[Note]

Hydrogen Production by Decomposition of Hydrocarbons over Ni/Ca/Carbon Catalysts Using Membrane-type Reactor

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In order to clarify the effectiveness of the Ni/Ca/carbon catalyst/Ag-Pd membrane-type reactor (PMR) system on decomposition of hydrocarbons such as ethane and gasoline, the decomposition of these hydrocarbons was investigated. The combined system was found to be more effective for hydrogen production at 550–750 K than the fixed-bed reactor (FBR) system. In fact, the use of PMR resulted in the formation of a smaller amount of methane (< 10% yield) as a major by-product than that in the FBR (10–50% yield). It could be postulated because, first, the direct decomposition of ethane to form hydrogen in the PMR system occurs predominantly by ethane cracking to give methane, carbon, and hydrogen and, second, the permeation of hydrogen prevents recombination of hydrogen with the carbon products to give methane. The Ni/Ca/C catalysts/PMR system was found also to be effective for the formation of hydrogen by decomposition of commercially available gasoline at temperature as low as 573 K.

1. Introduction

Hydrogen is expected to be used as an energy source for fuel cells such as proton-exchange membrane (PEM) type. At present, hydrogen is typically produced via steam reforming (SR) and/or partial oxidation of hydrocarbons or alcohols. In these cases, however, carbon monoxide is a co-product, which must be eliminated (< 1 ppm) in the current fuel cell to prevent poisoning of the Pt catalyst of the cells. An alternative route is to directly decompose the hydrocarbons into hydrogen and carbon. In this case, no CO_x is formed, and the need for such subsequent reactions as water-gas shift and CO oxidation, is eliminated^{1),*1)}. We have already reported that carbon-based catalysts are effective for methane decomposition to form hydrogen in the range of 800–1300 K²⁾. For the use as on-site fuel cells, further lowering of the decomposition temperature will be required. In the course of our research on the carbon-based catalysts, we have recently found that the metal-free graphite is effective for decomposition of ethane³⁾ and the reaction has also been found to be accelerated by elimination of the *in situ* hydrogen formed in the Ag-Pd alloy tube. However, even in these systems, the reaction temperature was still as high as 850–1050 K.

Ishihara *et al.*⁴⁾ has already reported that Ni/SiO₂/Palladium membrane (PMR) is an excellent system for decomposition of methane at 650–800 K. Also, we have recently reported that Ni/Ca/carbon catalysts are effective for methane reactions using fixed-bed reactor⁵⁾ in the same temperature range. Thus, the purpose of the present work is to clarify the effectiveness of the Ni/Ca/carbon catalyst/PMR system on decomposition of other hydrocarbons such as ethane and gasoline. In this study, we have reported that ethane conversion was over 90% at temperature as low as 673 K but the production of methane as a by-product was negligible.

2. Experimental

Commercially available activated carbon (Aldrich, AC Darco KB-B) as support was 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 K₂CO₃, in the presence of activated carbon, followed by drying at 373 K. For the fixed-bed reactor (FBR), a quartz reaction tube (12 mm, inner diameter) was used. The catalyst (1 g) was diluted with quartz sand (5 g) and placed in the tube. An electric furnace was used for heating. The Ni/Ca/carbon catalyst used was pretreated in air at 573 K for 4 h and subsequently reduced in H₂ at 673 K for 3 h. After cooling the tube to room temperature, the premixed gases of nitrogen and ethane (2–20 vol% C₂H₆, 20 mL min⁻¹) was introduced at atmospheric pressure (*W/F* = 20.5 g-cat.h.mol⁻¹) and the temperature was raised again to the prescribed temperature (6°C/min).

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*1) In this case, chemical or physical processes could be assumed as those for on-site removal of carbon products. These processes would consist of a combustion of carbon by some oxidants such as H₂O, CO₂ and a separation by centrifuge. However, further research will be required on carbon separation.

For the Ag-Pd membrane reactor (PMR), a double-tubular type arrangement was used: the inner and outer tubes were Pd-Ag alloy (90Pd10Ag) (250 μm thick and 9.5 mm in inner diameter) and quartz (1.5 mm thick and 19.5 mm inner diameter), respectively. The catalyst was placed between the inner and outer tubes. The catalyst pretreatment was the same as that described above. The premixed gases were passed into the catalyst bed at atmospheric pressure ($W/F = 20.5 \text{ g-cat.h.mol}^{-1}$), and Ar gas (1500 mL.min^{-1}) was fed through the inside of Ag-Pd alloy tube at atmospheric pressure to remove the permeated hydrogen. The organic and hydrogen products were analyzed by gaschromatography (GC) on Porapak Q and 5 Å molecular sieve columns after 30 min on-stream at each temperature, and the yield of carbon was estimated by mass balance of carbon (Eq. (1)). Decomposition of commercially available gasoline was carried out by bubbling nitrogen through the gasoline reservoir into the catalyst bed.

