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HYDROGEN PRODUCTION BY DECOMPOSITION OF LIGHT PARAFFINS OVER Ni/Ca/CARBON CATALYSTS IN THE ABSENCE OR PRESENCE OF IMPURITIES

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Abstract

The decomposition of light paraffins was investigated using a Ni/Ca/carbon-based catalyst and an Ag-Pd membrane-type reactor (PMR). The use of this combined system resulted in the formation of smaller amounts of methane (<10% yield) than in fixed-bed reactor systems (10-50% yield). The initial activity of CH_4 decomposition seems to be little affected by these impurities such as NO, SO_2, CO_2, and H_2O. The activity in the presence of SO_2, however, was found to be completely lost after 250 min.

Keywords: Ethane, decomposition, hydrogen, Ag-Pd membrane reactor

INTRODUCTION

Hydrogen is expected to be used as the energy source for fuel cells such as the proton-exchange membrane (PEM) types. At present, hydrogen is typically produced through steam reforming and/or partial oxidation of hydrocarbon fuel [1]. Alcohols are used as precursors to hydrogen [2]. In these cases, however, carbon monoxide is a co-product. Therefore, the current PEM fuel cells require essential elimination of carbon monoxide (<1 ppm) from hydrogen stream in order to prevent poisoning of Pt catalyst of the cells. An alternative route is to directly decompose light paraffins into hydrogen and carbon. In this case, no

CO_2 is formed in the first reaction step and the need for reactions such as water-gas shift and CO oxidation is eliminated. In the present work, the decomposition of these paraffins over the Ni/Ca/carbon catalysts was examined in the absence and presence of impurities such as NO, SO_2, CO_2, and H_2O and the catalytic nature of these systems was investigated.

EXPERIMENTAL

Commercially available carbon materials, such as activated carbon (Aldrich), graphite (Alfa) were dried at 493 K *in vacuo* for 3 h, prior to use. Carbon catalysts with Ni/Ca were prepared by co-precipitation of Ni and Ca nitrates with K_2CO_3, in the presence of activated carbon, followed by drying at 373 K. Catalyst thus prepared (1 g) was diluted with quartz sand (5 g) and placed in a quartz tube [12 mm (id), the fixed-bed reactor (FBR)]. The carbon catalysts were pretreated in N_2 at 873 K for 3 h, while the Ni/Ca/carbon catalysts were pretreated in air at 573 K for 4 h, followed by reduction in H_2 at 673 K for 3 h. After cooling the tube to room temperature, the premixed gases of N_2-light paraffins (2 vol.%, 20 mL min^{-1}) were introduced at atmospheric pressure and the temperature was raised again to the prescribed temperature (6°C/min). The gaseous impurities were NO, SO_2, CO_2 and H_2O. For comparison, the Ag-Pd membrane reactor (PMR) was also used. The experimental details have been mentioned elsewhere [3]. The organic and hydrogen products were analyzed by gas-chromatography (GC) on Porapack Q and MS 5A columns, after 30 min on-stream at each temperature, and the yield of carbon was estimated by the mass balance of carbon.

RESULTS AND DISCUSSION

Decomposition of ethane over carbon and Ni/Ca/C Catalysts

Pyrolysis of C_2H_6 (2) occurred at 850-1050 K in the presence of activated carbon (AC), catalyst and hydrogen, and a small amount of organic material (methane, ethylene,

$$CH_4 \rightarrow 2H_2 + C \tag{1}$$
$$C_2H_6 \rightarrow 3H_2 + 2C \tag{2}$$
$$2H_2 + C \rightarrow CH_4 \tag{3}$$

