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One-pot synthesis of Ni-nanoparticle-embedded mesoporous titania/silica catalyst and its application for CO_2-reforming of methane

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Abstract

Ni-nanoparticle-embedded mesoporous titania/silica catalyst was successfully synthesized in a one-pot process using homogeneous impregnation in sol–gel-derived titanium-silica gel, without any other organic additives and/or templating agents. The catalyst with NiO loading of 10 wt% and TiO_2/SiO_2 (wt) of 50:50 is highly catalytic active and stable for CO_2 reforming of methane and its physico-chemical properties were investigated by means of BET, H_2-TPR, XRD, TEM and TG/DTA techniques, respectively. Under the condition of an atmospheric pressure at 850 °C and a gas hour space velocity (GHSV) of 1.8×10^4 ml h^{-1} g_{cat}^{-1}, the conversion of CH_4 and CO_2 over 10 (wt%) $NiO/TiO_2–SiO_2$ (50:50) catalyst remained almost constant, at about 88% and 97%, for 30 h, respectively. The high activity and stability are attributed to the strong metal-support interactions, such as in $Ni_{2.44}Ti_{0.72}Si_{0.07}O_4$.

Keywords: $Ni/TiO_2–SiO_2$ catalyst; Sol–gel; CO_2-reforming of methane

1. Introduction

Carbon dioxide reforming of methane recently has received considerable attention since it converts greenhouse gases (methane and carbon dioxide) simultaneously to useful syngas with a low hydrogen/carbon monoxide ratio, which is suitable for Fischer–Tropsch synthesis [1,2]. In the previous studies, supported metal catalysts such as Ni, Ru, Rh, Pd, Ir and Pt are known as active catalysts for CO_2 reforming of methane [1–4]. Noble metal catalysts show good resistance to carbon formation compared to nickel catalysts, but their low availability and high cost make them unsuitable for industrial size operations. Thus nickel is considered as the most promising catalyst for CO_2/CH_4 reforming due to low price; however, nickel catalysts easily induced formation of carbon via the Boudouard reaction ($2CO \rightarrow C + CO_2$) or methane decomposition ($CH_4 \rightarrow C + 2H_2$), causing catalyst deactivation and plugging of a reactor [5].

Several studies have been performed in order to develop nickel catalysts with improved performance; lower coke deposition on the metal surface and higher stability against metal sintering [6–14]. It has been reported that the nature of the supports significantly affects the catalytic performance of Ni catalysts in CO_2/CH_4 reforming [15,16]. Strong metal-support interactions have been proven to reduce nickel sintering which can accelerate coke formation [17]. Therefore the modification of catalyst supports is efficient way to improved Ni catalysts. Furthermore, optimizing metal and support properties can be directly linked to improved catalyst method preparations.

Titanium silicate mesoporous mixed oxides, in which titanium is substituted into a silicate framework and the

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interaction between titania and silica can produce new active sites [18], is an important material that is used as a support for catalysts [19]. However, the Ni catalyst of TiO_2–SiO_2 (TiO_2–SiO_2 will be referred to as "TS" hereafter) as a support for CO_2/CH_4 reforming has not been reported. Further, besides the troublesome and time-consuming preparation procedures and the very severe pretreatment conditions needed to prepare Ni-embedded mesoporous inorganic materials generally by introducing Ni metal precursors into the mesoporous materials via impregnation [20] or ion exchange [21] or by directly incorporating Ni metal precursors into sols [22], an organic additive and/or a templating agent must be used to obtain mesostructure in the resulting inorganic materials.

Herein we describe a novel convenient method for preparing highly active Ni/TS catalyst in a one-pot process using homogeneous impregnation in sol–gel-derived titanium-silica gel for CO_2/CH_4 reforming, without any other organic additives and/or templating agents.

