Tri-reforming of Methane over Ni/$La_{0.1}Zr_{0.9}O_2$ Catalysts at Low Temperatures in Electric Field

Tomohiro Yabe, **Task Oguri, Kensei Yamada, Shuhei Ogo, Yasushi Sekine***
Faculty of Science and Engineering, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, 169-8555 Japan
**Corresponding author: +81-3-5286-3114, ysekine@waseda.jp*

Abstract: Tri-reforming of methane (a mixed reaction with steam reforming, dry reforming and partial oxidation of methane) for syngas production was conducted over Ni supported $La_{0.1}Zr_{0.9}O_{2-\delta}$ (Ni/La-ZrO_2) catalysts in an electric field at low temperatures as 473 K. In order to suppress methane combustion for energy recovery by endothermic reactions, an addition of alkali-earth metal to Ni/La-ZrO_2 was investigated and Mg added catalyst showed the highest enthalpy gain while suppressing combustion. From various characterizations, Mg-addition stabilized NiO on Ni/Mg/La-ZrO_2 catalyst even in the reaction atmosphere thanks to form an adjacent structure of NiO and MgO, and it contributed to suppress combustion.

Keywords: Tri-reforming, Electric field, Combustion suppression.

1. Introduction

Syngas production is an important step in the process of producing chemical feedstocks such as methanol, ammonia and hydrocarbons. Tri-reforming of methane (TR, a mixed reaction with steam reforming (SR), dry reforming (DR) and partial oxidation of methane) is attractive syngas production with desired H_2/CO ratios using O_2, H_2O and CO_2 in the flue gases without CO_2 pre-separation1). Considering the utilization of exhaust gases and the heat of low exergy rate from vehicles, SR (1) and DR (2) are endothermic reactions and can gain enthalpy, but the partial oxidation and complete combustion of methane (3) are large exothermic reactions and loses enthalpy, as presented in the following equations.

$$\text{SR:} \quad CH_4 + H_2O \rightarrow 3H_2 + CO \qquad \Delta H_0^{298} = 205.9\ \text{kJ mol}^{-1} \qquad (1)$$

$$\text{DR:} \quad CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H_0^{298} = 247.2\ \text{kJ mol}^{-1} \qquad (2)$$

$$\text{Combustion:} \quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_0^{298} = -890.4\ \text{kJ mol}^{-1} \qquad (3)$$

Therefore, a selective reforming reaction with suppressed methane combustion is necessary to gain enthalpy. In this study, screening tests over various Ni catalysts on La doped ZrO_2 were conducted for preferential reforming2). As a result, we succeeded in promoting SR and DR with suppressing methane combustion even at 473 K in the electric field. Then, in order to clarify the reason for the suppressed combustion on these catalysts, we conducted characterizations using XRD, TEM, H_2-TPR, XAFS etc.

2. Experimental

10 mol% La doped ZrO_2 oxide supports were prepared using a polymerized complex method with citric acid and ethylene glycol. Supported Ni metal was loaded on the support using an impregnation method. The metal precursors were nitrates. Activity tests were carried out using a fixed bed flow-type reactor. Two electrodes were inserted contiguously to the top and bottom of the catalyst bed for applying the electric field. In addition, alkali-earth metals were supported as a second metal on the Ni/La-ZrO_2 catalyst for investigating the effect of the impregnation order on the catalytic performance. To investigate the precursor effect on a Ni particle dispersion, Ni(acac)/Mg/La-ZrO_2 was also prepared. In activity tests, the reactant feed gases were methane, oxygen, carbon dioxide, H_2O, and Ar (CH_4:O_2:CO_2:H_2O:Ar = 6:1:2:2:9, the total flow rate of 200 SCCM). The applied current was 3.0 mA. The exit gases were analyzed using GC-FID and GC-TCD. Characterizations were conducted using XRD, TEM, BET, Raman, XPS, XAFS (BL14B2, SPring-8) and H_2-TPR.

3. Results and discussion

First, to discover suitable catalysts for the TR reaction, catalysts with various supported amounts of Ni on La-ZrO_2 (A) and various kinds of alkali-earth metal addition to 1wt%Ni/La-ZrO_2 (B) to suppress methane combustion in the electric field were investigated. Next, we elucidated the effects of impregnation sequences of Ni and Mg on catalytic activity. For comparison with Ni-Mg/La-ZrO_2 (co-impregnation), Ni/Mg/La-ZrO_2 (Mg→Ni) and Mg/Ni/La-ZrO_2 (Ni→Mg) were prepared using a sequential impregnation method (C). In order to investigate the effect of Ni precursor in the Ni/Mg/La-ZrO_2 on the catalytic activity, Ni(acac)/Mg/La-ZrO_2 catalyst using Ni-(acac) as a precursor was also prepared for comparing to Ni/Mg/La-ZrO_2. Table 1 presents catalytic activities for these catalysts.