benzene) were formed. The C_2H_6 conversion was as low as 47% at 948 K in case of the fixed bed reactor (FBR) (Fig. 1a,■). In contrast, the C_2H_6 conversion was found to be over 90%, after removal of hydrogen through a
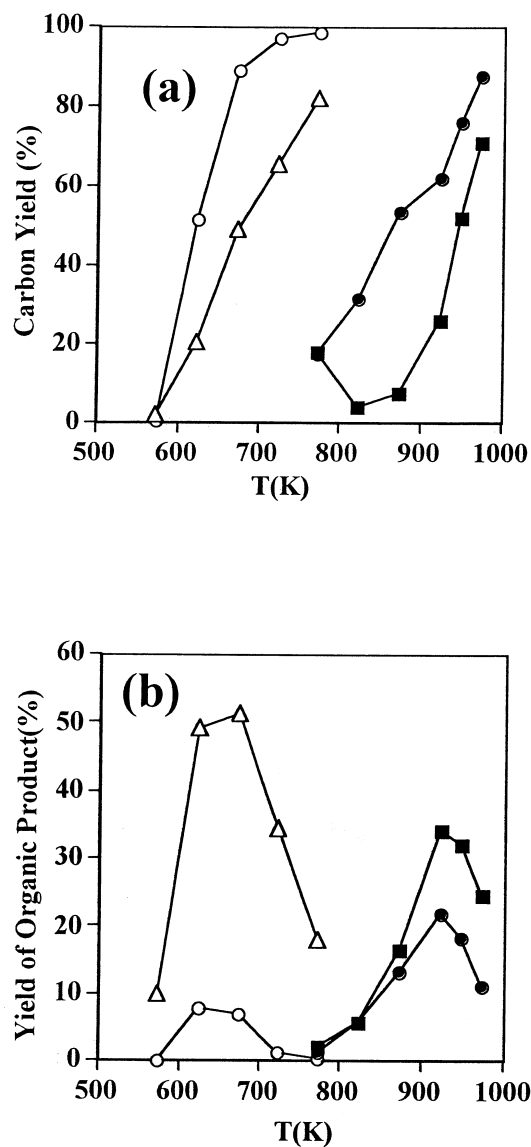
Fig. 1. Temperature dependence of ethane decomposition and product yields.
W/F=20.5 g-cat h mol^{-1}, feed gas: C$_2$H$_6$/N$_2$=1/9,
Catalyst: 10 wt.%Ni/10wt.%Ca/AC Darco KB-B (Ni/Ca/C)
(a): Carbon yield (%), (b): Yield of organic products (%)
■ AC KB-B//FBR   ● AC KB-B//PMR   △ Ni/Ca/C//FBR
O Ni/Ca/C//PMR

Ag-Pd membrane tube (PMR)(Fig. 1a,●). In the PMR system, the carbon yield was dependent on the carbon catalysts employed. The yield was in the order: graphite>AC Darco G-60>AC Darco KB-B > C60 soots > quartz sand. On the graphite catalyst, in particular, organic by-products were formed only in *ca*.4% yield. On the activated carbons, the yield of organic products was *ca*.15%, although their carbon yields were close to that in graphite. The use of fixed-bed reactor (FBR)/AC system resulted in the formation of a larger amount of organic products (>35% yield) than in PMR/AC. Thus, the graphite/PMR system could be a candidate of carbon-based catalysts suitable for pyrolysis of C_2H_6.

When the activated carbon-supported Ni/Ca (Ni/Ca/C) catalyst was used, the decomposition of ethane occurred at 550-750 K, being lower temperature than the case of AC catalyst (Fig. 1a,○,Δ). Hydrogen, carbon and methane were formed and the yields of other organic by-products were negligible. On these catalysts, the carbon yield for AC/PMR system (Fig. 1a,○) was found to be higher than that in the AC/FBR system (Fig. 1a, Δ), while the yield of organic products (*), mainly methane in the PMR was <10%, being much less than that in the FBR [10-50% methane yield, Fig. 1b(○,Δ)]. A similar tendency was observed for the activated carbon catalyst [Fig. 1b(●,■)]. This indicated that, in the PMR system, the decomposition of ethane to form hydrogen and carbon (eq.1) occurred predominantly over ethane cracking to give methane, carbon and hydrogen (eq.4(**)). Also, permeation of hydrogen, where over 90% of the hydrogen formed was eliminated from the reactant gas into argon, possibly appears to prevent a recombination reaction of hydrogen with carbon products (eq.3), which was confirmed by measuring the temperature-programmed reduction (TPR) profile (***) on the used Ni/Ca/C catalyst [3]. Thus, in case of ethane reactant, the

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(*) The yield of organic products was estimated on the basis of the number of carbon atoms in compounds: Ethane conversion (%): $10^2(\Sigma\alpha_iP_i)/2N_0$. Selectivity(%) for a product i: $10^2(\alpha_iP_i)/\Sigma\alpha_iP_i$. Total selectivity to organic products: Σ (Selectivity for product i). The yield of organic products(%) is 10^{-2}(conversion x total selectivity). The values N_0, P_i and α stand for the amount of ethane at the reactor inlet, the partial pressure and the number of carbon atoms in product i, respectively.

