Low temperature dry reforming of methane in an electric field over La-doped Ni/ZrO_2 catalysts

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Introduction

Dry (CO_2) reforming of methane (DRM), as shown in the following equation, is a 'green' hydrogen/syngas production process from the viewpoint of an environment and energy. [1]

$CH_4 + CO_2 \rightarrow 2CO + 2\ H_2$

$\Delta H_0^{298} = 247.2$ kJ mol^{-1}

DRM requires high temperatures: also, catalysts are easily deactivated and carbon deposition on catalysts is unavoidable.

Recently, utilization of an electric field has been reported for lowering reaction temperatures for several catalytic reactions. [2, 3] So, we conducted catalytic DRM in the electric field in order to achieve high CH_4 and CO_2 conversion even at low temperatures, over La-doped Ni/ZrO_2 catalysts.

Experimental

Catalyst-supports, 10 mol%La-ZrO_2 (La-ZrO_2) were prepared using a complex polymerized method. Then a supported metal was loaded on La-ZrO_2 with 1wt% using an impregnation method. Calcination was conducted at 973 K. These catalysts are designed as X/La-ZrO_2 (X = Fe, Co, Ni, Cu, Pd or Pt.)

Charging amount of catalyst for DRM activity tests were 100 mg. In the screening tests, the feed gas was supplied at CH_4:CO_2:Ar = 1:1:2; the total flow rate was 100 mL min^{-1}. Products were analyzed using a GC-FID and a GC-TCD. The electric field was applied using a DC high-voltage power supply.

Results and discussion

To discover suitable catalysts for DRM in the electric field, various metal-supported La-ZrO_2 oxide catalysts were investigated to assess their catalytic activities. (as shown in Table 1) Among these catalysts, higher CH_4 were obtained over Co/La-ZrO_2, Ni/La-ZrO_2, and Pt/La-ZrO_2 catalysts than other listed catalysts. We specifically chose Ni/La-ZrO_2 catalyst because of high H_2/CO ratio (=0.83). To investigate the carbon deposition on DRM reaction in the electric field, the catalytic activity test was conducted in conditions of high CH_4 conversion. (as shown in Table 2) The amount of the carbon deposits after DRM in the electric field was low thanks to the low reaction temperature.

Conclusion

Ni/La-ZrO_2 catalyst was the most appropriate catalyst for DRM in the electric field. High DRM selectivity, high H_2/CO ratio and low amounts of carbon deposition were demonstrated even in conditions of high CH_4 conversion.

Table 1 Catalytic activities for DRM in an electric field over X/La-ZrO_2 catalysts. [4]

Catalyst	Temp. (K)	Field Intensity (V mm^{-1})	CH_4 conv. (%)	CO_2 conv. (%)	CO sel. (%)	H_2/CO (–)
La-ZrO_2	596	151	1.9	1.9	74.4	0.76
Fe/La-ZrO_2	649	228	6.9	14.6	91.2	0.23
Co/La-ZrO_2	619	292	20.3	31.2	99.4	0.57
Ni/La-ZrO_2	555	243	22.8	24.8	100	0.83
Cu/La-ZrO_2	626	256	3.9	3.6	88.5	0.99
Pd/La-ZrO_2	533	125	6.4	9.8	100	0.52
Pt/La-ZrO_2	580	271	21.0	23.6	100	0.80

Table 2 Catalytic activities and amounts of carbon deposition under a high conversion condition on DRM. [4]

		Power (W)	CH_4 conv. (%)	CO_2 conv. (%)	H_2 / CO (-)	Carbon deposition (mg g_{cat}^{-1})
not imposed EF	initial	-	63.5	52.9	1.2	＞39.6
	140 min	-	64.0	77.0	0.81	
imposed EF	initial	8.1	74.5	85.3	0.87	1.5
	140 min	6.9	77.2	87.6	0.88	

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