Table 1. Catalytic activities for TR reaction in the electric field at 473 K.

	Various metals supported on La-ZrO_2	Power / W	CH_4 Conversion / % Total	Combustion	Reforming	O_2 Conv. / %	Reforming sel. / –	H_2/CO / –	ΔH_r / kJ min^{-1}
(A)	La-ZrO_2	2.7	3.7	1.9	1.8	27.9	46.9	1.8	-0.033
	0.25wt%Ni	3.4	12.8	7.0	5.8	91.1	44.9	1.2	-0.113
	0.50wt%Ni	4.1	18.2	7.5	10.7	80.4	58.2	1.6	-0.079
	1wt%Ni	2.6	20.7	8.2	12.5	100	56.3	2.7	-0.091
	5wt%Ni	1.8	18.7	7.6	11.2	100	55.8	3.6	-0.098
(B)	1wt%Mg	2.5	4.5	1.9	2.6	27.1	56.7	1.6	-0.038
	1wt%Ni-1wt%Mg	2.0	15.7	3.9	11.8	54.6	74.6	2.2	-0.020
	1wt%Ni-1wt%Ca	1.8	9.6	3.8	5.8	57.9	39.5	2.7	-0.051
	1wt%Ni-1wt%Sr	2.4	16.4	6.7	9.7	92.9	50.1	3.8	-0.090
	1wt%Ni-1wt%Ba	1.3	15.5	7.2	8.2	100	26.3	3.3	-0.112
(C)	1wt%Ni-1wt%Mg	2.0	15.7	3.9	11.8	54.6	74.6	2.2	-0.020
	1wt%Ni/1wt%Mg	2.6	17.8	4.0	13.8	55.8	77.4	2.4	-0.022
	1wt%Mg/1wt%Ni	3.2	13.5	4.1	9.4	55.8	68.8	1.8	-0.036
	1wt%Ni(acac)/1wt%Mg	2.9	19.7	3.9	15.8	47.4	79.8	2.2	0.004

As (A) part of Table 1, bare La-ZrO_2 catalyst showed low TR activity. When the supported amounts of Ni on La-ZrO_2 catalysts were increased to 1wt%, CH_4 conversion for reforming increased monotonically, which indicated that the active site of the reaction is the supported Ni particle. Furthermore, the highest activity for tri-reforming was achieved over 1wt%Ni/La-ZrO_2 among these catalysts with various Ni loadings. XRD patterns of these catalysts after reaction with the electric field are not markedly different from the patterns of as-made catalysts, which indicates that the structure is stable under the reaction conditions.

As (B) part of Table 1, O_2 conversion decreased by adding alkali-earth metal, indicated that methane combustion was suppressed in the following order: bare Ni=Ba<Sr<Ca<Mg. Moreover, the combustion activity for Ni-Mg/La-ZrO_2 catalyst declined to less than that for Ni/La-ZrO_2 catalyst. However, the reforming activity for Ni-Mg/La-ZrO_2 catalyst was almost equal to that for Ni/La-ZrO_2 catalyst, although the reforming activity decreased in catalysts for Ba, Sr and Ca added to Ni/La-ZrO_2. Therefore, the addition of Mg to Ni/La-ZrO_2 suppressed methane combustion while maintaining reforming activity, thereby minimizing enthalpy loss by combustion.

As (C) part of Table 1, by comparing with Ni-Mg/La-ZrO_2, Ni/Mg/La-ZrO_2 and Mg/Ni/La-ZrO_2, methane combustion activities for these catalysts were almost identical but the impregnation sequences affected the methane reforming activity. Therefore, the surface Ni functioned as a activity site for reforming and Mg addition played an important role for suppressing methane combustion. In addition, Ni(acac)/Mg/ La-ZrO_2 catalyst showed higher reforming activity than Ni/Mg/La-ZrO_2 and brought an endothermic reaction. From the results of H_2-TPR, Ni oxide was stabilized on Ni(acac)/Mg/La-ZrO_2 by virtue of the formation of an adjacent structure for MgO particle with NiO, suppressing NiO reduction.

4. Conclusions

Tri-reforming of methane (TR) was conducted in an electric field. Results of screening tests showed that $La_{0.1}Zr_{0.9}O_{2-\delta}$ (Ni/La-ZrO_2) catalyst was the most appropriate support. Then, Ni(acac)/Mg/La-ZrO_2 catalyst, prepared using acetone as an impregnation solvent, selectively proceeded methane reforming with high dispersion of NiO particle and suppressed methane combustion. From the results of several characterizations, Ni oxide was stabilized on Ni/Mg/La-ZrO_2 by virtue of the formation of an adjacent structure for MgO particle with NiO, suppressing NiO reduction.

References

1. C. Song, W. Pan, *Catal. Today* 98 (2004) 463.
2. T. Oguri, K. Sugiura, T. Yabe, S. Ogo, Y. Sekine, *J. Jpn. Petrol. Inst.* 60 (2017) 232.