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Catalytic dehydrogenative coupling of methane on active carbon

Effect of metal supported on active carbon

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Abstract

Ethane, ethene, ethyne and hydrogen are obtained in good yields via dehydrogenative coupling of methane in the presence of active carbon as a catalyst. The product yield is increased by supporting metal on active carbon.

Keywords: Carbon catalysts; Dehydrogenative coupling; Metal support

1. Introduction

Natural gas is considered as a clean energy resource and a cheap raw material for chemical industries. Methane (CH_4), main constituent of natural gas, is a very stable molecule and its effective conversion to the chemical feedstock is difficult. Oxidative coupling of CH_4 to C_2 hydrocarbons has been extensively investigated and CO_2 is formed as an unavoidable by-product [1–6]. In this regard, dehydrogenative coupling of CH_4 without oxygen is advantageous. High temperature pyrolysis of CH_4 was investigated in the past [7,8]. Recently, a practical C_2 hydrocarbon production by thermal coupling of CH_4 has been reported [9–12] and a thermal diffusion reactor system has been proposed [13].

We have already reported that dehydrogenative coupling of methane proceeded in the presence of active carbon as catalysts [14]. CH_4 is converted to ethane, ethene, ethyne and hydrogen as shown in the following equations (Eq. (1)–(3)).

$$2CH_4 \rightarrow C_2H_6 + H_2 \quad (1)$$

$$2CH_4 \rightarrow C_2H_4 + 2H_2 \quad (2)$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \quad (3)$$

In the present work, we studied the effects of operating parameters on dehydrogenative coupling of CH_4 on active carbon and also studied the effects of metals supported on active carbon.

2. Experimental

A conventional flow type reactor with a fixed catalyst bed was employed. Commercial active carbon (AC, Futamura Chemical Taiko-CG8, specific surface area; 1350 m^2/g) made from wood and metal oxides (SiO_2, ZrO_2; Wako Pure Chemical Industries Ltd., MgO; Nacalai

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Tesque, Inc., Al_2O_3; Catalysts and Chemicals Ind. Co., Ltd.) were used as catalysts without further treatment. Metal supported on AC was prepared by impregnation of AC with an aqueous solution of metal nitrate (Wako Pure Chemical industries, Ltd.). CH_4 diluted with H_2 was supplied to the catalysts in a tubular (id 11 mm) alumina reactor and the effluent gases were analyzed with gas chromatography.

3. Results and discussion

Fig. 1 shows the results of the dehydrogenative coupling of methane in the presence of active carbon (AC) and metal oxides as catalysts. Ethane (C_2H_6), ethene (C_2H_4) and ethyne (C_2H_2) were formed as products. AC gave the highest C_2 hydrocarbon yields and the activities of tested catalysts were in the following order: AC > Al_2O_3 > SiO_2 > ZnO > MgO.

The effects of operating parameters on the dehydrogenative coupling of CH_4 on AC were investigated. Fig. 2 shows the effect of contact time (W/F). To reduce the reactor wall effect and residence time, we employed a reactor with a thin diameter (id 4 mm) in this experiment. The product yields increased with an increase in W/F and active carbon is clearly active in the title reaction. We think that the first step of the reaction is extraction of hydrogen atom from CH_4 to form methyl radical, which is promoted by the surface radicals of AC. The reaction mechanisms are described in the later paragraph. In the absence of AC ($W/F = 0$), dehydrogenative coupling of CH_4 proceeded thermally at a small rate as reported in the literatures [11,12].

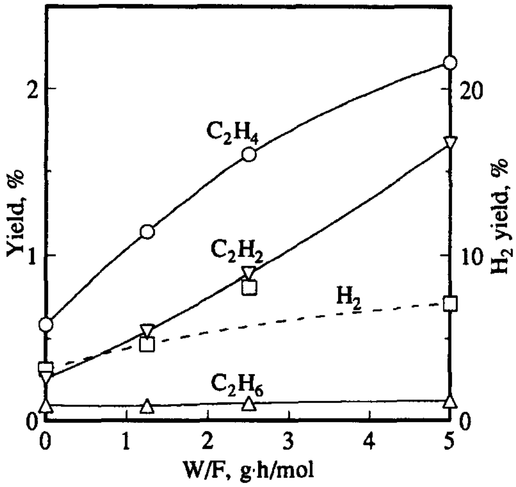

Fig. 2. Effect of contact time (W/F). Catalyst: AC, T: 1100°C, CH_4/H_2: 1:1.

