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La-promoted Ni/Mg-Al catalysts with highly enhanced low-temperature CO_2 methanation performance

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ABSTRACT

In this paper, we investigated the effect of adding lanthanum on the structure and low-temperature activity of the Ni/Mg-Al catalyst for CO_2 methanation. A series of La-doped Ni/Mg-Al catalysts with different La loadings were synthesized by urea hydrolysis method. The results showed that La-promoted NiLax (x = 2, 5 and 8 wt%) catalysts exhibited higher low-temperature activity than the Ni catalyst without La added. In particular, the NiLa5 catalyst performed the best, getting as high as 61% CO_2 conversion and nearly 100% CH_4 selectivity at 250 °C, 0.1 MPa, and a WHSV of 45,000 mL g^{-1} h^{-1}. Characterization results revealed that La effectively increased Ni dispersion and decreased Ni particle size. In addition, La could significantly increase the amount of moderate basic sites, which contributed to enhanced CO_2 adsorption capacity. Compared with coprecipitation method, urea hydrolysis method was proved to be a more efficient approach for the Ni-based catalyst preparation, getting the Ni-based catalyst with higher Ni dispersion, larger CO_2 adsorption capacity and thereby better catalytic performance.

Introduction

Global warming and wastage of conventional resources are the two hot issues in our social and economic development process. As reported, CO_2 makes up 82% of the total greenhouse gases [1], so the transformation of carbon dioxide into valued products is a promising technology to alleviate the global warming as well as the waste of resources. CO_2 hydrogenation to methane, known as CO_2 methanation, is an alternative approach to recycle CO_2 with promising commercial application and environmental benefit [2]. In addition, CO_2 methanation has potential utilization as chemical storage of the excess H_2 generated from renewable energy resources such as solar energy, biomass and hydropower. Many metals including Ru [3–5], Rh [6,7], Ni [8–10] and Co [11] are effective to catalyze CO_2 methanation reaction. Among them, noble metal catalyst Ru or Rh performs the best activity. Unfortunately, the high price and limited resource of these two metals are big problems for their further application. Hence, Ni-based catalysts with comparable catalytic performance and lower cost have been widely investigated for CO_2 methanation. Usually, a high reaction temperature is needed to achieve the maximum CO_2 conversion, which results in undesirable effect

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on the stability/lifetime of the catalysts as well as increased energy input [2]. Therefore, the key point for Ni-based catalyst is to improve the low-temperature catalytic performance for CO_2 methanation [12].

The Ni/Mg-Al catalysts prepared by coprecipitation method have been widely investigated in many reactions, such as CO_2 reforming of CH_4 [13,14] and CO_2 methanation [15] due to their low cost and excellent catalytic performance. It has been confirmed that the addition of MgO to Al_2O_3 contributed to forming $MgAl_2O_4$ phase, which could effectively increase both the reducibility of active species and the CO_2 adsorption capacity [13]. Herein, hydrogen dissociation and carbon dioxide activation could be promoted simultaneously, resulting in improved catalytic activity for CO_2 methanation. However, the low-temperature CO_2 methanation activity of the Ni/Mg-Al catalyst is still less than expected and needs to be improved. Since urea hydrolysis method showed several advantages over coprecipitation method, it was also used for preparing Ni-based catalyst [16]. As a precipitant, urea can form a homogeneous solution with metal nitrates at low temperature. As temperature increases, urea is decomposed slowly with gradual increase of pH value in the solution. This process can sustain the pH value in every part of the solution at a homogeneous level and overcomes the drawback of coprecipitation method [17].

Promoter plays a crucial role in electron mobility, crystal structure, metal dispersion and thermal stability of heterogeneous catalysts. Some promoters such as Ce [10], Zr [18], V [19], Mn [20] and La [21] have been studied in Ni-based catalysts for CO_2 methanation. Among them, La was found a good promoter that can effectively improve Ni dispersion and the amount of reduced active nickel species [21,22]. In addition, La as an electron promoter can modify the electron environment surrounding Ni atoms, which facilitates CO_2 activation [22]. However, there is little information reported about the effect of La species on the Ni/Mg-Al catalyst prepared by urea hydrolysis method for CO_2 methanation, which should be further studied since La is expected to be a potential promoter for enhancing CO_2 methanation performance at low temperature.

