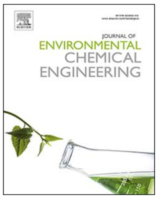
Journal of Environmental Chemical Engineering 6 (2018) 745–753

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece



Comparative study of Ni-Ce loading method: Beneficial effect of ultrasonic-assisted impregnation method in CO_2 reforming of CH_4 over Ni-Ce/SBA-15

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ARTICLE INFO

Keywords:
Ni-Ce/SBA-15
CO_2 dry reforming
Ni-Ce loading methods
Ultrasonic-assisted impregnation
Metal-support interaction

ABSTRACT

A series of Ni-Ce/SBA-15 catalysts with 6 wt% Ce and 5 wt% Ni were synthesized using conventional impregnation (Ni-Ce/SBA-15(C-IM)), ultrasonic-assisted impregnation (Ni-Ce/SBA-15(US-IM)) and reflux-assisted impregnation (Ni-Ce/SBA-15(R-IM)) methods The samples were characterized using XRD, TEM, SEM, BET, FTIR, H_2-TPR, XPS and TGA. The characterization results showed that Ni-Ce loading methods greatly influence the properties of Ni-Ce/SBA-15 whereby the homogeneity of metal dispersion and strength of metal-support interaction followed the order of Ni-Ce/SBA-15(C-IM) < Ni-Ce/SBA-15(R-IM) < Ni-Ce/SBA-15(US-IM). The smaller metal particle size and higher metal dispersion in Ni-Ce/SBA-15(US-IM) have led to the stronger metal-support interaction and further decreased the surface area and porosity of the catalyst. The activity and stability of catalysts followed the order of Ni-Ce/SBA-15(C-IM) < Ni-Ce/SBA-15(R-IM) < Ni-Ce/SBA-15(US-IM), with the conversion of CH_4 and CO_2 over Ni-Ce/SBA-15(US-IM) was about 96.3% and 93.5%, respectively, and H_2/CO ratio of 1.02 at reaction temperature of 800 °C and almost remained constant during 48 h of reaction. The superior catalytic performance of Ni-Ce/SBA-15(US-IM) probably was related with the smaller metal particles, stronger metal-support interaction and more homogenous metal dispersion, which altered the properties of catalyst towards an excellent catalytic performance. The characterization of spent catalysts showed the lowest carbon formation in Ni-Ce/SBA-15(US-IM) catalyst, demonstrating the positive role of ultrasonic effect on alteration of catalyst properties towards carbon resistance. This study provides new perspective on the preparation of Ni-Ce/SBA-15 towards an excellent performance of CO_2 reforming of CH_4.

1. Introduction

The global warming due to greenhouse gases emissions is a major concern of modern societies. In order to combat the problem of global warming, researchers had proposed the idea of producing the syngas from greenhouse gases. There are several ways can be used to produce syngas such as ethanol dry reforming [1], glycerol steam reforming [2], partial oxidation of CH_4 [3,4] and CO_2 reforming of CH_4 [5–8]. Among the proposed synthesis routes, CO_2 reforming of CH_4 is the most promising process whereby two major greenhouse gases (CO_2 and CH_4) are consumed to produce syngas (CO and H_2). In addition, the syngas produced has low equimolar ratio (1:1) which is preferred for the production of liquid hydrocarbon through Fischer-Tropsch synthesis [6]. The CO_2 reforming of CH_4 is expressed in the equation as below [9]:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^\circ = 247.3\,\text{kJ/mol} \qquad \Delta G^\circ = 61770 - 67.32T\,\text{kJ/mol} \tag{1}$$

The CO_2 reforming of CH_4 has been studied extensively using numerous types of catalysts including noble metal-based catalysts and transition metal-based catalysts [10]. However, transition metal-based catalysts, especially Ni-based catalyst is more feasible as it exhibits high catalytic activity, readily available and cost effective. In particular, Ni supported on SBA-15 has attracted intense interest for CO_2 reforming of CH_4 owing to the properties of SBA-15 that possesses hexagonal structure of mesopores with size of 4.6–30 nm, large surface area (600–1000 m^2/g), thicker walls (3.1–6.4 nm) and high thermal stability [8,11,12]. However Ni-based catalyst is always accompanied by coke formation and sintering of Ni metal particles, which causes a severe deactivation of the catalyst [5]. Therefore, it is highly necessary to design stable and active Ni-based catalysts.