Temperature-programmed reduction was carried out in a flow of 28 mL.min^{-1} of 10% hydrogen in argon. Methane analysis was performed by GC, as mentioned above, and a sample was taken for analysis every 14 min.

3. Results and Discussion

3.1. Decomposition of C_2H_6 over Carbon-supported Ni/Ca Catalysts

3.1.1. Effect of Reaction Temperature on Ethane Conversion and Product Yields

As shown in Fig. 1 (a), the decomposition of C_2H_6 over the activated carbon-supported Ni/Ca catalyst (1) occurred at 550-750 K ($\circ$, $\triangle$), but the formation of hydrogen, carbon, and methane over the carbon catalyst above ($\bullet$, $\blacksquare$) occurred at 800-1000 K. In all these runs, the carbon yield estimated from the mass balance was in good accord with that calculated by weighing after the reaction. With the Ni/Ca/carbon catalyst, ethane conversion in the PMR (Fig. 1 (a) ($\circ$)) was close to that in the FBR system (Fig. 1 (a) ($\triangle$)). With the carbon catalyst, however, the conversion in PMR (Fig. 1 (a) ($\bullet$)) was higher than that in FBR ($\blacksquare$).

Effects of temperature on product yields are exhibited in Fig. 1 (b), (c). Methane was a by-product and the yields of other organic by-products were negligible. The carbon yield in PMR (Fig. 1 (b) ($\circ$)) was found to be higher than that in FBR (Fig. 1 (b) ($\triangle$)), while the yield of organic products, mainly methane, in PMR was < 10% (Fig. 1 (c) ($\circ$)), being much less than that in FBR (10-50% methane yield, Fig. 1 (c) ($\triangle$)). A

$W/F = 20.5 \text{ g-cat.h.mol}^{-1}$ ($F = 20 \text{ mL.min}^{-1}$, Cat. 1.0 g), feed gas: $\text{C}_2\text{H}_6/\text{N}_2 = 1/9$.
Ni/Ca/AC = 10 wt% Ni/10 wt% Ca/AC Darco KB-B.

Fig. 1 Temperature Dependence on Ethane Decomposition and Product Yields

similar tendency was observed for the activated carbon catalyst (**Fig. 1 (b), (c)** (●, ■)). This indicated that, in the PMR system, the decomposition of ethane to form hydrogen and carbon (Eq. (1)) occurred predominantly by ethane cracking to give methane (Eq. (2)^{*2}), carbon and hydrogen (Eq. (2)). Also, permeation of hydrogen, where over 90% of hydrogen formed had been eliminated from the reactant gas by argon, would possibly prevent the recombination reaction of hydrogen with carbon products (Eq. (3)).

Catalyst: 30 wt%Ni/30 wt%Ca/AC Darco KB-B, 1 g.
Feed gas: H₂/Ar = 1/9 (vol%), 28 ml.min⁻¹.

Fig. 2 Temperature-programmed Reduction of Fresh and Used Catalysts

In order to shed light on the recombination of carbon product with hydrogen, temperature-programmed reduction (TPR) measurements were carried out by using the Ni/Ca/carbon catalyst at 400-700 K. As shown in **Fig. 2**, the rate of hydrogenation of carbon product into methane, the rate of which reached a maximum at *ca.* 620 K and then decreased, was much faster than that of activated carbon (AC Darco KB-B). These findings indicated that recombination (Eq. (3)) could occur under the reaction conditions employed.

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

3.1.2. Effect of PMR Conditions

In order to examine the characteristics of Ni/Ca/carbon catalyst/PMR systems, the effect of reaction parameters on ethane decomposition was examined. Influences of flow modes of sweep argon and reactant gas on the activity are shown in **Fig. 3 ((a), (b))**. Under the conditions used in this study (Ar/feed = 75), the activity in the countercurrent flow mode was found slightly higher than that in the concurrent flow mode, as in the dehydrogenation of cyclohexane to form benzene and hydrogen⁶). However, the formation of methane as a by-product in the concurrent flow mode appeared to be less than that in the countercurrent flow mode. Since recombination of carbon and hydrogen would occur under the conditions indicated in footnote^{*2}), it may possibly be closely associated with the rate of hydrogen permeation from the reactant gas by argon. In fact, when the flow rate of Ar was decreased (Ar/feed = 40), the yield of methane was increased even in the concurrent flow mode (**Fig. 3 (c)**). On this point, however, further investigation will

W/F = 20.5 g-cat.h.mol⁻¹, Feed gas: C₂H₆/N₂ = 2/98 (vol%). Catalyst: 30 wt%Ni/30 wt% Ca/AC Darco KB-B. (a) Concurrent flow, Ar/feed = 75 (*F*_{Ar} = 1500 ml.min⁻¹), (b) Countercurrent flow, Ar/feed = 75, (c) Concurrent flow, Ar/feed = 40.

