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Short Communication

A novel Ni–Mg–Al-LDHs/γ-Al_2O_3 Catalyst Prepared by in-situ synthesis method for CO_2 reforming of CH_4

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ABSTRACT

A novel Ni–Mg–Al catalyst derived from layered double hydroxides (LDHs) which was prepared on γ-Al_2O_3 by in-situ synthesis method. The catalyst was evaluated by CO_2 reforming of CH_4 and a better catalytic performance was obtained compared with a reference catalyst of Ni/MgO/γ-Al_2O_3 prepared by impregnation. The novel catalyst was also characterized by XRD, N_2-adsorption-stripping, TEM, TG and AAS (atomic absorption spectrum). The results showed that the excellent performance of the catalyst benefited from its larger specific surface area and smaller active-crystal grain which is due to the molecular-order dispersion of active components over the LDHs precursor.

1. Introduction

Syngas prepared by CO_2 reforming of CH_4 is a developing technology for the efficient utilization of resources and environmental friendship [1–4] since the technology not only makes use of the CO_2, but also greatly reduces the consumption of CH_4 to obtain equal amount of CO compared with steam reforming. Nickel-base catalyst is a promising catalyst for the reforming reaction due to its high activity and economic feasibility. However, the deactivation caused by carbon deposition on such catalysts blocks its practical application [5–8].

Layered double hydroxides (LDHs) are lamellar mixed hydroxides containing positively charged main layers and undergoing anion exchange chemistry. Its layered structure is shown in Fig. 1. The general formula of LDHs can be expressed as $[M^{2+}_{1-x} M^{3+}_{x} (OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent positive ions such as Ni^{2+}, Mg^{2+}, Al^{3+} respectively to form the main layer of LDHs with OH-octahedral; A^{n-} is the anion of valence "n" such as NO_3^- to form interlayer with crystal water; the value of "x" is the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$. The identities of M^{2+}, M^{3+}, x and A^{n-} may vary over a wide range, therefore various materials with different physicochemical properties can be prepared by LDHs synthesis method [9–11].

Researches reveal that LDHs have high specific surface area, inherent metal atom dispersion and alkalinity, which is very possible to become a good candidate catalyst material. Serving as catalyst, the LDHs are usually used in organic reaction, such as ethanol steam reforming, degradation of organic pollutant and partial oxidation of methane [12,13]. Recently, it has been attracted in the field of CO_2 reforming of CH_4. A. I. Tsyganok et al. [14] investigated dry reforming of methane over catalysts of nickel-containing Mg–Al LDHs, methane conversion of 95% and CO_2 conversion of 98% were achieved in 6-h reaction. Serrano-Lotina et al. [15] carried out dry reforming of methane over catalyst of La-promoted hydrotalcite clay. The catalyst was deactivated after 120-h test at 700 °C. Also, K. Takehira et al. [16] and K. Nagaoka et al. [17] did auto-thermal reforming of CH_4 over mono- and bimetal catalysts of Ni–Mg–Al hydrotalcite, respectively. However, as low mechanical strength of unsupported LDHs, it seems not to meet the requirements for such high temperature and long time of these reforming reactions.

To improve the mechanical strength of LDH catalyst, as well as its high temperature characteristics, a novel Ni–Mg–Al-LDHs catalyst is provided in this article. The divalent cation was offered by $Ni(NO_3)_2$ and $Mg(NO_3)_2$, and the trivalent cation was offered by γ-Al_2O_3, which also served as a substrate for LDHs to grew on its outer and inner surface. The Ni–Mg–Al-LDHs/γ-Al_2O_3 was calcined and reduced by the atmospheric H_2/Ar cold plasma to obtain target catalyst, which was evaluated by CH_4–CO_2 reforming reaction.