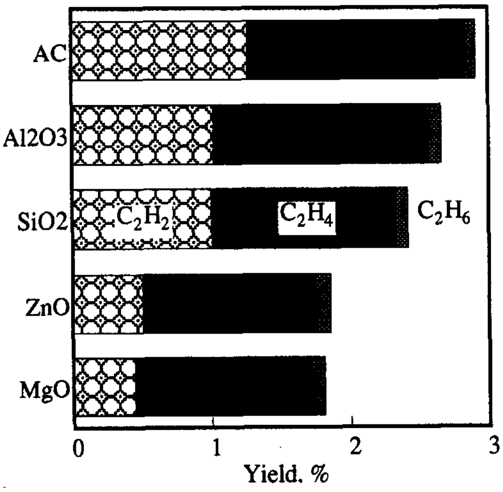

Fig. 1. Dehydrogenative coupling of methane. T: 1100°C, W/F: 2.5 g h/mol, CH_4/H_2: 1:1 (molar ratio).

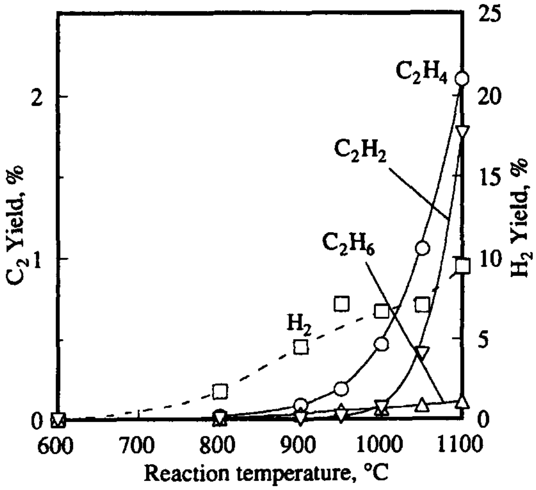

Fig. 3. Effect of reaction temperature. Catalyst: AC, W/F: 2.5 g h/mol, CH_4/H_2: 1:1 (molar ratio).

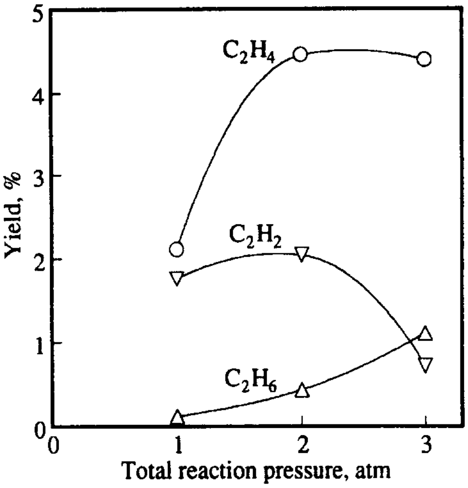

Fig. 4. Effect of total reaction pressure. Catalyst: AC, *T*: 1100°C, *W*/*F*: 2.5 g h/mol, CH_4/H_2: 1:1 (molar ratio).

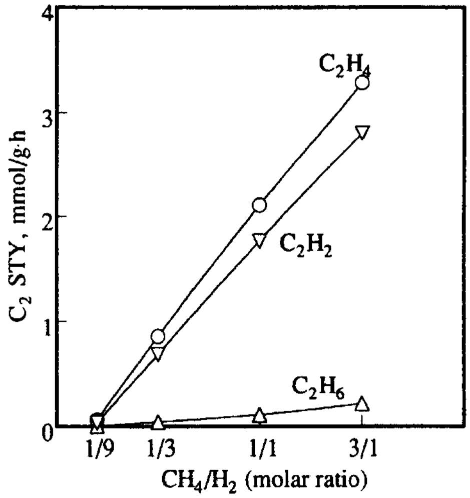

Fig. 5. Effect of CH_4/H_2 feed molar ratio. Catalyst: AC, *T*: 1100°C, *W*/*F*: 2.5 g h/mol.

Fig. 3 shows the effect of reaction temperature on the product yields, where the product yields increased with increasing reaction temperature. In particular, the yields of C_2H_4 and C_2H_2 rose sharply at temperature above 1000°C. This behavior is in good agreement with the fact that dehydrogenative coupling of CH_4 is endothermic.

Fig. 4 shows the effect of total reaction pressure on the yields of C_2 hydrocarbons. At pressures below 2 atm, the yields of C_2 hydrocarbons increased with increasing pressure. On increasing the pressure above 2 atm, the yield of C_2H_4 was leveled off while that of C_2H_2 decreased, suggesting an inhibition of the reaction by H_2. The yield of C_2H_6 increased monotonously in the tested pressure range.

Fig. 5 shows the effect of the CH_4/H_2 feed molar ratio on the product yields. An increase in CH_4 proportion in the reactant mixture promoted C_2 hydrocarbon yield. When the proportion of CH_4 is very small, the yields of C_2 hydrocarbons are almost zero. As suggested on the effect of total reaction pressure, H_2 strongly inhibited the dehydrogenative coupling. The composition of C_2 hydrocarbons did not change within the range of CH_4/H_2 feed molar ratio examined. It was proved that the results of the dehydrogenative coupling of CH_4 is drastically affected by the operating parameters.

