Improved catalytic performance of Ni catalysts for steam methane reforming in a micro-channel reactor

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Abstract

Milliseconds process to produce hydrogen by steam methane reforming (SMR) reaction, based on Ni catalyst rather than noble catalyst such as Pd, Rh or Ru, in micro-channel reactors has been paid more and more attentions in recent years. This work aimed to further improve the catalytic performance of nickel-based catalyst by the introduction of additives, i.e., MgO and FeO, prepared by impregnation method on the micro-channels made of metal-ceramic complex substrate. The prepared catalysts were tested in the same micro-channel reactor by switching the catalyst plates. The results showed that among the tested catalysts Ni-Mg catalyst had the highest activity, especially under harsh conditions, i.e., at high space velocity and/or low reaction temperature. Moreover, the catalyst activity and selectivity were stable during the 12 h on stream test even when the ratio of steam to carbon (S/C) was as low as 1.0. The addition of MgO promoted the active Ni species to have a good dispersion on the substrate, leading to a better catalytic performance for SMR reaction.

1. Introduction

Hydrogen is an efficient, clean and safe energy carrier as well as a raw material in many important industrial processes (e.g., oil refining, ammonia synthesis and methanol synthesis) [1]. Nowadays, there are various hydrogen production processes derived from different kinds of feedstock such as fossil fuels, biomass and water [2−4]. However, as a mature and effective technology, steam methane reforming (SMR) process is the dominant industrial route for hydrogen production [5] and nearly about 48% hydrogen around the world is produced in this way nowadays [6].

Meanwhile, the traditional SMR technology (e.g., a large scale packed bed reactor with Ni catalyst supported on Al_2O_3 pellets) since its first industrial application in 1930s always suffers from its poor heat transfer behavior, which inevitably results in large gradients in terms of temperature and/or pressure in axial and radial directions in the reactor due to the endothermic nature of SMR reaction. As a result, the efficiency of SMR process has been severely limited even though many different kinds of promoters and supports have been applied to improve the catalytic performance [7−15]. Besides, coke formation and sintering, as well as oxidation of the active sites

easily and frequently occur on Ni catalysts during the reaction according to the thermodynamic analysis [16]. Although several methods have been suggested and discussed to improve the resistance to coke of the catalyst [17−19], the low thermal conductivity in packed catalyst bed still limits the overall reactor hydrogen production efficiency.

It is acknowledged that micro-channel reactors have great potential for the process intensification on fast catalytic reactions such as highly exothermic or endothermic gas phase reactions under harsh conditions (e.g., high temperature and high pressure) due to their superior mass and heat transfer properties [20,21]. In recent years, both Velocys and Pacific Northwest National Laboratory (PNNL) have paid much more attention to the milliseconds SMR process in micro-channel reactors, but all reported results were based on Rh catalysts [22−25]. In order to greatly reduce the catalyst cost in industrial applications, Zhai et al. [26] reported that Ni catalyst coatings on FeCrAlloy plates shows excellent catalytic performance for SMR reaction. Therefore, milliseconds process can also be successfully implemented in micro-channel reactors based on Ni catalyst. However, optimization of such a catalyst technique has not been discussed in detail. In addition, as one of the fundamental challenges to fully explore the

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kinetic potential of a catalyst in micro-channel reactors, how to reduce or even avoid the problem of catalyst fall-off, which tends to take place at high temperature due to the difference of thermal expansions between the metallic substrate and the coated catalyst layer, must be seriously considered in practical applications [27,28]. In a previous study [26] we reported that thermal spray method could be applied to manufacture the metal-ceramic complex substrates as the walls of micro-channels; then the catalyst carrier layer and the Ni catalyst could be loaded on each substrate in sequence. As a result, enhanced binding force between the catalyst layer and the Fe-CrAlloy substrate could be realized. Consequently, the catalyst plates prepared by this means had a neglectable fall-off rate after they underwent high-temperature reaction and vigorous ultrasonic treatment. In the present study, we aim to further improve the catalytic performance of Ni catalyst by introducing additives of iron and magnesium oxides. MgO is widely used as a structure promoter in SMR process [29,30], while Ni-Fe bimetallic catalyst exhibits high catalytic activity in ethanol steam reforming, water-gas shift (WGS) and methanation process [31−34]. Moreover, both magnesium and iron have been demonstrated to be effective promoters for Ni-based catalyst with high coke resistance in dry reforming process [35,36]. These two new catalysts, namely Ni-Mg catalyst and Ni-Fe catalyst will be prepared by impregnation method, and then tested for SMR reaction in micro-channel reactors to evaluate the catalytic performances in comparison with the pristine Ni catalyst. Extensive characterizations of these catalyst plates, such as N_2 adsorption-desorption, TPR, SEM, TEM and XRD have been performed to get a better understanding of the catalytic performance of SMR reaction in micro-channel reactors.

