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Preparation of La_2NiO_4/ZSM-5 catalyst and catalytic performance in CO_2/CH_4 reforming to syngas

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Abstract

A La_2NiO_4/ZSM-5 catalyst was prepared by the sol–gel method, which ensured high dispersion of the metal and high activity in the CO_2 reforming of methane. The catalytic performance, catalyst stability and coke deposition as well as the influence of the doped La species on the Ni/ZSM-5 catalyst were investigated. The results show that the conversion of CO_2 and CH_4 to syngas and the selectivity of CO and H_2 observed over the La_2NiO_4/ZSM-5 catalyst were significantly higher than those over a Ni/ZSM-5 or $La_2NiO_4/\gamma\text{-}Al_2O_3$ catalyst. Such results suggest that the doping of the rare earth ion (La^{3+}) in the ZSM-5 not only enhanced the stability of the catalyst, but also increased the catalytic activity. In addition, the catalysts were characterized by X-ray diffraction (XRD), BET and thermogravimetic and differential thermal analysis (TG/DTA). The X-ray diffraction (XRD) studies revealed that the prepared catalyst, La_2NiO_4, exhibited a typical spinel structure and was uniformly dispersed both on the surface and in the ZSM-5 zeolite channels. During the CO_2/CH_4 reforming, the La_2O_3 generated from the La_2NiO_4 decomposition was transformed into $La_2O_2CO_3$ in an atmosphere of CO_2, which promoted CO_2 adsorption on the surface of the catalyst. The TG/DTA results indicate that the amount of carbon deposition on the La_2NiO_4/ZSM-5 catalyst was smaller than the amount on the Ni/ZSM-5 catalyst, and that there were at least two kinds of carbon deposition on the used La_2NiO_4/ZSM-5 catalyst. However, only one kind of carbon deposition existed on the used Ni/ZSM-5 catalyst.

Keywords: La_2NiO_4/ZSM-5 catalyst; Dispersion of Ni; Coke formation; Sol–gel technique; CO_2/CH_4 reforming

1. Introduction

In recent years, there has been an increasing interest in the catalytic transformation of carbon dioxide, a greenhouse gas, into more useful or valuable chemicals; especially, important is the CO_2 reforming of methane, the cheapest carbon-containing feed stock, into synthesis gas (i.e. CO + H_2), which can be used in chemical energy transmission systems or utilized in the Fisher–Tropsch synthesis to produce liquid hydrocarbons [1,2]. The CO_2/CH_4 reforming has been studied over numerous supported metal catalysts, such as Ni-based [3–7] and noble metal catalysts [8–10]. However, when one considers the high cost and limited availability of noble metal, it is more practical, from the industrial standpoint, to develop Ni-based catalysts that not only possess high stability and activity, but also are able to resist carbon deposition during the reaction. A number of studies on CO_2/CH_4 reforming over supported Ni [3,11,12] catalysts have indicated that metal- doped supports, such as La-doped Ni/Al_2O_3 [3] and Ni/yttria-doped ceria catalyst [11] play an important role in the catalytic activity and in the coking resistance of the catalysts. The effect of lanthanum doped supports on nickel catalysts to suppress carbon deposition has been attributed to the dispersion of the doped species on the Ni surface, which segregates the active centers at the metal-support interfaces [13,14]. Although the effect of a doped support on nickel catalysts has been recognized, there have been very few reports of CO_2/CH_4 reforming over rare earth-doped Ni/ZSM-5 catalysts. Because of its large specific surface area and its well-defined structure, ZSM-5 is an ideal candidate for a catalyst support, since it allows a high dispersion of active metal on the surface. Metal atoms on the surface of the support are

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segregated into tiny islands. The driving force for this is to minimize the surface free energy and to maximize spreading on the support.

Previously, we reported the catalytic performance of La_2NiO_4/γ-Al_2O_3 [3,15] and La_2NiO_4 [6] catalysts for CO_2/CH_4 reforming. It was found that the La_2NiO_4 catalyst exhibited excellent catalytic activity and stability. However, the specific surface area of these catalysts did not meet the requirements for industrialization. The aim of our present work was to investigate the activity and stability of La_2NiO_4/ZSM-5 and Ni/ZSM-5 catalysts by introducing ZSM-5 zeolite for the CO_2/CH_4 reforming to syngas. In addition, the effect of La doping on the Ni/ZSM-5 catalyst as well as the optimal reaction conditions (gas hour space velocity (GHSV) and reaction temperature) were investigated. Thermogravimetry (TG) was used to study the nature of the carbon deposition on La_2NiO_4/ZSM-5 (sol–gel) and Ni/ZSM-5 (*imp*) catalysts after the CO_2/CH_4 reforming.

