ノート

Fe$_3$C を構築した鉄のメタン分解活性

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Catalytic methane decomposition over iron grains with and without Fe$_3$C prepared via an *ex situ* process

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Abstract

Fe$_3$C supported on iron grains (Fe$_3$C/Fe) was prepared by the solid-solid reaction of iron grains (Fe-pw) and carbon that had been sputter deposited on the Fe-pw surface. Fe$_3$C/Fe showed slightly higher methane decomposition activity as compared to the bare Fe-pw at 750 ℃.

Research note

Over the last several decades, hydrogen has received increasing attention as a potential energy carrier, using methane (natural gas) or water as hydrogen sources [1-3]. Although water is a plentiful hydrogen source, its standard enthalpy of formation ($\Delta_f H^o$: -285.8 kJ/mol) is lower than that for methane (-74.4 kJ/mol) [4], indicating that the conversion of water to H_2 requires a greater energy input. While methane is currently obtained as a fossil fuel, recent progress in research regarding biomass methane will likely increase its importance as a hydrogen source. Even though the $\Delta_f H^o$ value for methane is relatively small, the poor reactivity of methane requires the application of high temperatures. As a result, the most cost effective means of hydrogen production is currently the steam reforming of methane [5,6].

Another option that has become of interest is catalytic methane decomposition to generate hydrogen and carbon nanomaterials. This process does not produce carbon monoxide and so does not require the separation of hydrogen and carbon monoxide. Many studies of this process have been performed, and have considered the use of nickel, iron and cobalt as active metals for catalytic methane decomposition, as well as the use of activated carbon [1,7]. In work with Fe_2O_3 supported on Al_2O_3 (with Fe_2O_3 loadings above 38.5 wt%), the iron species in the deactivated catalyst following methane decomposition at 800 °C was found to be Fe_3C, and so this has been proposed as the active component [8]. However, Fe_3C alone does not exhibit methane decomposition activity [9]. Thus, the conditions used to prepare Fe_3C, such as the precursor materials or the thermal treatment (including pre-activation), may affect its catalytic activity. In the present study, the *ex situ* preparation of Fe_3C on an iron grain surface was attempted, based on the barrel-sputter deposition of carbon on the iron grain followed by thermal annealing. The methane decomposition activity of the resulting iron-supported Fe_3C was subsequently investigated.

Iron powder with grain diameters in the range of 3–5 μm (referred to as Fe-pw herein) was

purchased from the KOJUNDO Chemical Laboratory Co., Ltd., and stored under N_2. Carbon was deposited on the Fe-pw using a barrel sputtering apparatus [10,11], employing a Fe-pw mass of approximately 3.0 g, a radio frequency power of 200 W, an Ar pressure of 2.0 Pa and a sputtering duration of 4.5 h. The resulting material is referred to herein as C/Fe. The X-ray diffraction (XRD) pattern of Fe-pw was shown in Figure 1(a). The original Fe-pw showed the signals at 2θ values of 44.6° and 65.0º that can be assigned to the 111

Fig. 1 The XRD patterns of the (a) Fe-pw, (b) C/Fe and (c) Fe$_3$C/Fe samples. The triangle marks the peaks that can be assigned to α-Fe.

and 220 planes of α-Fe, respectively (Figure 1(a)). The carbon coating to form the C/Fe did not lead to any significant differences in the diffraction pattern (Figure 1(b)). Also, neither sample showed the presence of impurities such as iron oxides.