(**) From the thermodynamic point of view, the ethane conversions of eq. 1 are 54.3% at 298.2 K, 99.9% at 400 K and the conversion of eq.2 is 99.9% at 298.2 K.

(***) The temperature-programmed reduction (TPR) measurement was carried out using a Ni/Ca/C catalyst at 400-700 K. The rate of hydrogenation of carbon product to methane, the rate of which reached a maximum at *ca*.620 K and then decreased, was much faster than that of the activated carbon support (AC Darco KB-B). These findings indicated that the recombination (eq. 3) could occur under the reaction conditions employed.

$$C_2H_6 \quad \rightarrow CH_4 + C + H_2 \tag{4}$$

combined use of Ni/Ca/carbon catalyst and the PMR system was very effective for hydrogen production by ethane decomposition at 550-750 K.

Decomposition of methane over Ni/Ca/carbon catalysts in the presence of impurities

Naturally occurring natural-gas contains some impurities such as NO, SO_2, CO_2, and H_2O. CH_4-containing gas mixtures obtained from combustion of waste plastics also include impurities. So, the effects of some impurities on the
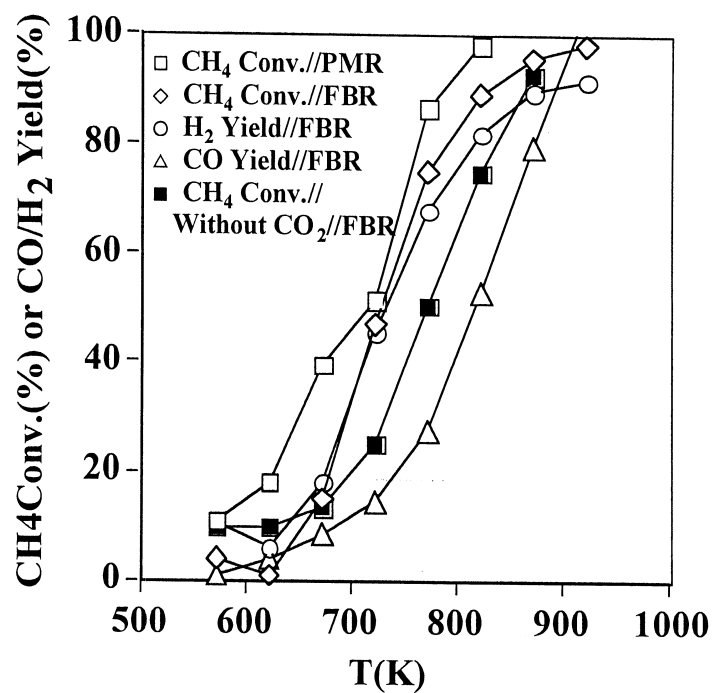

Fig. 2. Temperature dependence of CH_4 decomposition in the presence of CO_2.
W/F=20.5 g-cat h mol^{-1}, feed gas: $CH_4/CO_2/N_2$=2/1.3/96.7
Catalyst: Ni/Ca/C (same as Fig. 1)

pyrolysis of CH_4 would be important from an industrial point of view. In the absence of impurities, pyrolysis of CH_4 (1) occurred at 1100-1400 K over a carbon-based catalyst. Over the Ni/Ca/carbon catalyst, the conversion of CH_4 was > 80% even at temperatures as low as 873 K [Fig. 2,(∎)] [4].

