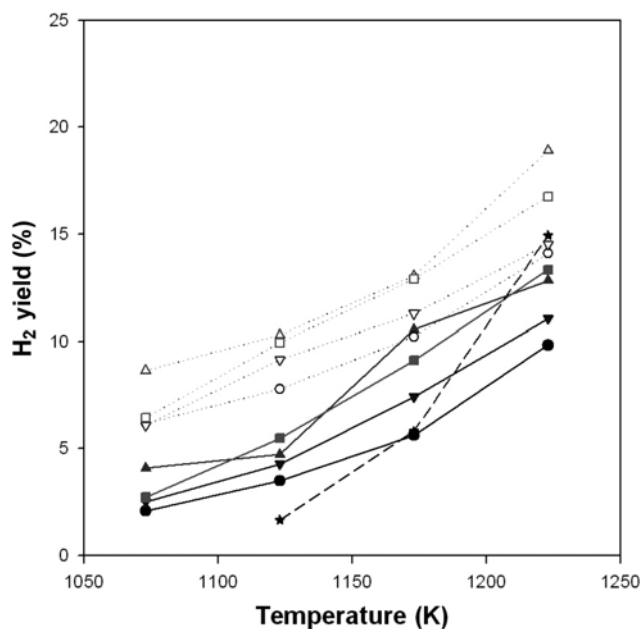


Fig. 5.  $H_2$  yield in non-catalytic reaction and in the presence of catalysts at different temperatures (VHSV=18,000  $cm^3 CH_4/h \cdot g_{CB}$ ;  $C_2H_6/CH_4$  feed ratio=5/95 (solid symbols): non-catalytic (●), N330(P) (▼), N330(F) (▲), HI-900L (■);  $C_2H_6/CH_4$  feed ratio=15/85 (open symbols): non-catalytic (○), N330(P) (▽), N330(F) (△), HI-900L (□);  $C_2H_6/CH_4$  feed ratio=0/100 over N330(F) (★), adopted from [21] and corrected for the given VHSV).

cause the  $C_2H_6$  conversion at 1,123 K (92-96%) is considerably higher than that at 1,073 K (70-82%), while the  $CH_4$  selectivity at 1,123 K is almost equal to or higher than that at 1,073 K. As a consequence, if it is assumed that the  $CH_4$  selectivity from  $C_2H_6$  remains the same whether the feed is pure  $C_2H_6$  or not (but actually it is expected that the  $CH_4$  selectivity from  $C_2H_6$  will change if the  $C_2H_6$  partial pressure changes), a rough estimation predicts that the amount of  $CH_4$  produced from  $C_2H_6$  at 1,123 K is higher by 0.5-1 mole per 10 moles of  $C_2H_6$  fed than that produced at 1,073 K, which could result in a decrease of the net  $CH_4$  conversion by approximately 0.5-1%, although a slightly more  $CH_4$  is decomposed at a higher temperature. The lower net  $CH_4$  conversion at 1,173 K with the feed ratio  $C_2H_6/CH_4$  of 15/85 than that at 1,123 K can be explained in the same manner, especially by the higher  $C_2H_6$  fed. The increase of the net  $CH_4$  conversion with temperature from 1,073 or 1,123 K to 1,223 K is due to the higher extent of  $CH_4$  decomposition with increasing temperature.

The  $H_2$  yields are shown in Fig. 5. Again the data with the feed ratio  $C_2H_6/CH_4$  of 10/90 are not shown here for brevity because they were between those with the  $C_2H_6/CH_4$  feed ratios of 5/95 and 15/85. As the feed ratio  $C_2H_6/CH_4$  increased, the  $H_2$  yield increased although the net  $CH_4$  conversion decreased. This is because most of the  $H_2$  is produced from  $C_2H_6$  owing to high  $C_2H_6$  conversion and low  $C_2H_4$  selectivity, while the net  $CH_4$  conversion is quite low or even negative. For example, if the relative contributions of  $C_2H_6$  and  $CH_4$  to the  $H_2$  yield at the highest temperature of 1,223 K in this study were estimated from the material balances of hydrogen and carbon by using the  $C_2H_6$  conversion, net  $CH_4$  conversion and  $C_2H_4$  selectivity, the relative contributions of  $C_2H_6$  were roughly 50% with the  $C_2H_6/CH_4$  feed ratios of 5/95, 80% with the  $C_2H_6/CH_4$  feed ratios of 10/90, and near 100% with the  $C_2H_6/CH_4$  feed ratios of 15/85; at lower temperatures they were even higher [20]. The estimated relative contributions to the  $H_2$  yields are listed in Tables 1-3. Due to the negative net  $CH_4$  conversions or more production of  $CH_4$  from  $C_2H_6$  in several cases, negative contributions by  $CH_4$  decomposition were estimated.

