INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

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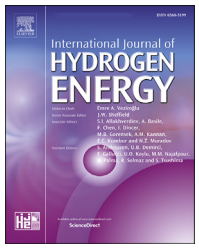

Synthesis of nanocrystalline mesoporous $Ni/Al_2O_3–SiO_2$ catalysts for CO_2 methanation reaction

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ARTICLE INFO

Article history:
Received 2 May 2018
Received in revised form
17 August 2018
Accepted 24 August 2018
Available online xxx

Keywords:
Nanocatalyst
Sol-gel
Alumina-silica composite
Methanation
Carbon dioxide

ABSTRACT

A series of nanocrystalline mesoporous $Ni/Al_2O_3–SiO_2$ catalysts with various SiO_2/Al_2O_3 molar ratios were prepared by the sol-gel method for the carbon dioxide methanation reaction. The synthesized catalysts were evaluated in terms of catalytic performance and stability. The catalysts were studied using XRD, BET, TPR and SEM. The BET results indicated that the specific surface area of the samples with composite oxide support changed from 254 to 163.3 m^2/g, and an increase in the nickel crystallite size from 3.53 to 5.14 nm with an increment of Si/Al molar ratio was visible. The TPR results showed a shift towards lower temperatures, indicating a better reducibility and easier reduction of the nickel oxide phase into the nickel metallic phase. Furthermore, the catalyst with SiO_2/Al_2O_3 molar ratio of 0.5 was selected as the optimal catalyst, which showed 82.38% CO_2 conversion and 98.19% CH_4 selectivity at 350 °C, high stability, and resistivity toward sintering. Eventually, the optimal operation conditions were specified by investigating the effect of H_2/CO_2 molar ratio and gas hourly space velocity (GHSV) on the catalytic behavior of the denoted catalyst.

Introduction

Widespread use of energy sources and topical need to deduction carbon oxides emission have led to progress in methanation applications since 10 years ago [1,2]. On the other hand, carbon dioxide is the most common greenhouse gas in the atmosphere, and its uncontrolled emission leads to global warming and outstanding climate change [3,4]. Subsequently, serious actions need to be implemented to reduce the amount of CO_2 emerged by combustion of fossil fuels. Accordingly, CO_2 separation, capture and its storage have gained attention in industries [5]. Besides, ethanol, methanol, formic acid, formates, dimethyl ether, higher hydrocarbons, etc. can be produced by means of carbon dioxide methanation [6,7]. The purification of hydrogen from carbon oxides in petrochemical and refining industries, where the high purity hydrogen is needed for the process is another application of methanation reaction [7,8].Various metals in methanation reaction including transition and noble metals as an active

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https://doi.org/10.1016/j.ijhydene.2018.08.163
0360-3199/

phase and Al_2O_3 [9], SiO_2 [10], ZrO_2 [11] and zeolites [12] as the support have been studied. Among these catalysts, the nickel based catalysts are considered as commercial catalysts, due to low price, high availability and acceptable catalytic performance [7,13]. Among the supports, alumina has unique characteristics such as high specific surface area and appropriate interaction with active metal [9,14]. These characteristics can be modified and lead to higher activity and stability in this reaction [15].

The performance of the Ni-based catalysts is related to various factors such as the content of Ni, type of promoters and carriers, catalyst synthesis method, and reaction conditions [16]. The physicochemical characteristics of the Ni-based catalysts can be influenced by the catalyst preparation method. There are several methods for the preparation of nickel-based catalysts [17]. Among these methods, it is noteworthy to elucidate that the prepared samples by sol-gel route have higher stability and the dispersion of nickel is higher compared to the other preparation methods such as co-precipitation, deposition-precipitation, etc. [18]. In fact, sol-gel method can be considered as an effective method to produce powders with high purity, high surface area, chemical homogeneity and the ability of the control of the particle size [18–21].