Effect of CO_2

In the presence of CO_2, the catalytic activity of CH_4 pyrolysis, where the CH_4/CO_2 ratio was 1.5, was found to be higher than that in the absence of CO_2 [compare Fig. 2,(∎) with (◊)]. This indicates that CO_2 reforming with CH_4 could occur even under the conditions of low temperature of 873 K(*). In fact, both H_2 and CO were formed (Fig. 2, O and Δ) The reaction was accelerated by H_2 permeation when using a PMR reactor (□). Thus, the pyrolysis reaction is found not to be inhibited by CO_2.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad\qquad (5)$$

Effect of NO

As is shown in Fig. 3, the pyrolysis of CH_4 in the presence of NO (0.07%) occurs in a similar manner as in the absence of NO (compare □ and ◊) and hydrogen yields are also almost the same (Fig. 3, inset). The reaction was slightly accelerated by NO/H_2O (Δ). However, the pyrolysis was found to be dramatically inhibited by removal of H_2 by the PMR reactor: This could be due to an irreversible 'partial' oxidation over Ni/Ca/C catalyst surface by NO. In fact, the results of time dependence of catalytic activity are consistent with this postulate (Fig. 4). Without NO, the CH_4 conversion over Ni/Ca/C catalyst at 773 K was constant at *ca*. 36.3% for 300 min (Fig. 4,□), while the conversions in the presence of NO decreased as the reaction proceeded [25.2% to 18.1% (Ni/Ca/C, Fig. 4◊), 30.6% to 24.5% (Ni/SiO₂, ∎]. In the presence of H_2O/ NO, the activity seems to be constant (Fig. 4 O,Δ). In this point, further study is required for the effects of NO on the nature of surface Ni. For comparison, SiO_2-based catalysts instead of carbon support were tested for the reaction. The Ni/SiO₂ catalyst (∎) was active, but Fe/SiO₂ (●) and Co/SiO₂ (◆) were not so effective.

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(*) Generally, CO_2 reforming with CH_4 over Ni-based catalysts could occur at temperatures of *ca*.1000 K (eq.5) [5].
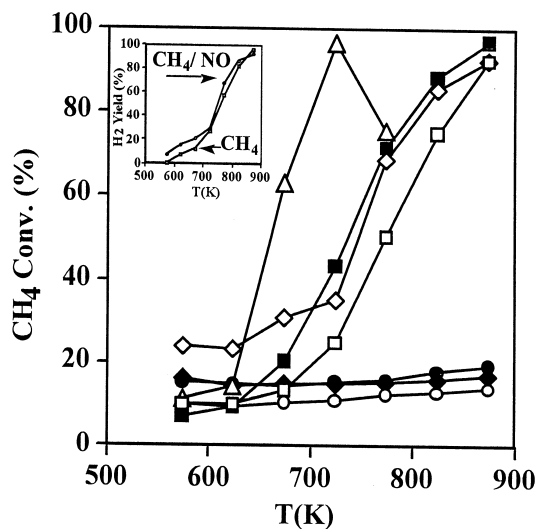
Fig. 3. Effect of NO on CH_4 decomposition. W/F=20.5 g-cat h mol^{-1}, feed gas:
$CH_4/NO/N_2$=2/0.07/97.93, H_2O (9%), Catalyst: Ni/Ca/C (same as Fig.1).
Without NO, ◊ NO, O NO/PMR, NO/H_2O, ■ Ni/Si/NO, ◆ Co/Si/NO,
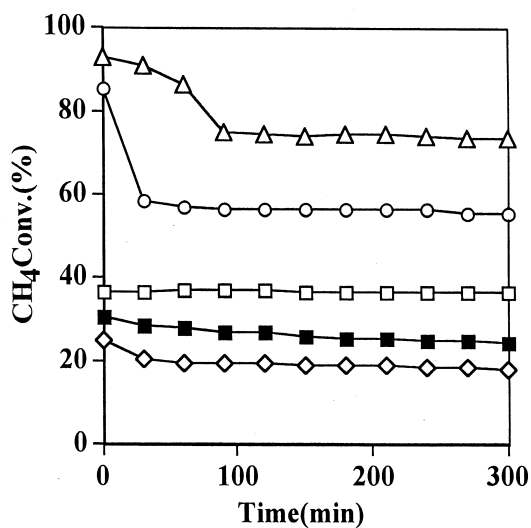● Fe/Si/NO. Inset: H_2 yield in the CH_4 decomposition