For the purpose of comparison, the  $H_2$  yields obtained in decomposition of pure  $CH_4$  over N330(F), which are adopted from [21] and corrected for the same VHSV, are also presented in Fig. 5. At and below 1,173 K, these yields were lower than those with the  $C_2H_6/CH_4$  feed ratios of 5/95. As mentioned before, this was mainly due to the easy decomposition of  $C_2H_6$ . However, at 1,223 K the  $H_2$  yield

**Table 1. Relative contributions to  $H_2$  production by  $CH_4$  and  $C_2H_6$  decomposition ( $C_2H_6/CH_4$  feed ratio=5/95)**

Catalyst	Source	Relative contribution, %			
		1,073 K	1,123 K	1,173 K	1,223 K
Non-catalytic	$CH_4$	9	11	31	52
	$C_2H_6$	91	89	69	48
N330(P)	$CH_4$	9	14	35	56
	$C_2H_6$	91	86	65	44
N330(F)	$CH_4$	46	14	52	53
	$C_2H_6$	54	86	48	47
HI-900L	$CH_4$	3	19	37	53
	$C_2H_6$	97	81	63	47

**Table 2. Relative contributions to  $H_2$  production by  $CH_4$  and  $C_2H_6$  decomposition ( $C_2H_6/CH_4$  feed ratio=10/90)**

Catalyst	Source	Relative contribution, %			
		1,073 K	1,123 K	1,173 K	1,223 K
Non-catalytic	$CH_4$	0	-13	5	15
	$C_2H_6$	100	113	95	85
N330(P)	$CH_4$	3	-9	8	20
	$C_2H_6$	97	109	92	80
N330(F)	$CH_4$	20	-6	18	26
	$C_2H_6$	80	106	82	74
HI-900L	$CH_4$	-1	-1	18	26
	$C_2H_6$	101	101	82	74

**Table 3. Relative contributions to  $H_2$  production by  $CH_4$  and  $C_2H_6$  decomposition ( $C_2H_6/CH_4$  feed ratio=15/85)**

Catalyst	Source	Relative contribution, %			
		1,073 K	1,123 K	1,173 K	1,223 K
Non-catalytic	$CH_4$	-9	-25	-26	-12
	$C_2H_6$	109	125	126	112
N330(P)	$CH_4$	-7	-22	-20	-9
	$C_2H_6$	107	122	120	109
N330(F)	$CH_4$	29	-16	-13	4
	$C_2H_6$	71	116	113	96
HI-900L	$CH_4$	-9	-18	-15	-4
	$C_2H_6$	109	118	115	104

in decomposition of pure  $CH_4$  was quite high, higher than that with the  $C_2H_6/CH_4$  feed ratios of 5/95 but lower than that with the  $C_2H_6/CH_4$  feed ratios of 15/85. The high  $H_2$  yield in decomposition of pure  $CH_4$  at 1,223 K can be explained as follows.  $CH_4$  is more difficult to decompose than  $C_2H_6$ , which means that the activation energy of  $CH_4$  decomposition is much higher. As the temperature increases, the  $CH_4$  decomposition rate increases more rapidly and hence the  $CH_4$  conversion can be that high at 1,223 K. Another aspect to consider is that the amount of  $C_2H_6$  is limited and almost all the  $C_2H_6$  is decomposed above 1,123 K as shown in Fig. 1. Thus, the contribution of  $CH_4$  to the  $H_2$  yield becomes greater with further increase of the temperature as seen in Tables 1-3.

N330(F) was observed to be more effective for  $CH_4$  decomposition than HI-900L on the whole (Figs. 3 and 4) while the latter is more effective for  $C_2H_4$  decomposition (Fig. 2). Therefore, the  $H_2$  yields obtained over N330(F) and HI-900L were similar to each other, but these were higher than those over N330(P) and even higher than those for the non-catalytic decomposition.