Fig. 3 Effects of PMR Conditions on the Carbon Yield

^{*2}) From the thermodynamical point of view, the ethane conversion of Eq. (1) is 54.3% at 298.2 K and 99.9% at 400 K, respectively, and the conversion in Eq. (2) is 99.9% at 298.2 K.

W/F = 20.5 g-cat.h.mol⁻¹, Feed gas: C₂H₆/N₂ = 2/98 (vol%), Temp.: 673 K.
Catalyst: 30 wt%Ni/30 wt%Ca/AC Darco KB-B.

Fig. 4 Change in the Catalytic Activity as a Function of Time

W/F = 20.5 g-cat.h.mol⁻¹, Carrier gas: N₂, Total hydrocarbons/N₂ = 1/9 (vol%). Catalyst: 30 wt%Ni/30 wt%Ca/AC Darco KB-B.

Fig. 5 Temperature Dependence on the Decomposition of Commercially Available Gasoline

be required. Lower ethane concentrations (2-20%), and higher ethane conversions in the temperature range from 550 to 750 K are in agreement with thermodynamic predictions.

3.1.3. Catalytic Activity as a Function of Time

In the Ni/Ca/carbon catalyst/PMR system, ethane conversion at 673 K decreased as reaction proceeded (100% → 83% (6 h)) (Fig. 4 (a)) due to the decrease in the yield of methane (23 to 8%). The yield of carbon was, however, decreased moderately and the yield was still *ca.* 80% even after 6 h-reaction. When the reaction was carried out in the presence of H₂O (5 kPa), part of the carbons formed *in situ* was allowed to react with H₂O to give CO_x under the conditions employed (Fig. 4 (b)). As a result, the decrease in the catalytic activity with H₂O was much less than that without H₂O.

3.2. Decomposition of Commercially Available Gasoline

From the thermodynamic point of view, the decomposition of liquid hydrocarbons occurs at temperature lower than that of ethane. We conducted catalytic pyrolysis of commercially available gasoline consisting mainly of C₄, C₅, C₆, and BTX, using the Ni/Ca/carbon catalysts. Figure 5 shows the temperature dependence on the composition of pyrolyzed gas. In the FBR system, the successive reaction of carbon products and hydrogen formed by decomposition to form methane occurred as follows. The formation of C₂⁺ and/or methane predominated over hydrogen production, in which the highest composition was approximately 30% at 573-673 K (Fig. 5 (a)). On the other hand, in the PMR system, the hydrogenation of carbon formed was

prevented by hydrogen permeation. As a result, the molar fraction of the total amount of hydrogen consisting of permeated hydrogen and the hydrogen, which was estimated from the sum of organic products, was found to be as high as *ca.* 85% in the range 573-773 K, and methane composition was extremely low (**Fig. 5 (b)**).

Investigation of **Figs. 1, 3 and 4** demonstrated that the PMR system was effective for predominant formation of hydrogen over methane in the decomposition of hydrocarbons. The PMR process studied can be the basis for the development of compact catalytic units for on-site CO₂-free production of hydrogen from natural-gas and/or liquid hydrocarbon fuels.

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要 旨

メンブレンリアクターを用いた Ni/Ca/炭素触媒上での炭化水素の分解による水素製造

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エタンや液状炭化水素のようなメタン以外の炭化水素の分解に対する Ni/Ca/C 触媒/Ag-Pd メンブレンリアクター (PMR) 系の有効性を調べるために, これらの炭化水素の分解が行われた。これらの系は 550~750 K の温度で, 固定床 (FBR) の系より水素生成に対して有効であり, 実際 PMR 系では副生するメタンは 10% 以下であるのに対して, FBR 系では 10~50% のメタンが生成した。この理由として, PMR 系では, 第一に

エタンの水素と炭素への直接分解が, エタンの解裂によるメタン, 水素および炭素の生成反応よりも優先的に起こること, 第二には水素の系外への除去により, 一度生成した水素と炭素の再結合反応が抑制されることを推定した。本 Ni/Ca/C/PMR 系は, 573 K という低温でのガソリン中の揮発成分の分解による水素製造にも有効であることが併せて見いだされた。

Keywords

Natural gas, Gasoline, Hydrogen, Decomposition, Nickel carbon catalyst, Membrane reactor