2. Experimental

2.1. Preparation of target catalyst

The LDHs catalyst was prepared by following steps: 10 g of γ-Al_2O_3 support was firstly cleaned by plasma jet and then impregnated with 100 ml aqueous solution of $Ni(NO_3)_2$ (7.0 g), $MgNO_3$(2.5 g) and

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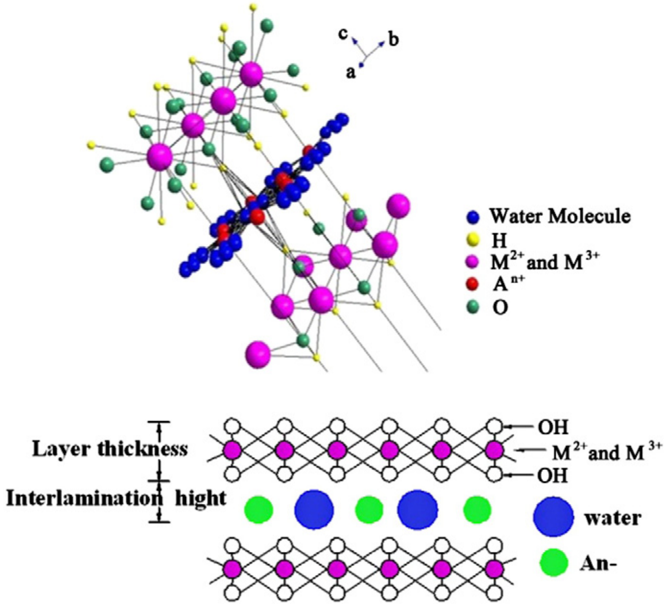

Fig. 1. Schematic representation of the LDHs structure.

NH_4NO_3(1.0 g) by string at 60 °C for 24 h to activate the surface of γ-Al_2O_3, followed by adjusting the PH value of the solution with 1 wt.% ammonia water. Once the PH value reached at 7.5, the impregnated γ-Al_2O_3 was quickly fished out and washed by 100 ml solution of NH_4NO_3 and ammonia water with PH value of 7.5 by Buchner filter. After being aged for 1 h in air, LDHs would organize on the activated surface of γ-Al_2O_3 and then the wet sample was washed with deionized water until the eluate was neutral. After that, the sample was dried at 70 °C for 12 h to obtain Ni–Mg–Al-LDHs precursor. In this case, $Ni(OH)_x$, $Mg(OH)_x$, and $Al(OH)_x$ form LDHs according to determinate chemical stoichiometry, and Ni element is dispersed chemically on γ-Al_2O_3 support. The precursor was calcined at 400 °C for 3 h and reduced by atmospheric cold plasma jet for 15 min to obtain the target catalyst denoted as C-LDHs/γ-Al_2O_3. The evolvement of in-situ synthesized C-LDHs/γ-Al_2O_3 is shown in Fig. 2. Detected by atomic absorption spectrum (AAS), the Ni content of C-LDHs/γ-Al_2O_3 catalyst is 5.5 wt.%. A reference catalyst Ni(12 wt.%)/MgO(2 wt.%)/γ-Al_2O_3, which was optimal catalyst for drying reforming of methane in our lab before, was prepared by step-impregnation method as reported in reference [18].

2.2. Catalyst evaluation

The evaluation test for C-LDHs/γ-Al_2O_3 was carried out in a fixed-bed flow reactor. The reactor made of quartz with 6 mm internal diameter was mounted horizontally inside a tube furnace. 200 mg of catalyst was put in the quartz tube. The bed was controlled at 800 °C and the feed gas composed of CH_4 and CO_2 with the mole ratio of 4/6 and the gas space velocity (GHSV) of 30 l/(g h). The effluent passed through a trap to remove trace water and then was analyzed by an on-line gas chromatography (GC-7900) with TCD detector. The conversions of CH_4 and CO_2 and the selectivities of H_2 and CO were calculated as the following formulas:

$$X(CH_4)\% = \frac{F(CH_4)_{in} - F(CH_4)_{out}}{F(CH_4)_{in}} \times 100\%$$

$$X(CO_2)\% = \frac{F(CO_2)_{in} - F(CO_2)_{out}}{F(CO_2)_{in}} \times 100\%$$

$$S(H_2)\% = \frac{F(H_2)_{out}}{2\left[F(CH_4)_{in} - F(CH_4)_{out}\right]} \times 100\%$$

$$S(CO)\% = \frac{F(CO)_{out}}{\left[F(CH_4)_{in} - F(CH_4)_{out}\right] + \left[F(CO_2)_{in} - F(CO_2)_{out}\right]} \times 100\%$$

Where, X, S and F express the conversion, selectivity and gas flow, respectively.

2.3. Characterizations

X-ray diffraction (XRD) of the precursors and the catalysts was recorded with an X-ray diffractometer (DX-1000, Dandong, China) using Cu Kα X-ray source at 40 kV and 25 mA. Data were recorded over a 2θ range of 2° to 80° with a step size of 0.06° at a scanning speed of 0.06º/s. Transmission electron microscopy (TEM) images were carried out with a FEI Tecnai G^2 20 instrument operated at 200 kV. The BET surface area, pore volume and average pore diameter of the catalysts were measured by N_2 adsorption at the temperature of −196 °C using a Micromeritics ASAP 2020 surface and porosity analyzer. The pore size distribution was calculated from desorption branch of the isotherm by BJH method. Thermogravimetric (TG) analysis of used catalysts was performed on the TGA-Q500 instrument. The sample was loaded onto the thermo-balance and heated from room temperature to 820 °C at 10 °C/min under the oxidative atmosphere (60 ml/min of air). Atomic absorption spectrum (AAS) analysis of catalyst content was performed on the Spectr-AA 220FS (VARIAN company, US).

3. Results and discussions

3.1. The catalytic performance of C-LDHs/γ-Al_2O_3 catalyst

The performance of C-LDHs/γ-Al_2O_3 catalyst and reference catalyst Ni/MgO/γ-Al_2O_3 is presented in Fig. 3. Under the same conditions, both exhibit good activity and stability during 160-h reaction at 800 °C, but the former has more excellent performance. In the whole process, the conversions of CH_4 and CO_2 are about 95% and 75% for Ni/MgO/γ-Al_2O_3 catalyst while they are about 95% and 65% for C-LDHs/γ-Al_2O_3 catalyst. In view of the feeding ratio of $CH_4/CO_2 = 4/6$, the ratios of converted methane and carbon dioxide are about 0.97 and 0.84 by C-LDHs/γ-Al_2O_3 and Ni/MgO/γ-Al_2O_3, respectively. However,

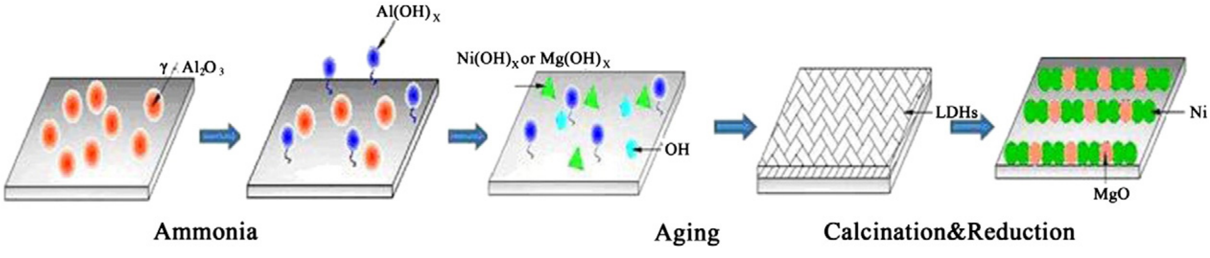

Fig. 2. Evolvement of in-situ synthesized C-LDHs/γ-Al_2O_3.