In this study, La-doped Ni/Mg-Al catalysts were prepared by urea hydrolysis method for CO_2 methanation process. The catalysts were characterized by a series of techniques including inductively coupled plasma optical emission spectrometer (ICP-OES), N_2-physisorption (BET), X-ray diffraction (XRD), transmission electron microscopy (TEM), hydrogen temperature programmed desorption (H_2-TPD), hydrogen temperature programmed reduction (H_2-TPR) and carbon dioxide temperature programmed desorption (CO_2-TPD). The effects of La loading, preparation method and Ni loading on the catalytic performance as well as the structure-activity relationship were investigated.

Experimental

Catalyst preparation

All chemicals with analytical grade including magnesium (II) nitrate hexahydrate ($Mg(NO_3)_2\cdot 6H_2O$), aluminum(III) nitrate nonahydrate ($Al(NO_3)_3\cdot 9H_2O$), nickel (II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$), lanthanum (III) nitrate hexahydrate ($La(NO_3)_3\cdot 6H_2O$) and urea were purchased from Tianjin Kermel Co., LTD of China and used without any further purification.

Urea hydrolysis method was used to synthesize the catalysts with 15 wt% Ni and 55 wt% MgO. Firstly, specified amounts of $Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $La(NO_3)_3\cdot 6H_2O$ and urea as the precipitant were dissolved in deionized water to form a homogeneous and transparent solution. And then the solution was transferred into an autoclave and crystallized statically at 110 °C for 10 h, followed by filtering and washing with deionized water until the pH value of the filtered solution became 7. Finally, the obtained solid was dried at 110 °C for 12 h and calcined at 600 °C for 6 h with a heating rate of 3 °C/min. The prepared catalyst was denoted as NiLax (x = 0, 2, 5 and 8) where x represented the La loading.

For comparison, the NiLa5-C catalyst with 15 wt% Ni, 55 wt % MgO and 5 wt% La was prepared by coprecipitation method as described in the literature [23].

Catalytic activity test

The catalytic activity tests for CO_2 methanation were performed in a fix-bed reactor equipped with an 8 mm I.D. quartz lining tube under atmospheric pressure. The catalyst bed was filled with 0.2 g catalyst (20–40 mesh) diluted with 0.4 g quartz sand (40–60 mesh). Prior to the reaction, the fresh catalysts were reduced at 700 °C for 2 h with the mixed gas H_2 (30 mL/min) and N_2 (30 mL/min). The $H_2/CO_2/N_2$ gas mixture (volume ratio = 72/18/10) was introduced into the reactor with the total flow rate 150 mL/min, which is equivalent to a WHSV of 45,000 mL g^{-1} h^{-1}. N_2 was chosen as the internal standard for GC quantitatively analysis, making up 10% of the total flow rate. The volume ratio of H_2/CO_2 was set as 4. During reaction, the gas mixture composition was analyzed by a gas chromatograph equipped with a TCD detector. CO_2 conversion and CH_4 selectivity were calculated according to equations (1) and (2):

$$X_{CO_2}(\%) = \frac{F(CO_2)_{in} - F(CO_2)_{out}}{F(CO_2)_{in}} \times 100 \quad (1)$$

$$S_{CH_4}(\%) = \frac{F(CH_4)_{out}}{F(CO_2)_{in} - F(CO_2)_{out}} \times 100 \quad (2)$$

where F_{in} and F_{out} are the flow rates (mL/min) of the inlet and outlet gas mixture, respectively.

Catalyst characterization

The elemental analysis of the catalysts was performed on an inductively coupled plasma optical emission spectrometer (ICP-OES) (VISTA-MPX, Varian) to investigate the actual loadings of Ni and La. About 20 mg catalyst was dissolved in the mixed acid solution (3 mL HCl and 1 mL HNO_3) and then the solution was diluted to 50 mL with deionized water before measurement.

N_2 adsorption-desorption was performed by a TriStar 3000 (Micromeritics, USA) at −196 °C. Prior to measurement, the samples were degassed by N_2 at 90 °C for 1 h and 300 °C for 3 h. The specific surface area was calculated using Brunauer