



Sol–gel synthesis of titanium oxide supported nickel catalysts for hydrogen and carbon production by methane decomposition



Yi Shen ^{a, b, *}, Aik Chong Lua ^{b, **}

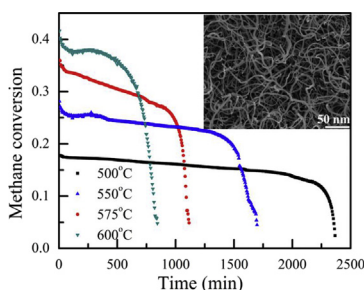
^a College of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, PR China

^b School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798 Republic of Singapore

HIGHLIGHTS

- TiO₂-supported NiO was synthesized using sol–gel method for hydrogen production.
- The Ni/TiO₂ catalyst showed enhanced catalytic activity for methane decomposition.
- TiO₂ support showed a critical role on the high activity of the catalysts.
- A methane conversion of 0.16 and a carbon yield of 312 g C per g Ni were achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 November 2014

Received in revised form

14 December 2014

Accepted 9 January 2015

Available online 10 January 2015

Keywords:

Hydrogen production

Catalytic decomposition of methane

Supported nickel catalysts

Titanium oxide support

Sol–gel synthesis

Metal-support interaction

ABSTRACT

TiO₂-supported NiO hybrids have been synthesized by the sol–gel method and further processed into catalysts for hydrogen production by methane decomposition. The structures of the metal oxides and catalysts are characterized using field emission electron microscopy, transmission electron microscopy, X-ray diffraction, energy dispersive X-ray spectroscopy and N₂ adsorption-desorption test. The catalytic performance of the catalysts is evaluated in terms of hydrogen yield rate, methane conversion and carbon yield. It is found that the TiO₂-supported catalysts show better catalytic performance when compared with the unsupported catalyst, which is attributed to the uniform dispersion of ultrafine nickel particles as well as the appropriate metal-support interaction. The catalyst performance is dependent on the ratio of NiO and TiO₂. The 1NiO–2TiO₂ exhibits the highest carbon yield of 321.1 g C g⁻¹ Ni at 500 °C. The structures of the produced carbons are characterized by transmission electron microscopy and X-ray diffraction. It is found that the resulting filamentous carbon materials exhibit uniform diameters and various morphologies including hollow tube, platelet, bow-like and herringbone structures.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author. College of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, PR China

** Corresponding author. School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Republic of Singapore.

E-mail addresses: feyshen@scut.edu.cn (Y. Shen), maclua@ntu.edu.sg (A.C. Lua).

1. Introduction

Due to the ever-increasing energy consumption and great concern on environmental impacts of fossil fuels, renewable energy technologies have attracted extensive attention to reduce the emission of greenhouse gases and boost the global economic development. Being an efficient and environmentally friendly energy carrier, hydrogen has been considered to be a promising replacement for fossil fuels [1]. Hydrogen fueled fuel cells are promising candidates

for potential applications in transportation and portable electronic devices due to their inherent simplicity of operation, high energy efficiency, and low emissions [2]. To date, many efforts have been devoted to developing efficient, economical, and environmentally-friendly approaches for hydrogen production [3]. For several decades, steam reforming of natural gas has been the most widely used process for hydrogen production. However, hydrogen production by this multistep process results in high emission of carbon dioxide and the end-products always contain some quantities of carbon monoxide, which prevents the direct utilization of the resulting hydrogen in fuel cells. Alternatively, catalytic decomposition of methane (CDM) is technologically a simple one-step process with negligible or no carbon dioxide emission [4–7]. The produced CO-free hydrogen is favorable for fuel cell applications without further separation and purification. In addition, carbon is sequestered in the form of a stable valuable solid carbon rather than as a notorious greenhouse gas in the form of carbon dioxide.

So far, nickel has been identified as the most active catalyst for CDM process due to its unique 3d-orbital structures. However, the efficiency of single nickel catalyst is significantly limited by the low reaction temperatures. The sintering and encapsulation of nickel particles inevitably occur at high reaction temperatures, leading to low activity and poor stability. To enhance the operating temperature of Ni, one common strategy is to utilize support materials such as Al_2O_3 [8], SiO_2 [9], zeolite [10] and carbon nanofibers (CNFs) [11]. It has been confirmed that the utilization of such support materials, not only promotes the dispersion of nickel nanoparticles, but also increases its stability, resulting in enhanced methane conversions and carbon yields. For instance, Li et al. [12] prepared the catalysts via co-precipitation method using Feitknecht compound precursors. It was found that the Al_2O_3 -supported NiO catalyst was active while the unsupported NiO catalyst was inactive for CDM. Takenaka et al. [13] prepared a 40 wt.% Ni/ SiO_2 catalyst which showed an outstanding carbon yield of $491 \text{ g C g}^{-1} \text{ Ni}$ at 500°C . Gallego et al. [14] prepared the La_2O_3 -supported nickel catalyst from LaNiO_3 , which showed a remarkable methane conversion of 75% at 700°C . Recently, Shen and Lua [15] prepared carbon nanotube-supported nickel (Ni/CNT) catalysts by the polyol-assisted reduction method. The resulting Ni/CNT catalyst showed a carbon yield of $358 \text{ g C g}^{-1} \text{ Ni}$ and methane conversion of 37% at 575°C . It is demonstrated that the catalyst support greatly affects the dispersion and stability of nickel nanoparticles and that the selection of catalyst supports with appropriate metal-support interaction is critical to achieve high catalytic performance of the catalysts. Takenaka et al. [16] prepared a series of supported nickel catalysts by an impregnation method and found that the catalyst supported by SiO_2 , TiO_2 and graphite showed better catalytic performances than those supported by Al_2O_3 , MgO and $\text{SiO}_2\text{-MgO}$. It was suggested that the activity of the catalysts was closely related to the states of nickel. In addition, Ashok et al. [17] employed an incipient wetness impregnation method to prepare supported nickel catalysts by HY, USY, SiO_2 and SBA-15. The authors found that the 30 wt.% Ni/HY catalyst showed superior catalytic performance, resulting from the Ni particle size and the acidity of the support. So far, oxides, such as SiO_2 [9,16–18], Al_2O_3 [8,12,16,19], TiO_2 [9,16], CeO_2 [20,21], MgO [16,22–24] and spinel MgAl_2O_4 [25–27], zeolite [10,17,28] and carbon-based materials [11,15,29] have been widely studied as supporting materials in the preparation of catalysts for CDM.