2. Experimental

2.1. Catalyst preparation

Ni/TS composite xerogel catalyst was prepared using impregnation combined sol–gel method. Nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), tetrabutyl titanate (TBOT) and teraethylorthosilicate (TEOS) were used as precursors of nickel, titania and silica, respectively. Ethanol was used as a mutual solvent. The corresponding molar ratios of NiO:SiO_2:TiO_2:EtOH:H_2O were z:x:y:7(x+y):10(x+y). In a typical procedure, $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in a solution containing H_2O and half of the required EtOH by stirring for 0.5 h. After homogenization of the mixture solution, the pH (value) was adjusted to ~2 by adding diluted HCl, and the TEOS was prehydrolyzed for 3 h in this strongly acidic solution. Then the mixed solution of TBOT and half of the required EtOH was added dropwise into the partially hydrolyzed TEOS solution, followed stirring for 2 h. After that, the mixture was refluxed by stirring at 90 °C for 18 h, and the resultant wet gel was dried at 120 °C for 12 h. All samples were calcinationed at 700 °C in air for 5 h and marked with xNi/TS(y), in which x displayed the weight percentage of NiO in fresh samples and y displayed the TiO_2/SiO_2 (wt). All catalysts were finally pressed, crushed and sieved through 24–40 meshes.

2.2. Catalyst characterization

The BET specific surface area was determined by nitrogen physisorption data at −196 °C on a Thermo Finnigan Sorptomatic 1990 instrument. The total pore volume and the average diameter of pore were obtained by the Barrett–Joyner–Halenda (BJH) method. Temperature programmed reduction (TPR) measurement was carried out with 50 mg of the calcined catalyst from room temperature to 800 °C, at a rate of 10 °C min^{-1} in flowing H_2/Ar gas (10:90 v/v mixture with a total flow of 30 ml min^{-1}). The hydrogen consumption was monitored with a TCD. The XRD patterns were collected on a Rigaku D/Max-2400 X-ray diffractometer equipped with a rotating anode and using Cu Kα radiation (40 kV, 30 mA). The transmission electron microscopy (TEM) micrographs of used catalyst were observed on a Hitachi H-600 microscopy operating at 100 kV. The TG/DTA studies were carried out on a Perkin Elmer Pyris Diamond TG/DTA thermogravimeter. A spent catalyst was heated from room temperature to 800 °C at the rate of 10 °C min^{-1} under static air. Nickel loading in the catalyst was measured by atomic absorption spectroscopy (AAS;Varian,Spectr AA-20 Plus). The NiO particle size was determined using the Scherrer equation.

2.3. Catalyst testing

The CO_2-reforming of CH_4 was carried out in a vertical fixed-bed flow reactor made of quartz glass with an inner diameter of 12 mm and a length of 150 mm, under an atmospheric pressure. The reactant gas mixture with CO_2:CH_4 volume ratio of 1:1 was fed at 60 ml min^{-1} during the reaction. The catalyst samples were reduced in hydrogen stream (30 ml min^{-1}) at 700 °C for 1 h before the reaction. The gaseous effluent was cooled in an ice–water trap and analyzed by an on-line gas chromatography (PE, Autosystem XL) with thermal conductivity detector (TCD) using a TDX-01 packed column.

3. Results and discussion

3.1. Catalytic activity of Ni/TS catalysts containing different Components

The CO_2 reforming reaction data over the 10 wt% NiO/TS catalysts with various TiO_2/SiO_2 weight ratios are presented in Table 1. The 10Ni/TS (50:50) catalyst exhibited much higher catalytic activity and stability. Furthermore, CO_2 conversion was always greater than that of CH_4 because the production of synthesis gas from CH_4 and CO_2 was probably influenced by the occurrence of the reverse water–gas shift (RWGS) reaction and H_2/CO ratio was approximately constant and equal to 1 over the 10Ni/TS (50:50) catalyst [23]. On the contrary, it also can be observed that the catalysts containing Ni supported on pure oxides (TiO_2 and SiO_2) presented lower catalytic activities. In addition, rapid deactivation was observed from the start in the reaction process over 10Ni/TS (70:30) and 10Ni/Ti so as to plug a reactor. The high H_2/CO ratio (1.15–1.29) over the 10Ni/TS (70:30) and 10Ni/Ti catalysts within 1 h of reaction, shown in Table 1, indicates that carbon deposition is occurring [24]. In addition, a little higher CH_4 and CO_2 conversion may thus result from significant coke deposition, since coke deposition was not included in the calculation of catalytic activity [25]. Then the poor catalytic performance may be attributed to carbon deposition on the catalyst surface.