An Ultra Stable Ni-Co Catalyst for CO_2 Reforming of CH_4

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Introduction

Since industrial revolution, the atmospheric CO_2 concentration has been rising so rapidly that it leads to global warming and destructive climate change [1]. CO_2 reforming of CH_4 will make a technology that enables to convert emitted CO_2 into usable chemicals and fuels should there is an economically effective catalyst over which the reforming reaction takes place [2]. This abstract reports an ultra stable catalyst of Ni-Co-Al-Mg composite made by coprecipitation, which has undergone a test of 2000 h time on stream without tendency of deactivation. The conditions of the test of catalyst life were 750°C, 1 atm, and 110000 mL h^{-1} g_{cat}^{-1} (N_2:CO_2:CH_4=1:1:1). The catalyst screening, effect of preparing conditions, the activity evaluation, the characterization, and the catalyst life test are to be discussed.

Materials and Methods

The catalysts were prepared using co-precipitation method from the precursors of an aqueous solution of nickel nitrate (98%, Lancaster Synthesis Inc.), cobalt nitrate (99%, Aldrich Chemical Company), magnesium nitrate (EMD Chemicals Inc.) and aluminium nitrate (EMD Chemical Inc.). The precipitate was formed by adding aqueous ammonia solution (27~30%, Mallinckrodt Baker Inc.) in it, washed with de-ionized water and dried overnight in air at 120ºC, and then calcined in air at various temperatures between 400 and 1100ºC for 6 h. The composition of the catalysts was determined by inductively-coupled plasma-mass spectrometry (ICP-MS). The catalyst evaluation was conducted in a bench-top, fixed-bed quartz micro-reactor (Autoclave) with an i.d. of 6 mm. The gas composition was analyzed by an on-line Agilent 6890N GC equipped with TCD and a GS-GASPRO capillary column (J&W Scientific). The characterization methods include BET, XRD, TG/DTA, TPR, TEM, and XAS in the Canadian Light Sources (CLS) synchrotron.

Results and Discussion

The catalyst design idea is to generate synergetic effects by forming a composite of every involved component, *i.e.,* high activity of Ni, thermal stability of MgO, large surface of Al_2O_3, inhabitation of carbon deposition by Ni-other-metal alloy and strong metal-support interaction from the composite. Table 1 shows the screening results, and the Ni-Co-Al-Mg composite gives the best catalytic performance. Calcination temperature has strong impact on the activity and stability of the catalysts. As shown in Fig. 1, catalyst of Ni-Co-Al-Mg composite catalyst has the best activity and stability. TG/DTA indicates that this catalyst caused the least carbon deposition. BET and TPR reveal that this catalyst has sufficient surface area and uniform active sites. The life test shows the catalyst has undergone 2000 h time on stream without tendency of activation (Fig. 2). Synchrotron XAS shows that the catalyst became chemically and structurally stable after 200 h time on stream. Based on the observations, it is certain that the catalyst will have even longer stability. And its activity and H_2, CO selectivity are even better than the reported catalysts up to date [3-5].

Table 1. Initial performance of Ni, Co based catalyst for CO_2-CH_4 reforming

Catalyst Composition	Conversion (%)		Selectivity (%)	
	CH_4	CO_2	H_2	CO
$Ni_{0.06}Al_{0.29}Mg_{0.65}O_{1.145*}$	89.8	91.7	85.6	99.1
$Co_{0.09}Al_{0.26}Mg_{0.66}O_{1.13}$	90.9	93.4	84.7	99.7
$Ni_{0.06}Co_{0.09}Al_{0.28}Mg_{0.57}O_{1.14}$	**91.4**	**91.1**	**98.3**	**99.97**
$Ni_{0.06}Mn_{0.09}Al_{0.28}Mg_{0.57}O_{1.14}$	85.0	91.7	92.8	97.9
$Ni_{0.06}Cu_{0.06}Al_{0.3}Mg_{0.58}O_{1.15}$	53.9	62.9	82.5	92.5
$Ni_{0.06}Fe_{0.07}Al_{0.3}Mg_{0.57}O_{1.15}$	15.3	25.8	75.5	95.8
$Co_{0.09}Mn_{0.09}Al_{0.26}Mg_{0.56}O_{1.13}$	35.5	52.1	81.1	97.2

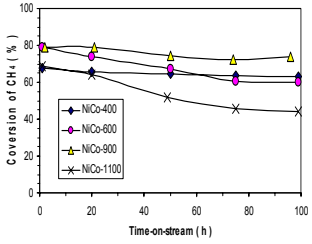

Fig. 1. Activity and stability of catalysts calcined at 400, 600, 900, and 1100ºC (Test condition: 750°C, 1 atm, 183,000 mL h^{-1} g_{cat}^{-1})

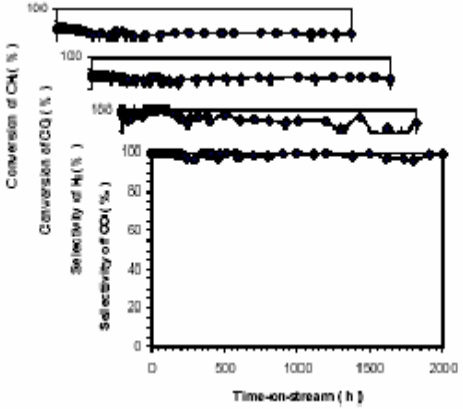

Fig. 2. 2000 h time on stream test of Ni-Co-Al-Mg.

Significance

The development of Ni-Ci-Al-Mg composite catalysts has provided an ultra stable catalyst for CO_2 reforming of CH_4. Why this catalyst is stable has been attempted from the material science point of view. Larger scale experimental research is ready to proceed to push forward the commercialization of CO_2 reforming of CH_4 for CO_2 emission in energy sector.

References

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