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Bio-syngas methanation towards synthetic natural gas (SNG) over highly active Al_2O_3–CeO_2 supported Ni catalyst

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ABSTRACT

The Al_2O_3–CeO_2 composite supported Ni catalyst was developed for synthetic natural gas (SNG) from bio-syngas methanation. The physico-chemical properties of the Ni-based catalysts were characterized by BET, H_2-TPR, XRD, SEM and TG. The methanation tests showed that Ni/Al_2O_3–CeO_2 presented the highest methanation performances at low temperature (91.6% CO conversion with 92% CH_4 selectivity at 350 °C) compared with Ni/Al_2O_3, Ni/ZrO_2 and Ni/Al_2O_3–SiO_2, etc. The characterization results indicated that combination of CeO_2 with Al_2O_3 restrained the entering of Ni species into the inside, increasing the Ni species amounts and promoting the dispersion of NiO on the surface of Al_2O_3–CeO_2. In addition, adding CeO_2 into Ni/Al_2O_3 weakened the interaction of NiO–Al_2O_3 via the strengthening of NiO–CeO_2 interaction, promoting the reduction of NiO and formation of active metallic Ni. All of these factors improved the catalytic activity for bio-syngas methanation to SNG and the resistance to carbon deposition for Ni/Al_2O_3–CeO_2.

1. Introduction

Natural gas as the cleanest fossil fuel is the world's fastest growing energy, which increases in consumption at an average rate of 1.6% since 2008 [1,2]. Production of synthetic natural gas (SNG) from coal or biomass has attracted more and more attention recently due to increasing demand and price volatility of natural gas [3,4]. Especially, gasification of residual biomass or non-food crops produces syngas with lower H_2/CO ratio, which can be adjusted by water-gas shift reaction for complete conversion of carbon oxides to methane [5]. Methanation of syngas ($CO + 3H_2 \rightarrow CH_4 + H_2O$, $\Delta H^o_{298} = -206$ kJ/mol) is highly exothermic and thermodynamically feasible [6,7]. The syngas methanation is extensively investigated over noble- and transition-supported catalysts. In order to improve methanation performances and overcome carbon deposition and particles' sintering, suitable catalysts need be developed.

Compared to other metals such as Ru, Rh, Co and Fe [8–11], the use of Ni-based catalysts is more attractive for methanation of CO to SNG due to their higher activity and selectivity to methane and lower cost [12–14]. Abundant efforts have been made to modify methanation performances for Ni-based catalysts by adjusting promoters and supports [13–15]. Especially, modification of supports has attracted much attraction because it plays an important role in affecting metal–support interaction as well as the bonding and reactivity of chemisorbed species. Various oxides such as Al_2O_3, TiO_2, SiO_2, SiC and CeO_2 have been used extensively to act as supports for optimizing methanation performances [16–19]. The results of Erdöhelyi et al. [20] indicated that the activity of CO methanation was two times higher for TiO_2 supports than MgO. Some researchers suggested that Ni supported on Al_2O_3 catalysts presented higher catalytic activity than that for Ni/SiO_2 catalysts [21–23]. However, the sintering of Ni nanoparticles and carbon deposition formed on the surface of Ni/Al_2O_3 catalysts at higher temperature results in rapid deactivation [24]. Zhang et al. [25] reported that the Ni/SiC catalyst was more stable than the Ni/Al_2O_3 catalyst. Therefore, it is necessary to optimize supports of Ni-based catalysts for improving the activity and selectivity of syngas methanation.

The composite support has many properties such as high redox property, excellent thermal stability and resistance to sintering, which has been promoted to be a very promising catalyst support in heterogeneous catalysis reaction [26,27]. The composite supports have been used widely in many different reactions, e.g., methane reforming [28], hydrodesulfurization [29], olefin polymerization [30], isomerization [31] and Fischer–Tropsch synthesis [32]. However, the composite oxide as support for Ni based catalysts is less employed in the methanation reaction. Fan et al. [33] reported that Mg–Al oxide supported Ni catalysts showed higher activity at low temperature and excellent thermal stability compared to the Ni/MgO and Ni/Al_2O_3 catalysts. The results of Guo et al. [34] indicated that the ZrO_2–Al_2O_3 modified Ni catalyst improved the anti-carbon

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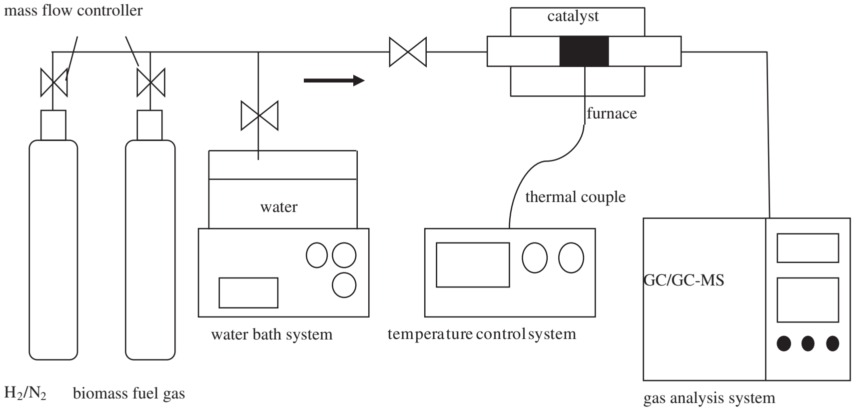