The solid-solid reaction of the carbon and iron on the Fe-pw surface to form iron carbide was achieved by annealing the C/Fe under an Ar flow (50 cm^3/min) at 500 ºC for 30 min. The XRD pattern of the resulting material is also provided in Figure 1(c). This pattern exhibits signals assignable to Fe$_3$C in the 2θ region of 35°–60º, based on indexing to the JCPDS 34-0001 standard. These results suggest the successful formation of Fe$_3$C on the Fe-pw, and this sample is referred to as Fe$_3$C/Fe hereafter. Quantitative analyses of the carbon concentrations in the Fe$_3$C/Fe and C/Fe samples by combustion were unsuccessful because the Fe-pw could not be fully oxidized to iron oxides even at 1000 ºC, but rather produced a mixture of metallic Fe and Fe$_2$O$_3$. It was also difficult to determine whether Fe$_3$C was present on the iron grain surface as a complete uniform layer or as inhomogeneous patches. Further experiments are required to obtain a better understanding of this material.
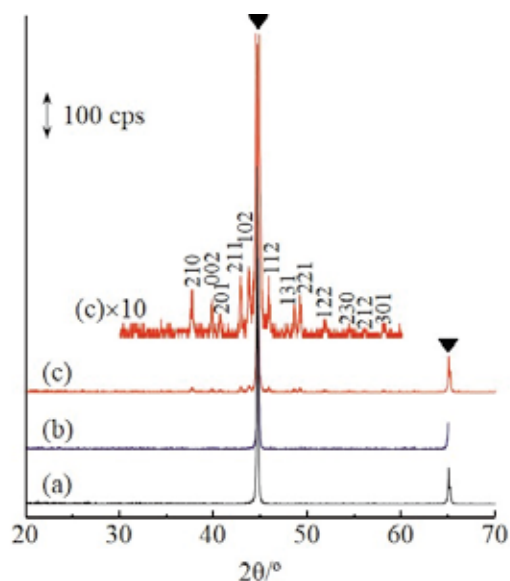
Catalytic methane decomposition was performed over both the Fe₃C/Fe and Fe-pw using a conventional fixed-bed flow reactor. The gas-phase product was analyzed *via* an on-line gas chromatographs (Shimadzu; GC-8A) equipped with an activated carbon column and a thermal conductivity detector (TCD) or a Porapak Q column and flame ionization detector (FID). In this study, the catalyst (approximately 0.5 g) was pre-treated by heating to 750 °C at a rate of 10 ºC/min under a H_2(50 %)/N_2-balance gas (50 cm³/min) followed by a hold at that temperature for 0.5 h. Subsequently, the gas flow was switched to a CH_4(90 %)/N_2-balance gas (50 cm³/min) at the same temperature. The effluent gases were analyzed using the gas chromatograph, so as to evaluate the decomposition activity. The extent of methane conversion was calculated from the equation:

$$CH_4 \text{ conversion} = \frac{([CH_4]_{in} - [CH_4]_{out})}{[CH_4]_{in}} \times 100$$

where $[CH_4]_{in}$ and $[CH_4]_{out}$ are the concentrations of CH_4 in the inflow and the effluent gases, respectively. The gas phase product was found to be primarily H_2 (as determined by TCD), with small amounts of ethane and ethene (as determined by FID).

The methane conversions obtained over the Fe-pw and Fe₃C/Fe catalysts as functions of time are plotted in Figure 2(A). It is evident that the methane conversion initially increased slightly over time in both cases. However, during the final stage of the reaction, the gas flow was found to decrease significantly because the reactor was blocked by carbon deposition. As a result, the methane
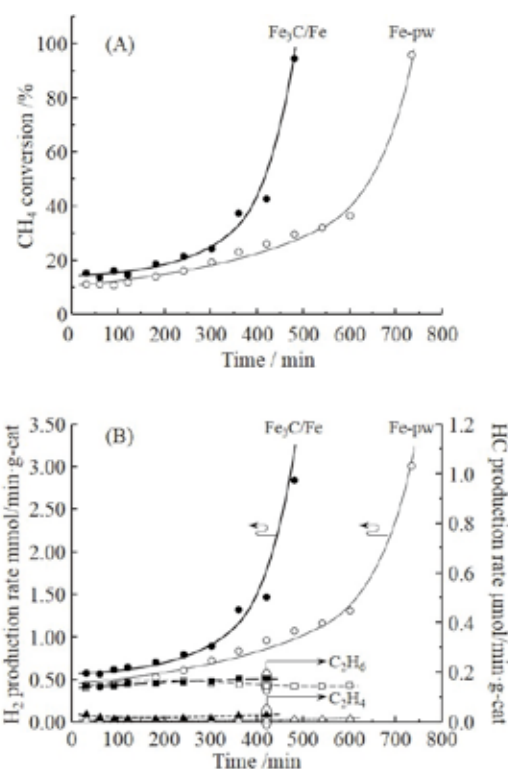

Fig. 2 (A) Methane conversion and (B) H_2 and hydrocarbon production rates as functions of time, over the Fe₃C/Fe (filled symbols) and Fe-pw (empty symbols).

conversion rose almost to 100 %, at which point the reaction was stopped. A greater degree of carbon deposition was observed when using the Fe$_3$C/Fe, suggesting higher methane decomposition activity over this material. This superior activity is confirmed by the H$_2$ production rate data in Figure 2(B). The H$_2$ production rate over the Fe$_3$C/Fe is seen to be greater than that over the Fe-pw, indicating that the presence of Fe$_3$C on the Fe effectively promoted this reaction. In addition, both catalysts were found to produce ethane and ethene, although at rates three orders of magnitude smaller than the H$_2$ production rate (Figure 2(B)). Propane and propene were also found in the effluent, but at very low generation rates (below 0.01 μmol/min·g-cat).

In conclusion, Fe$_3$C synthesized *via* a solid-solid reaction on an iron grain surface showed improved methane decomposition activity, giving a higher H$_2$ production rate than that obtained from the bare Fe-pw. The results of this work suggest that decreasing the Fe$_3$C/Fe grain size might enhance the methane decomposition activity of this material. This study also demonstrates that new catalysts can be fabricated by reforming catalytic surfaces through solid-solid reactions.

Acknowledgements

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