

Reforming of biomass-derived CO₂ by composite iron with nickel and/or copper

Takashi Sagawa and Takashi Morii

Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Tel: +81 774 38 3511 E-mail: t-sagawa@iae.kyoto-u.ac.jp

1. INTRODUCTION

Plenty of studies have been reported to clarify the roles of iron or composite iron with other metals for Fischer-Tropsch synthesis [1, 2], reforming of natural gas [3], or surface reaction with CO₂, CO, or H₂ [4] since iron is one of the promising candidates for hydrogenation of CO₂ into alcohols or hydrocarbons. For example, Ando *et al* examined the reactivity of iron catalyst for alcohol formation in hydrogenation of CO₂ [4]. However, this CO₂ reforming system requires higher-pressure conditions from several tens to hundreds atm in order to achieve high-yield and selectivity for alcohol production. To the best of our knowledge, there is no direct reforming of CO₂ with iron by the combination of water as reducing agent under the relatively mild conditions of atmospheric pressure and at around 300-500°C. In the present work, fundamental aspects of biomass-derived carbon recycle system with composite iron have been examined. We developed CO₂ reforming system by using composite materials of Fe/Al₂O₃ through CO₂-reduction to CO, dissociation of water into hydrogen at atmospheric pressure. In particular, we seek to develop the modified CO₂ reforming system by using Ni and/or Cu doped Fe/Al₂O₃ in order to produce CO, CH₄, carbon, and/or alcohols more efficiently and selectively.

2. METHODOLOGY

Fe microparticles with ca 20-30 μm in diameter were commercially available. Composite materials of Fe/Al₂O₃ were prepared by core-precipitation method from Fe(NO₃)₃ · 9H₂O with granular Al₂O₃, which were 10 μm in size [1]. The CO₂ reforming was carried out with a fixed-bed reactor made of stainless-steel tube with 8-mm i.d. Analysis of the gas was done using on-line column gas chromatographs with thermal conductivity detector or flame ionization detector.

3. RESULTS & DISCUSSION

Two steps conversion of CO₂ of dry and wet reforming by Fe produced small amount of CH₃OH (only 0.08% yield from the starting material of CO₂). From XRD analyses of the iron surface, iron carbide was detected and such Fe₃C was relevant to the formation of CH₃OH in the presence of H₂O. Dry and wet reforming of CO₂ and steam reforming of CO₂ produce almost the same amount of H₂. CO yield for steam reforming was relatively higher than dry and wet method. At the temperature above 500°C, maximal and saturated yields of CO and H₂ were obtained. From the FT synthesis by using Fe under the atmospheric pressure, small amount of CH₃OH (4% yield from the starting material of CO) from synthetic gas was obtained though it was 50 times enhancement of the dry and wet reforming of CO₂. Optimized molar ratio of H₂/CO is 3 or 4 for CH₃OH production. It means that we need more H₂ from water through water-gas shift reaction. Cu doped iron was the most effective for water-gas shift reaction among the promoters examined. Hydrogenation of CO₂ was performed with Fe/Al₂O₃ at 500°C in order to increase the amount of produced CO and/or CH₄ as one of the candidates of reductants for iron-recycle in addition to H₂. When Ni instead of Fe was supported onto Al₂O₃, conversion of CO₂ was reduced to 76%, while, 9% of methane was detected. On the other hand, though the CO₂-conversion reduced half of Fe, the selectivity of CO from CO₂ increased up to 95% in the case of Cu. Therefore Ni was effective to produce CH₄ for hydrogenation of CO₂, while Cu was the highest selectivity of CO from CO₂.

[1] O'Brien, R., Xu, L., Bao, S., Raje, A., Davis, B., *Appl. Catal. A.*, **2000**, *196*, 173-178. [2] Dry, M. E., *Catal. Today*, **2002**, *71*, 227-241. [3] Kodama, T., Koyanagi, T., Shimizu, T., Kitayama, Y., *Energy & Fuels*, **2001**, *15*, 60-65. [4] Ando, H., Matsumura, Y., Souma, Y., *Appl. Organomet. Chem.*, **2000**, *14*, 831-835.