The reaction was investigated on metals supported on AC. As shown in Fig. 6, all the alkali metals supported on AC gave lower C_2 hydrocarbon yields than that of AC alone. Especially, the yields of C_2H_2 decreased on alkali metals supported on AC. The reason for the alkali metals depressing the dehydrogenative coupling is still unclear. By the SEM observation of the used catalysts, we confirmed that alkali metals melted on the surface of AC after the reaction.

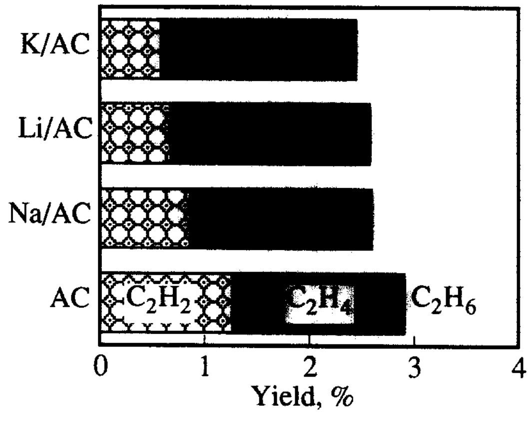

Fig. 6. Effect of supported alkali metal. Metal loading: 1 wt.-% as metal, *T*: 1100°C, *W*/*F*: 2.5 g h/mol, CH_4/H_2: 1:1 (molar ratio).

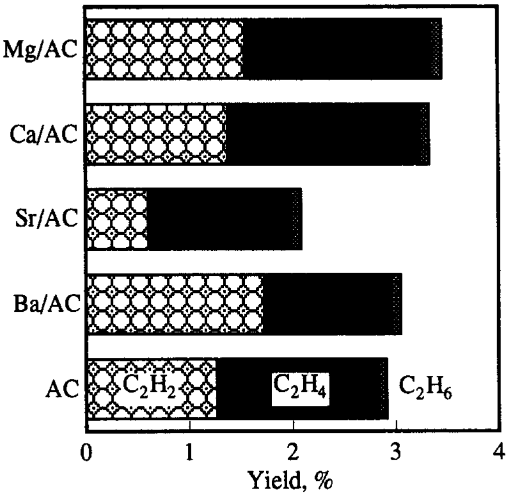

Fig. 7. Effect of supported alkali earth metal. Metal loading: 1 wt.-% as metal, T: 1100°C, W/F: 2.5 g h/mol, CH_4/H_2: 1:1 (molar ratio).

Fig. 7 shows the effects of alkali earth metals supported on AC. Except for strontium, the activities of alkali earth metals supported on AC are higher than that of active carbon itself. Mg/AC gave the highest activity and Ba/AC gave the highest C_2H_2 yield. In contrast to the alkali metals, alkali earth metals promoted the dehydrogenative coupling of CH_4.

Based on the above results, a model of active site on Mg/AC is proposed in Fig. 8. Hydrogen, which is extracted from CH_4 on the surface of active carbon, moves slowly from active carbon surface to the vapor phase in the absence of metal. While in the presence of supported metal, hydrogen is quickly emitted to the vapor phase via metal species. The two methyl radicals bond and are successively dehydrogenated to give C_2 hydrocarbons in gas phase. Our reaction mechanism is based on the reverse-spillover effect of atomic hydrogen.

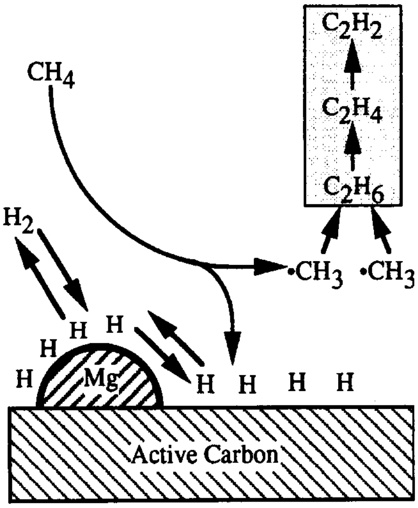

Fig. 8. Model of active site.

4. Conclusion

Catalytic dehydrogenative coupling of methane is proposed as a new process for converting natural gas to chemical feedstocks. Ethane, ethene, ethyne and hydrogen are obtained in good yields in the presence of active carbon as a catalyst. Alkali earth metals enhance the dehydrogenative coupling of methane on active carbon. In particular, magnesium is effective to increase the yields of C_2 hydrocarbons.

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