The catalyst support has an important role on the morphology of the active phase, adsorption ability and catalytic features [22]. The strong interaction between Ni and Al_2O_3 and the formation of $NiAl_2O_4$ spinel with low degree of reducibility is one of the most important challenges in development of the appropriate catalysts for methanation reaction. The modification of the catalyst support is one of the best ways to overcome this problem and prepare a catalyst with higher activity and reducibility [23]. Different support modifiers (ZrO_2, SiO_2, MgO, La_2O_3, CeO_2, and TiO_2) have been used and the catalysts possessed better conversion, higher redox property, high thermal stability and resistance against sintering due to their excellent properties. Favorable aspects of using composite oxide supports are the inherent desirable properties and the synergetic effect of all the individual supports. On the other side, interactions between nickel and the composite oxide support exert high effect on the methanation reaction. Likewise, composite oxide supports have better chemisorption capability owing to better dispersion of nickel species [14,24,25]. Aldana et al. [24] reported that ceria-zirconia composite oxide supported Ni-based catalysts prepared by the sol-gel method showed 80% CO_2 conversion and 99.3% CH_4 selectivity at 350 °C. Ding et al. [26] noted that the synthesized Ni/CeO_2–Al_2O_3 catalyst with 60 wt% of CeO_2 showed excellent performance in methanation reaction. Zhang et al. [27] reported that the Ni/SiO_2–Al_2O_3 catalyst prepared by the grinding-mixing method presented 76% CO conversion and 80% CH_4 selectivity at 350 °C. Chang et al. [28] prepared nickel catalysts on rice husk ash-alumina by incipient wetness impregnation method. They found that the reaction temperature of 500 °C might be the optimum temperature for CO_2 hydrogenation to give the maximum yield and selectivity of CH_4. Cui et al. [29] noted that Ni–Mg/SiO_2–Al_2O_3 catalysts prepared by combining co-precipitation and spray granulation showed 50% CO conversion and 87% CH_4 selectivity at 350 °C.

Alumina-silica composite oxide can be considered as a high potential catalyst support due to high thermal stability and high surface area at elevated temperatures. In addition, the silica particles restrict the contacts of Al_2O_3 particles by surrounding the γ–Al_2O_3, inhibiting its phase transition to α-Al_2O_3 [30]. In this study, a series of nanocrystalline nickel catalysts supported on alumina-silica composite oxides with different SiO_2 contents were prepared by the sol-gel method for the carbon dioxide methanation reaction.

Experimental

Ni-based catalysts supported on alumina-silica composite oxides with various silica/alumina (SiO_2/Al_2O_3) molar ratios were prepared by a facile sol-gel route. $Ni(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ were used as Ni and Al salt precursors, respectively. Additionally, sodium silicate (NS) as a silica source, ethanol as a solvent, and propylene oxide (PO) as a network forming agent were used.

Solvents are employed in this method as a media for the hydrolysis step in order to control the concentrations of constituents, which exerts a significant influence on the gelation kinetics. For this reason, solvent selection is a key factor in determining the rate of gel formation, its structure, and drying pattern [31]. Likewise, propylene oxide was used as a gelation promoter to facilitate the condensation procedure during the sol-gel method.

$30Ni/Al_2O_3$ and $30Ni/Al_2O_3.XSiO_2$ catalysts were prepared according to the method explained in our previous work [32]. Finally, the gel was calcined at 700 °C with a heating rate of 3 °C/min for 3 h under static air atmosphere. In all catalysts, the weight percent of the nickel was kept constant (30 wt%) and the SiO_2 content was varied and the catalysts were denoted as $30Ni/Al_2O_3.XSiO_2$, where X represents the silica/alumina (SiO_2/Al_2O_3) molar ratio (X = 0.25, 0.5, 0.75, 1 and 1.5).

Catalyst characterization

The BET area, pore volume and pore size of the prepared catalysts were determined using a Belsorb mini II instrument. A PANalytical X'Pert-Pro instrument was employed for the X-ray diffraction experiments.Hydrogen temperature programmed reduction (TPR) experiments were conducted using a Micrometrics chemisorb 2750 instrument. The detail conditions of the TPR analysis are reported in our previous work [32]. Scanning electron microscopy (SEM) analysis was done using a VEGA TESCAN microscope.

Catalytic tests

The methanation reaction was carried out in a quartz micro reactor (Id.: 10 mm) at ambient pressure. Before reaction, the catalyst powders were pressed into tablets and then crushed into particles with a size in the range of 0.25–0.5 mm.

Typically, 200 mg of the catalyst particles was charged into the reactor and reduced by a H_2 stream (25 ml/min) at 600 °C for 2 h. After that, the reactor was cooled to 200 °C and then a mixture of H_2 and CO_2 with favorable ratio was entered the reactor as reactant feed. The analysis of the effluent gases was

Please cite this article in press as: Moghaddam SV, et al., Synthesis of nanocrystalline mesoporous Ni/Al_2O_3–SiO_2 catalysts for CO_2 methanation reaction, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.08.163