Apart from catalyst support, the catalytic performance of catalysts is also dependent on the catalyst preparation method. Li et al. [20] prepared a 10 wt.% Ni/ CeO_2 catalyst using different methods and found that the catalysts prepared by impregnation and deposition-precipitation exhibited higher hydrogen formation rates than that prepared by the co-precipitation method. Up to now, considerable work has focused on catalyst preparation.

Impregnation [30–32], co-precipitation [33,34], and fusion method [35–37] have been extensively used to prepare active catalysts. Sol-gel technique is a well-established method to prepare various catalysts with high porosities and uniform dispersions of active components on supports [38]. However, limited work has been reported on the syntheses of catalysts by the sol-gel method for the CDM process [39,40]. It has been reported that the supported catalysts obtained by the sol-gel technique exhibit strong metal-support interaction, which can stabilize the active component at high reaction temperatures. In this work, TiO_2 -supported nickel oxide was synthesized by the sol-gel method using a nontoxic and biodegradable ethoxylated sorbitan ester as the structure-directing agent. After calcination and reduction, the TiO_2 -supported nickel hybrids were evaluated as catalysts for the CDM process. The structures and catalytic performance of the catalysts were fully studied. The effects of TiO_2 supports on the catalytic activity of the catalysts were also investigated.

2. Experimental section

2.1. Synthesis of NiO– TiO_2 hybrids

TiO_2 supported NiO mixed oxides were synthesized using the sol-gel method as reported in the authors' previous work [41]. In brief, 4 ml of surfactant ethoxylated sorbitan ester, namely, Tween 20, 40 mmol of acetate acid, and 24 mmol of HCl were dissolved in 60 mL of ethanol to form a stable solution. 30 mmol of metal precursors, i.e., nickel (II) nitrate hexahydrate and titanium (IV) butoxide were then added into the solution and subjected to vigorous stirring. The mixture was aged at 60°C in an oven for 2 days. After the complete evaporation of ethanol, the as-synthesized composite was calcined at 500°C in air for 5 h to obtain the oxides. Three different mole ratios of nickel (II) nitrate hexahydrate and titanium (IV) butoxide in the feedstock, that is, 1:2, 1:1 and 2:1, were used to prepare the hybrids, which were denoted as 1NiO–2 TiO_2 , 1NiO–1 TiO_2 and 2NiO– TiO_2 , respectively. For a good comparison, unsupported nickel oxide was also prepared.

2.2. Catalyst characterization

The morphologies of the samples were observed using a field emission scanning electron microscope (JSM-7600F, JEOL) and a transmission electron microscope (JSM2010, JEOL). The crystalline structures of the samples were examined by X-ray diffraction (XRD) patterns, which were obtained by a diffractometer (PW1830, Philips) equipped with $\text{CuK}\alpha$ radiation of 1.54 \AA . The N_2 adsorption-desorption isotherms were obtained using the accelerated and surface area porosimetry system (ASAP 2020, Micromeritics). The surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the pore volume was calculated by the Barrett–Joyner–Halenda (BJH) method. An energy dispersive X-ray (EDX) analyzer was used to analyze the elemental composition of the samples.

2.3. Catalytic activity characterization

The catalytic activities of the catalysts were tested by an experimental set-up as reported in the authors' previous works [42,43]. In a typical process, 50 mg of the oxide sample was loaded into the mid-section of a quartz tube reactor having an internal diameter of 10 mm and a length of 800 mm. The reactor was heated by an electric furnace fitted with a temperature programmed controller and the temperature of the reactor was accurately monitored using a K-type thermocouple. The flow rates of the gases were measured and controlled by mass flowmeters (Alicat

Download English Version:

<https://daneshyari.com/en/article/7733375>

Download Persian Version:

<https://daneshyari.com/article/7733375>

[Daneshyari.com](https://daneshyari.com)