2. Experimental

2.1. Catalyst plate preparation

As described in details in our previous work [26], thermal spray method was applied to develop a type of metal-ceramic complex substrate as the support to load catalyst in order to implement stable and active catalyst coatings for SMR reaction in micro-channels. A ceramic layer mainly consisting of α-Al_2O_3 nanoparticles was first sprayed on a FeCrAlloy substrate to form the metal-ceramic complex substrate by thermal spray method. Then, a carrier layer of γ-Al_2O_3 was coated on the substrate by dip coating method. This process can be repeated until the weight gain reached a desired value [37]. After that, the metal-ceramic complex substrate with γ-Al_2O_3 layer was impregnated into the prepared solution of $Mg(NO_3)_2$ (4.6 wt%) or $Fe(NO_3)_3$ (10 wt%) for 6 h at 80 °C, following with a drying process at 120 °C for 6 h and a calcination process at 600 °C for 6 h; the promoters were then loaded on the catalyst plate. At last, the metal-ceramic complex substrate with promoters was further impregnated into the prepared solution of $Ni(NO_3)_2$ (28 wt%) for 6 h at 80 °C following with the same process as the loading of promoters. After all of the above steps, Ni (without any promoters),

Ni-Mg and Ni-Fe catalyst plates with stable catalyst coatings were obtained. The catalyst loading was defined as the catalyst weight loaded on unit area of the micro-channel wall. By varying the concentration of $Ni(NO_3)_2$ solution and/or the times of impregnation, the catalyst Ni loading can be well controlled. To maintain the consistence in the catalytic performance evaluation, the same Ni catalyst loading on these three kinds of catalyst plates of about 6.8 g/m^2 was realized using $Ni(NO_3)_2$ solution with the same concentration, and so the catalytic evaluation on Ni, Ni-Mg and Ni-Fe catalyst plates was comparable each other.

2.2. Catalyst characterization

A self-constructed equipment connected with an on-line GC (GC-2014, Shimadzu) was used to perform temperature-programmed reduction with hydrogen (H_2-TPR) [37]. BET specific surface area was determined by nitrogen adsorption method (Autosorb-1-C, Quantachrome CO. LTD). Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance equipment, operating at 40 kV and 45 mA and employing nickel-filtered Cu K_α radiation ($\lambda = 0.1542$ nm). X-ray diffraction (XRD) patterns of the catalyst in bulks were recorded on MDI Jade 5.0 for their phase identification by comparing the collected pattern with the standard one in the database of PDF2004.

Scanning electron microscopy (SEM, JEOL, JSM-7401F) was used to characterize the catalyst morphology, and an energy dispersive X-ray spectroscopy (EDX) was coupled with SEM to analyze the element composition of selected points or areas. The average diameter of nickel particles of the catalyst was determined by a JEOL JEM2010 high-resolution transmission electron microscopy (HRTEM).

2.3. Catalyst test

All the plates were cut off to the same size of 2 cm×5.5 cm before the catalyst impregnation. After the impregnation, two catalyst plates were inserted into the slits of micro-channel reactor separately. Finally, a channel of 1.8 cm×5.5 cm×0.04 cm was formed between the two plates, as shown in Scheme 1. The assemble procedure of micro-channel reactor is easy and convenient.

During the experiments, the gas feed measured by mass flow controller was introduced into the system, while the steam was generated in a vaporizer using a pump to feed water. The micro-channel reactor was heated by a furnace with the maximum temperature of 1300 °C. A gas chromatograph (GC-2014, Shimadzu) equipped with a TCD was applied to on-line analyze the composition of effluent in gaseous phase after the complete gas liquid separation in a condenser. An in situ reduction process by a diluted hydrogen (10% H_2/Ar) at 900 °C for 60 min was required before SMR reaction. During the catalyst evaluation, CH_4/H_2O mixture with steam to methane (S/C) ratio ranging from 1.0 to 3.0 was introduced at different gas hourly space velocities (GHSV) (1.000×10^4–10.125×10^4 h^{-1}) into the micro-channel reactor.