Low Temperature Catalytic Dry Reforming of Methane over Ni/La-ZrO_2 in Electric Field

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Abstract: Dry reforming of methane was conducted over La-doped Ni/ZrO_2 catalyst in an electric field. The reaction mechanism and the effect of imposing the electric field on the catalytic activity were investigated. The periodic (CH_4-CO_2 cycling) operation test revealed that both the decomposition of CH_4 and the dissociation of CO_2 were promoted by imposing the electric field. The well-balanced promotion of the two reactions was attributed to suppression of catalyst deactivation due to carbon deposition.

Keywords: Dry reforming of methane, Electric field, Low temperature system.

1. Introduction

Syngas production is an important step in the process of producing chemical feedstocks such as ammonia, methanol and FT synthesis. The dry (CO_2) reforming of methane (DR, (1)) is attractive syngas production environmentally because both CH_4 and CO_2 are greenhouse gases.

$$CH_4+CO_2 \rightarrow 2CO+2H_2 \qquad \Delta H^0_{298}=247.2 \text{ kJ mol}^{-1} \qquad (1)$$

This reaction yields syngas with low H_2/CO ratios, which is especially suitable for the synthesis of long-chain alkanes (FT synthesis) or oxygenated chemicals. However, this reaction is a large endothermic reaction and necessitates high temperatures as 1073 K, which requires robustness of the reactor and causes catalyst deactivation due to carbon deposition. These problems would be crucial for commercialization of this process. Accordingly, we reported that DR over Ni/La-ZrO_2 catalyst was promoted at low temperatures as 423 K in the electric field1). In addition, it was found that operating at low temperature for DR made it possible to greatly reduce carbon deposition on the catalyst and maintain the catalytic activities. In this study, to elucidate the mechanism of DR with the electric field, the activity tests by changing the amount of CH_4 and CO_2 supplies and the periodic (CH_4-CO_2 cycling) tests were performed by imposing the electric field. In addition, the results were compared to that in a conventional catalytic system without the electric field to discuss the role of imposing the electric field.

2. Experimental

10 mol%La-ZrO_2 support was obtained by a complex polymerized method and 1wt% of Ni was loaded on the support using an impregnation method with water. The metal precursors were nitrates. The activity test was carried out using a fixed bed flow-type reactor. Two electrodes were inserted contiguously to the top and bottom of the catalyst bed during the reaction to apply the electric field. Catalysts were reduced at 1023 K in H_2:Ar = 1:3, the total flow rate 100 mL min^{-1} prior to the reaction. The applied current was 3.0 mA. The exit gases were analyzed using GC-FID and GC-TCD, which allowed for separation of H_2, CO, CH_4, CO_2. In the partial pressure change test, the catalyst weight was 20 mg, the reaction temperature was 823 K for the reaction without the electric field and 423 K with an electric field. CH_4 and CO_2 partial pressures were changed in the low conversion range and the total flow rate was 200 mL min^{-1} by diluted with Ar. In the cycle test of CH_4 or CO_2 flow, the catalyst weight was 200 mg, the reaction temperature was 773 K without the electric field and 423 K with the electric field. The total flow rate of the reaction gas was 100 mL min^{-1} (CH_4:Ar = 1:3 or CO_2:Ar = 1:3).

3. Results and discussion

To clarify the promoting effect for imposing the electric field on the catalytic activity, activity tests by changing CH_4 and CO_2 partial pressures with/without imposing the electric field were conducted. As a result, the reaction orders of the reaction assisted by the electric field differed from those of the conventional reaction. The application of electric field increased the reaction order of CO_2 both for the formation rate of CO from CH_4 from 0.05 to 0.22 and for the formation rate of H_2 from -0.42 to 0.34. On the other hand, the reaction order of CH_4 for the formation rate of H_2 decreased from 0.26 to zero. Zhang reported that reaction order of CO_2 for the formation rate of H_2 showed negative because intermediates formate species ($HCOO^-$) were stabilized by application of basic catalyst-supports[2)]. Therefore, the imposed electric field was supposed to promote the formation rate of H_2 from CH_4 and forming formate species.

Cyclic tests were performed in order to clarify the elementary reactions. Figure 1 shows H_2 and CO produced during CH_4 or CO_2 supply. Panel A and C show the products during only CH_4 supply, while panel B and D show the products during CO_2 supply. The first CH_4 supply (panel A) resulted in the production of H_2 at 447 K. The H_2 production stopped on 12 min due to carbon deposition. In the subsequent supply of CO_2 (panel B), CO and H_2 were produced at 573 K. The production of H_2 in panel B suggested that CH_x species formed on Ni metal during CH_4 supply. During the second CH_4 supply (panel C), H_2 production was observed again, indicating that CO_2 removed carbon from metal surface via carbon gasification (2).

$$C_{(s)}+CO_2 \rightarrow 2CO \qquad \Delta H^0_{298}=172.5\ \mathrm{kJ\ mol^{-1}} \qquad (2)$$

Stagg-Williams reported that the decomposition of CH_4 and the dissociation of CO_2 occurred via two independence pathways over Pt/ZrO_2 at 1073 K[3)]. Without the electric field, at low temperatures as 423 K, these reactions did not proceed. However, with the electric field, both CH_4 and CO_2 reacted, indicating that both the decomposition of CH_4 and the dissociation of CO_2 were promoted by imposing the electric field. The well-balanced promotions of CH_4 decomposition and carbon gasification were attributed to the suppression of catalyst deactivation due to carbon deposition.

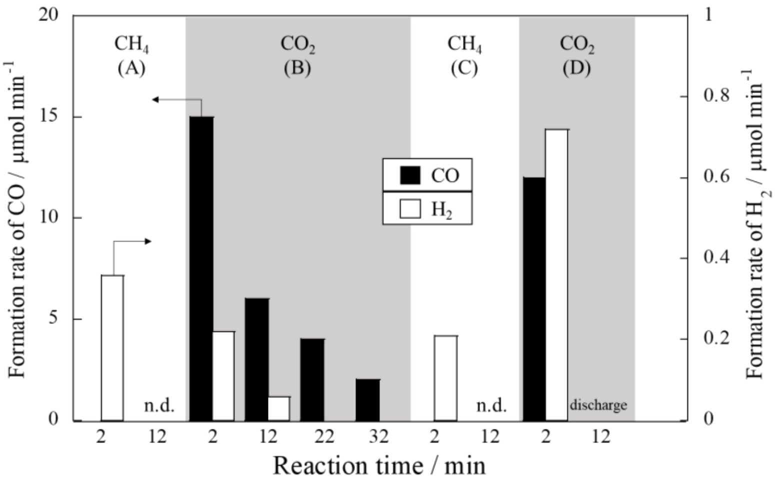

Figure 1. Results of periodic (CH_4-CO_2 cycling) operation test with an electric field

4. Conclusions

The mechanism of dry reforming of methane in an electric field and the effect of imposing the electric field on the catalytic activity were investigated. The activity tests by changing CH_4 and CO_2 partial pressure suggested that the applied electric field promoted the H_2 formation from CH_4 and forming formate species. The periodic (CH_4-CO_2 cycling) operation test indicated that both CH_4 decomposition and CO_2 dissociation were promoted by imposing the electric field. The well-balanced promotion of CH_4 decomposition and carbon gasification probably prevents catalyst from deactivating due to carbon deposition.

References

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