It has been reported that the addition of promoters such as cerium oxide (CeO_2) [5,7,13,14] and lanthanum oxide (La_2O_3) [15] played a significant role in improving the catalytic activity of the Ni-based catalyst and inhibit carbon deposition through modification of surface

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https://doi.org/10.1016/j.jece.2018.01.001
Received 28 September 2017; Received in revised form 19 December 2017; Accepted 1 January 2018

structure effects. In the case of CeO_2, the redox properties of CeO_2 ($Ce^{4+} \leftrightarrow Ce^{3+}$) promotes the formation of oxygen vacancies, thus enhancing the mobility of surface oxygen whose contributes to lower carbon deposition of the metallic particles. Besides, the basic characteristic of CeO_2 can suppress the carbon deposition by adsorbing the mild acidic CO_2 species on the catalyst surface and further interacting with deposited carbon [16]. In addition, the presence of Ce in catalyst improves support interactions and enhances the dispersion of metal species over the support [17]. It was also found that high nickel dispersion inside the support channels was obtained in the presence of Ce, thus resulted in more stable reaction, with minor carbon nanotubes formation [6].

The catalyst preparation procedure is one of the main factors that can alter the physicochemical characteristics and influence the catalytic performance of the catalyst. Aghamohammadi et al. [7] studied the effect of ceria promotion and synthesis methods on Ni/Al_2O_3-CeO_2 towards dry reforming of methane. They found that sol-gel method is more favored than sequential impregnation method with much improved catalytic activity and stability due to high dispersion of active phase. Albarazi et al. [18] investigated on three different synthesis routes: two sequential incipient wetness impregnation, one single impregnation and co-precipitation method for ceria-zirconia doped Ni/SBA-15. They also claimed that different synthesis routes strongly influenced the properties of the catalyst. In addition, Kaydouh and coworkers [19] reported that the "two solvents" deposition method favors the dispersion of NiO particles entrapped in the porous channels of SBA-15, thus inhibiting sintering and coke formation during the reaction. For Ni-Ce/SBA-15, CeO_2 nanoparticles are also highly dispersed and the catalyst shows high activity and stability towards CO_2 reforming of CH_4. The dispersion of Ni particle inside the pores of SBA-15 was also reported by Gálvex et al. [20] for Ni/SBA-15 prepared by precipitation method. In their study, three preparation method where considered: incipient wetness impregnation, precipitation and precipitation in the presence of ascorbic acid as reducing agent. The results showed that Ni/SBA-15 prepared by addition of ascorbic acid favors deposition of Ni particles inside the pores and thus resulted in higher activity, improved stability and enhanced selectivity towards CO_2 reforming of CH_4.

Despite the fact that several studies have disclosed the positive role of Ce on the coke resistance and influential of synthesis strategies, however searching for a suitable catalyst preparation methods are still required in order to facilitate the uniform dispersion of active compound in the catalyst, and thus promote the catalytic activity and inhibit carbon deposition of the catalyst. Owing to the fact that the methodologies of catalyst preparation will significantly influence the properties and catalytic activity of the catalyst, thus, the objective of this study is to investigate the influence of Ce-Ni loading methods on the properties and catalytic activities of Ce-Ni/SBA-15 towards CO_2 reforming of CH_4.

2. Materials and methods

2.1. Catalysts preparation

SBA-15 support was synthesized according to the method reported by Zhao et al. [21]. In concise, the triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$, Aldrich) was dissolved in the solution of deionized water and 2 M hydrochloric acid solution under stirring. Then, tetraethyl orthosilicate (TEOS, Merck) was added dropwise to the previous solution and stirred at 40 °C for 24 h, and the precipitate product was obtained. The precipitate product was filtered, washed with deionized water and dried overnight at 110 °C. The sample was calcined at 550 °C for 3 h to remove the triblock copolymer.