2. Experimental

2.1. Preparation of the catalysts

The La_2NiO_4/ZSM-5 catalyst was prepared from Ni $(NO_3)_2\cdot 6H_2O$, La $(NO_3)_3\cdot 6H_2O$ and ZSM-5 by means of a sol–gel technique. Nickel nitrate (1.22 g) and lanthanum nitrate (3.44 g) were dissolved in de-ionized water, and then citric acid and ethylene glycol were added to the solution. The molar amounts of citric acid and ethylene glycol were 1.5 times that of the total metal ions. The solution was then heated to 333 K with constant stirring, and ZSM-5 zeolite (2.0 g) was added to the solution. After the removal of the water by evaporation, a translucent green gel was formed. Next, the co-gel obtained was aged and dried in a beaker at room temperature (RT) for 3 days. This was followed by a two-step decomposition: first heating at 773 K for 5 h and then calcinating at 1073 K in air for 5 h, according to the method reported in the literature [6]. This sol–gel generated catalyst will be referred to as "La_2NiO_4/ZSM-5" hereafter. For comparison, Ni/ZSM-5 catalysts were prepared by impregnating ZSM-5 supports with an appropriate amount of an aqueous solution of Ni $(NO_3)_2\cdot 3H_2O$ (1.22 g). After the excess water was evaporated at 353 K, the catalyst was calcinated using the method mentioned above. In both the sol–gel- and imp-generated catalysts, the loaded amount of nickel on the support was ca. 9%. All catalysts were finally pressed, crushed and sieved through 40–60 meshes.

2.2. Characterization of the catalyst

The structure of the catalysts was characterized using X-ray diffraction (XRD), BET and thermogravimetic and differential thermal analysis (TG/DTA). The powder XRD patterns of the catalysts were recorded on a BDX3300 diffractometer with a Cu Kα radiation source (λ = 1.54056 Å) at a voltage of 30 KV and a current of 20 mA. The average size of Ni particles was calculated using the Scherrer equation. BET measurements were conducted using N_2 as the adsorbate with a NOVA-1200 instrument at 77 K. All samples were degassed with N_2 for 2 h at 623 K before measurement. The TG/DTA studies were carried out under an oxidative atmosphere (20 mL/min of air) with a WCT-1 analyzer. About 8 mg of sample was heated from RT to 1073 K at 15 K/min.

2.3. CO_2 reforming of CH_4

CO_2 reforming of methane was carried out at atmospheric pressure in a conventional fixed-bed quartz tubular reactor. The catalyst was placed between two quartz-wool plugs in the reactor, and the thermocouple by which the reaction temperature was controlled was placed at the center of the catalyst bed. Typically, 100 mg of the catalyst was reduced in a flow of H_2 at 973 K for 1 h before the reaction. The CO_2/CH_4 reforming was carried out at 973K with a GHSV of 4.8×10^4 mL h^{-1} $g_{cat}{}^{-1}$. The effluent was analyzed using on-line gas chromatography (102G) with a thermal conductivity detector (TCD). A TDX-01 column was used for the separation of H_2, CO, CH_4 and CO_2. The conversion of CO_2 or CH_4 was defined as converted CO_2 or CH_4 per total amount of CO_2 or CH_4. The selectivity of CO (calculated based on total carbon conversion) and H_2 (assuming that a molar CH_4 is converted into 2 mol. of H_2), as well as the yield of carbon (including the carbon of heavier hydrocarbons condensable in the transfer line) are defined as follows:

$$S_{CO}(\%) = 100 \times [CO]_o/(([CO_2]_i - [CO_2]_o) + ([CH_4]_i - [CH_4]_o))$$

$$S_{H_2}(\%) = 100 \times [H_2]_o/(2 \times ([CH_4]_i - [CH_4]_o))$$

$$Y_C(\%) = 100 \times (([CO_2]_i + [CH_4]_i) - ([CH_4]_o + [CO_2]_o + [CO]_o))/([CO_2]_i + [CH_4]_i)$$

where $[CO_2]_i$ and $[CH_4]_i$ are inlet flow rates, and $[CH_4]_o$, $[CO_2]_o$, and $[CO]_o$ are outlet flow rates [6].

3. Results and discussion

3.1. Structure of the Ni supported catalysts

The specific surface areas of the catalysts and the average sizes of Ni particles are listed in Table 1. The results indicate that the specific surface area of La_2NiO_4/ZSM-5 catalyst (119.7 m^2/g) is much larger than that of the La_2NiO_4/γ-Al_2O_3 catalyst reported in the literature (38–55 m^2/g) [3]. This is due to the high specific surface area (340 m^2/g [16]) and the stable structure of the ZSM-5 support. For the