Fig. 4. CH_4 decomposition as a function of time.
W/F=20.5 g-cat h mol^{-1}, feed gas: $CH_4/NO/N_2$=2/0.07/97.93, H_2O (9%),
Ni/Ca/C//without NO, ◊ Ni/Ca/C//NO, O Ni/Ca/C//NO/H_2O,
Δ Ni/Ca/C//NO(2%)/H_2O, ■ Ni/Si/NO

Effect of NO/SO$_2$

When the reaction was carried out in the presence of both NO (0.07%) and SO$_2$ (0.07%), the activity was slightly higher than that without these impurities (Fig. 5, inset). But the time dependence of the activity was found to be completely different from NO alone. After *ca.*200 min, the activity sharply fell to below 5%, despite the absence or presence of H$_2$O (Fig. 5, without H$_2$O □, with H$_2$O ▲). This is probably due to a formation of sulfur-containing Ni species [6]. Futher work is in progress to prepare sulfur-tolerant Ni catalysts.
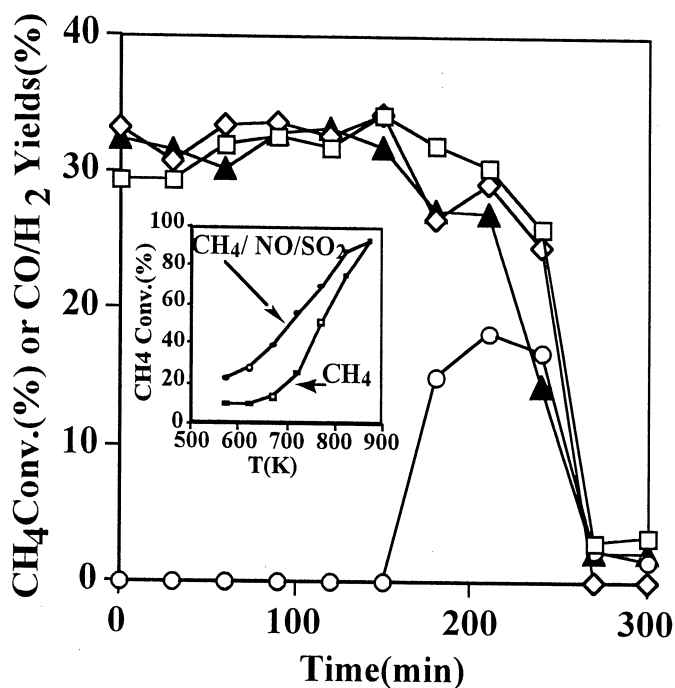

Fig. 5. Effect of NO/SO$_2$ on CH$_4$ decomposition. W/F=20.5 g-cat.h mol^{-1}, feed gas: CH$_4$/NO//SO$_2$/N$_2$=2/0.07/0.07/97.86, H$_2$O (9%), Catalyst: Ni/Ca/C.
□ CH$_4$ Conv. (%), ◊ H$_2$ yield (%), O COx yield (%), ▲ CH$_4$ conv.(%) in the presence of H$_2$O (9%). Inset: effect of NO/SO$_2$ as a function of temperature

Summary

Pyrolysis of C_2H_6 (2) occurred at 850-1050 K in the presence of carbon catalysts and at 550-750 K over Ni/Ca/C catalysts. Hydrogen and carbon were formed from organic compounds such as methane, ethylene, benzene. Over carbon catalysts, the graphite/PMR system could be one of the candidates suitable for pyrolysis of C_2H_6 to form hydrogen. With Ni/Ca/C catalyst, the PMR system is also more effective than the FBR system and the yield of organic products, mainly methane, in the PMR was <10%, being much less than that in the FBR (10-50% methane yield).

The effects of some impurities on the pyrolysis of CH_4 were examined. The temperature dependence on CH_4 conversion seems to be little affected by impurities such as NO, SO_2, CO_2, and H_2O, except for the PMR system. The time dependence of the activity was slightly increased by the presence of NO and/or NO/H_2O, while, in the presence of SO_2, the Ni/Ca/C catalyst was found to be completely deactivated after 250 min. Further work is currently underway to elucidate impurity effects.

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