Fig. 1. Schematic diagram of bio-syngas methanation reaction.

deposition and anti-sintering of Ni particles. In addition, the results of Li et al. [35] showed that the Ni/Al_2O_3–CeO_2 catalyst exhibited higher performances for biomass steam gasification than Ni/Al_2O_3. In the present study, the Al_2O_3-based composite supported Ni catalysts were developed for further investigating bio-syngas methanation performances. Because of the complexity of metal–support interaction, several techniques including N_2 physical adsorption, scanning electron microscopy (SEM), temperature-programmed reduction of hydrogen (H_2-TPR), X-ray diffraction (XRD) and a thermogravimetric analyzer (TG) were used together to characterize the catalyst samples.

2. Experimental

2.1. Catalyst preparation

Different single supports (SiO_2, CeO_2 and ZrO_2) were prepared with the following method. Appropriate amounts of $Na_2SiO_3 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Zr(NO_3)_3 \cdot 5H_2O$ were dissolved in distilled water respectively. With continuous stirring, ammonia solution was added dropwise into the solution of $Na_2SiO_3 \cdot 9H_2O$ until its pH reached an approximate value of 8.0, by which the $Si(OH)_4$ precipitate was prepared. According to the similar procedure, the $Zr(OH)_4$ and $Ce(OH)_3$ precipitates were prepared using ammonia as precipitator, respectively. After aging for 12 h at 75 °C, different precipitates were filtered and washed with distilled water until the filtrates were neutral, and then dried overnight at 120 °C and calcined at 500 °C for 5 h, by which SiO_2, ZrO_2 and CeO_2 were prepared, respectively. Different composite supports (Al_2O_3–SiO_2, Al_2O_3–CeO_2 and Al_2O_3–ZrO_2) were prepared using the similar procedure. Two kinds of precipitates were mixed and whisked. The mixed precipitate was aged for 12 h at 75 °C, and then filtered and washed with distilled water completely. Subsequently, solid obtained was dried 12 h at 120 °C and then calcined at 500 °C for 5 h. The complex oxide of Al_2O_3–SiO_2, Al_2O_3–CeO_2 or Al_2O_3–ZrO_2 with the mass ratio of 4:6 was prepared, respectively.

The catalysts were prepared by wet impregnation of the prepared supports using aqueous solutions of nickel nitrate. After impregnation, the samples were dried at 120 °C for 12 h and then calcined in air at 500 °C for 5 h. The Ni loading was 10 wt.% for all catalysts tested in this work.

2.2. Catalyst characterizations

BET surface area, pore volume and average pore diameter of the catalysts were measured by N_2 physisorption at −196 °C using a Micromeritics ASAP 2010 instrument. The samples were degassed under vacuum at 120 °C for 6 h prior to measurement.

Powder X-ray diffraction patterns (XRD) of the catalyst samples were measured on a D/max-RA X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation ($\lambda = 0.154$ nm) operated at 40 kV and 100 mA.

Temperature program reduction with hydrogen (H_2-TPR) was carried out in a U-tube quartz reactor with a hydrogen–argon mixture (containing 5 vol.% of hydrogen) as the reductive gas. The samples (50 mg) were flushed with an argon flow of 50 ml/min at 120 °C to remove water and then reduced in a flow of reductive gas at a rate of 10 °C/min with a programmable temperature controller. Hydrogen consumption was monitored by a thermal conductivity detector (TCD). The effluent gas was passed through a cold trap placed before TCD in order to remove water from the exit stream of the reactor.

The morphology of samples was obtained using an ESEM XL30 (FEI, USA) scanning electron microscopy (SEM). Elemental analysis was carried out to determine the surface composition and distribution of each element on the cross-sectional surface of catalyst particles using an Oxford INCA 300 energy dispersive X-ray spectroscope (EDXS).

Table 1
Textural properties of the fresh single and composite supported Ni catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume (ml/g)	Pore diameter (nm)	Particle size d_{Ni} (nm)[a]	Surface Ni (wt %)[b]
Ni/Al_2O_3	107.9	0.38	14.2	17.6	8.0
Ni/SiO_2	7.8	0.03	13.9	41.8	5.5
Ni/ZrO_2	4.8	0.06	52.7	34.2	9.3
Ni/CeO_2	9.6	0.06	23.9	32.2	12.0
Ni/Al_2O_3–SiO_2	134.5	0.37	11.2	20.0	6.4
Ni/Al_2O_3–ZrO_2	80.4	0.23	11.2	13.7	9.7
Ni/Al_2O_3–CeO_2	80.8	0.22	10.7	10.1	13.4

[a] Calculated by XRD; [b] calculated by EDS.

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