Efficient dry (CO_2) reforming of methane by current-assisted self-heating of metal/carbon catalysts†

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Abstract: A new catalytic system for highly energy-efficient CO_2 reforming of methane is suggested. The system is designed so that the catalyst bed can be exposed to electron flow in a modified reactor, and heat energy to activate reactants is generated from the interface of metal catalysts and conductive carbons. CO_2 reforming of methane are carried out at a temperature range of 100 – 250 °C with a voltage range of 5.0 – 6.5 V, which is a catalytic performance of a conventional reactor at 400 – 600 °C. Interestingly, the energy efficiency to obtain similar yield of H_2 is greatly enhanced about 6 times per each second by comparison with a conventional catalytic reactor.

Keywords: CO_2 reforming of methane, current-assisted self-heating system, energy saving

1. Introduction

Conversion of greenhouse gases such as CO_2 and CH_4 is an important issue for green technology, because the concern about global warming has been increased.[1] This is why the dry CO_2 reforming of methane (DRM) reaction has been considered to be one of the most advantageous green chemistries. Using this reaction, industrially valuable syngas can be obtained from greenhouse gases. The produced syngas can be converted into hydrocarbons through the Fisher-Tropsch synthesis,[2] and synthesized hydrogen can be used for fuel cell.

However, the DRM is highly endothermic process ($\Delta H^0 = 247$ kJ·mol^{-1}), and high temperature (> 600 ^oC) condition is required to reach high yield of products. Even if the catalytic reaction is green process, energy-intensive consumed process is not commercially and environmentally viable.

As an alternative of conventional catalytic (heating) system, use of a microwave dielectric heating[3] and a plasma-catalysis hybrid system[4] have been reported. However, reflected power were inevitably observed, because the input energy is applied from out of the catalyst bed, like as existing catalytic system. Therefore, they need excessive input energy to overcome an activation energy for a target reaction.

In this study, we suggest a new platform of catalytic system, which effectively transfers the energy to proceed the production of syngas from greenhouse gases. In the new catalytic system proposed here, heat is generated on each surrounding of active metals, which seems like countless nano-sized furnaces operate throughout the catalyst bed. Finally, we compare the efficiency of this catalytic system with the conventional catalytic system.

2. Experimental

Current-assisted self-heating system was constructed in a modified packed-bed-flow reactor. Carbon sheets were located from side to side of the catalyst bed, and they were linked by copper line to power supply. Thermocouple was put into the catalyst bed to measure apparent temperature during catalysis. The dry reforming of methane reaction was performed in a flow-type quartz reactor under atmospheric pressure at various temperatures. A 0.1 g sample of catalyst was loaded in the reactor. The reaction gas stream consisted of CH_4, CO_2, and N_2 with a volumetric ratio of 1:1:3, at a total flow rate of 50 mL·min^{-1}. The

products were analyzed using an on-line gas chromatograph (Younglin ACME 6500 model) equipped with a thermal conductivity detector (TCD) and a RESTEK ShinCarbon ST 100/120 column.

3. Results and discussion

The activities of the catalyst with and without electron flow were compared by using the same weight (0.1 g) of Ru/C in the reactor. The similar turn over frequency using current-assisted self-heating system was obtained under the only 5.0~6.5 V condition, which can be presented under the 500-600 ^{o}C in the conventional heating system. To identify the mechanistic difference between the conventional heating catalysis and the current-assisted catalysis, apparent activation energies were evaluated by examining Arrhenius plots. According to the Arrhenius plots, the apparent activation energies for CH_4 and CO_2 consumptions (17.8 kcal/mol and 14 kcal/mol, respectively) were very similar in two catalytic systems. This indicates that application of electron flow does not alter the reaction mechanism (or activation energies) for DRM.

In order to compare the energy consumptions in two catalytic systems, work done ($V \cdot I \cdot t$) by electrical energy during DRM reaction to obtain 40 % yield of H_2 in each catalytic system was calculated. The effective voltage and current were determined using Power meter. The amount of work done was thought to be partitioned by two processes, ramping and maintaining processes. In the conventional thermal system, 1 hour is needed for rising a temperature from room temperature to reaction temperature, 600 ^{o}C. The work done during this process was 4116 kJ. Contrary to this, temperature was quickly stabilized in current-assisted self-heating system. When the time for stabilization was estimated as 5 minutes, work done during ramping process in current-assisted self-heating system is 52.3 kJ. This is 78 times smaller than conventional thermal system. In the maintaining process, work done per a unit second is 1.14 and 0.184 kJ/s in conventional heating and current-assisted self-heating systems, respectively. This clearly shows that current-assisted self-heating system for DRM is 6 times efficient catalytic system than conventional thermal system. In addition, we calculated the TOF-E values (These were calculated by TOF/applied energy per a unit time) for each catalytic system. The productivity per a unit applied energy in current-assisted self-heating system is higher than that in the conventional catalytic system. From this result, it was concluded that the current-assisted self-heating system could effectively and directly supply the energy for dry reforming of methane.

4. Conclusions

It was demonstrated that new platform of catalytic system can effectively supply the energy for dry reforming of methane. According to the results of catalytic activity test, turn over frequency per a unit applied energy (TOF-E) is 6 times higher compared to that of conventional catalytic system. This is because, the electrical energy is converted into thermal energy at surrounding of every nano-active metals throughout the catalyst bed.

†This work was published in ChemSusChem 10 (2017) 3671.

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