### 3. Effect of Added $C_2H_6$ on the $H_2$ Production Rate from $CH_4$

Muradov et al. [11] reported in decomposition of  $CH_4$  over carbon catalysts that after a pulse of  $C_2H_4$  was injected into the reactor a sharp increase in  $CH_4$  decomposition rate was observed, followed by its gradual decrease over a period of half an hour. This increase was attributed to highly active small carbon crystallites deposited from  $C_2H_4$ . From this observation, an increase in the  $CH_4$  decomposition rate may be expected if  $C_2H_4$  is present. However, contrary to the expectation, when the  $H_2$  production rate from  $CH_4$  in

this study was compared with that in decomposition of pure  $\text{CH}_4$ , the former was estimated to be considerably lower than the latter. For example, at 1,223 K in the presence of N330(F), the overall  $\text{H}_2$  production rate with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio of 5/95 was 3.8 mmole/ $\text{min} \cdot \text{g}_{\text{CB}}$ , but approximately a half of this was contributed from  $\text{CH}_4$  as mentioned before, and thus the  $\text{H}_2$  production rate only from  $\text{CH}_4$  was estimated to be 1.9 mmole/ $\text{min} \cdot \text{g}_{\text{CB}}$ , while the  $\text{H}_2$  production rate in decomposition of pure  $\text{CH}_4$  was reported to be 4.0 mmole/ $\text{min} \cdot \text{g}_{\text{CB}}$  [10].

The lower  $\text{H}_2$  production rate from  $\text{CH}_4$  with added  $\text{C}_2\text{H}_6$  can be explained as follows. One reason is the difference in the experimental method between this study and the previous study [11]: in this study  $\text{C}_2\text{H}_6$  was continuously introduced into the reactor and  $\text{C}_2\text{H}_4$  was accordingly continuously produced, while in the previous study  $\text{C}_2\text{H}_4$  was injected in a pulse only for a short time. Initially, very small carbon crystallites may be formed from  $\text{C}_2\text{H}_4$ , but in this study due to the continuous deposition of carbon from continuously and rapidly decomposing  $\text{C}_2\text{H}_4$ , the carbon crystallites will rapidly grow and hence the high activity of the deposited carbon for the  $\text{CH}_4$  decomposition will be obscured in a short period. Another reason is the competition for the active sites between  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ . Decomposition of both  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  requires active sites on carbon, but adsorption of  $\text{C}_2\text{H}_4$  is much easier than  $\text{CH}_4$ . Therefore, adsorption of  $\text{CH}_4$  is inhibited by more reactive  $\text{C}_2\text{H}_4$  which occupies a greater part of the active sites and results in a lower rate of  $\text{CH}_4$  decomposition. This argument can also explain the lower contribution of  $\text{CH}_4$  to the overall  $\text{H}_2$  yield with the higher  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio [20]. Nonetheless, it is again notable that the added  $\text{C}_2\text{H}_6$  increases the overall  $\text{H}_2$  production rate.

## CONCLUSIONS

$\text{C}_2\text{H}_6$  contained in low concentrations in  $\text{CH}_4$  was first converted to  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  predominantly by non-catalytic reaction. The conversions of  $\text{C}_2\text{H}_6$  were very high at 1,073–1,223 K (around 70% to 99%) and were nearly the same regardless of the presence of the CB catalysts and the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio.  $\text{C}_2\text{H}_4$  was subsequently decomposed to solid carbon and  $\text{H}_2$ , and this decomposition was much more effectively facilitated by the CB catalysts than by the non-catalytic decomposition. Because some  $\text{CH}_4$  was produced from  $\text{C}_2\text{H}_6$ , the net  $\text{CH}_4$  conversions decreased as the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio increased, and moreover, the net  $\text{CH}_4$  conversion became negative depending on the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio and temperature. With the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratios of 10/90 and 15/85, the net  $\text{CH}_4$  conversions at intermediate temperatures of 1,123 and/or 1,173 K were lower than those at 1,073 K due to the higher  $\text{CH}_4$  production from  $\text{C}_2\text{H}_6$ . Nevertheless, the net  $\text{CH}_4$  conversions in the presence of the CB catalysts were higher than those in the non-catalytic reaction. The rate of  $\text{H}_2$  production from  $\text{CH}_4$  was decreased by the added  $\text{C}_2\text{H}_6$ . A reason for this is the competition for the active sites on CB between  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ , that is, adsorption of  $\text{CH}_4$  on the active sites is inhibited by more reactive  $\text{C}_2\text{H}_4$ , resulting in a lower rate of  $\text{CH}_4$  decomposition. However, in spite of a decrease of the net  $\text{CH}_4$  conversion, the  $\text{H}_2$  yield increased with an increase of the  $\text{C}_2\text{H}_6/\text{CH}_4$

feed ratio. This is because the contribution of  $\text{C}_2\text{H}_6$  dehydrogenation and subsequent  $\text{C}_2\text{H}_4$  decomposition to the  $\text{H}_2$  production is dominant over  $\text{CH}_4$  decomposition. The highest  $\text{H}_2$  yield was obtained in the presence of N330(F) and HI-900L with the  $\text{C}_2\text{H}_6/\text{CH}_4$  feed ratio of 15/85.

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