A series of Ni-Ce/SBA-15 catalysts were prepared by three types of preparation methods which are conventional wet impregnation method (C-IM), ultrasonic-assisted impregnation method (US-IM) and reflux followed with impregnation method (R-IM). For C-IM method, an appropriate amount of Ce salt precursor, $Ce(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich, 99%) was mixed with SBA-15, and then was heated slowly at 80 °C under continuous stirring until nearly all the water had evaporated. The solid residue was dried overnight at 110 °C followed by calcination at 550 °C for 3 h to produce Ce/SBA-15(C-IM). Subsequently, similar procedure was used to synthesis Ni-Ce/SBA-15(C-IM) by using Ce/SBA-15(C-IM) and Ni salt precursor, $Ni(NO_3)_2\,6H_2O$ (Merck, 99%). For the US-IM method, Ce/SBA-15(US-IM) was prepared by mixing of SBA-15 with appropriate amount of Ce salt precursor, $Ce(NO_3)_2.6H_2O$. The resulting slurry was immersed in the ultrasonic cleaner bath and was heated slowly at 80 °C until nearly all the water had evaporated. The solid residue was dried overnight at 110 °C followed by calcination at 550 °C for 3 h. Next, similar procedure was used to synthesis Ni-Ce/SBA-15(US-IM) by using Ce/SBA-15(US-IM) and Ni salt precursor, $Ni(NO_3)_2\,6H_2O$. Meanwhile, for the R-IM method, Ce/SBA-15(R-IM) was prepared by mixing of SBA-15 with appropriate amount of Ce salt precursor, $Ce(NO_3)_2{\cdot}6H_2O$, and was refluxed at 80 °C for 6 h. Then, the resulting slurry was heated at 80 °C under stirring until nearly all the water had evaporated. The solid residue was dried overnight at 100 °C followed by calcination at 550 °C for 3 h. Subsequently, similar procedure was used to synthesis Ni-Ce/SBA-15(R-IM) by using Ce/SBA-15(R-IM) and Ni salt precursor, $Ni(NO_3)_2\,6H_2O$. For all catalysts, the cerium content was fixed to 6 wt% and that of nickel to 5 wt%.

2.2. Catalyst characterization

The X-ray diffraction (XRD) analysis was recorded on powder diffractometer (Philips X' Pert MPD, 3 kW) using a Cu Kα radiation (λ = 1.5405 Å). The primary crystallite size of NiO and CeO_2 were calculated using the Scherrer equation at 2θ of 43.6° and 28.8°, respectively:

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{2}$$

where λ is the X-ray wavelength corresponding to Cu-Kα radiation (0.15405 nm), B is the broadening (in radians) of the metal reflection and θ is the angle of diffraction corresponding to peak broadening.

Transmission electron microscopy (TEM) was performed using JEM-2100 Electron Microscope. The sample was dispersed in ethanol by sonication, and deposited on an amorphous, hollow carbon grid. The elemental distribution mapping of the catalyst was observed using a Scanning Electron Microscope (FEI Quanta 450 Electron Microscope) operating at 10 kV.

The specific surface areas, total pore volume and average pore diameter were determined using AUTOSORB-1 model AS1 MP-LP instrument at −196 °C. Before each measurement, the sample was degassed in vacuum at 300 °C for 3 h.

The Fourier Transform Infrared (FTIR) analysis was carried out using Thermo Nicolet Avatar 370 DTGS model in KBr matrix in order to study the chemical properties of catalysts and to identify the interaction of metal species with SBA-15.

H_2-TPR analysis was carried out using Micromeritics Chemisob 2920 Pulse Chemisorption in 10% H_2/Ar at 10 °C/min. Prior to the chemisorption, 30 mg of the catalyst was reduced with pure H_2 (20 mL min^{-1}) at 850 °C for 1 h. The amount of hydrogen uptake was determined by injecting mixed gas (10% H_2/Ar) periodically into the reduced catalyst.

The X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Kratos Analytical XSAM HS spectrometer. XPS data were analyzed using CasaXPS software.

The amount of carbon deposited on the spent catalyst was determined using thermogravimetric analyzer (TGA Q500, TA Instruments), XRD (Philips X' Pert MPD, 3 kW) analyses and TEM (JEM-2100 Electron Microscope). TGA analysis was carried out under a mixture of air (20%O_2/80% N_2) with heating rate of 5 °C/min up to