Catalytic performance of Ni catalyst for steam methane reforming in a micro-channel reactor at high pressure

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ABSTRACT

Hydrogen has drawn much attention as both a kind of clean and efficient energy and an important chemical material. Among numerous production method, steaming methane reforming (SMR) accounts for most of the hydrogen production over the world. In this work, we investigated the behavior of Ni catalyst and performance of micro-channel reactor at high pressure for SMR process. The influences of various temperature, steam-to-methane ratio, GHSV at high pressure varied from 0.5 MPa to 2.0 MPa were studied in details. Even when the process was conducted at 240,000 h^{-1}, the methane conversion could still approach to the thermodynamics limitation at 900 °C and 2.0 MPa, which confirmed that micro-channel reactor with coated catalyst is not only feasible but high efficient for SMR process. Besides, we realized the hydrogen productivity of about 0.1 m^3/h in a single channel at 2.0 MPa, namely 1.95×10^4 m^3/(m^3 h) space time productivity.

1. Introduction

Hydrogen has been considered as the basis of sustainable energy system in the future due to its high mass based energy density, clean utilization and efficient transportation [1]. Although hydrogen can be generated from different energy sources (i.e. thermal, electrical, photonic and biochemical energy) and different natural substances (i.e. water, biomass, fossil fuels and hydrogen sulfide) nowadays, the steam methane reforming (SMR) on Ni-based catalysts is still the most cost-effective and highly developed industrial process among all the routes and supplies most of the hydrogen over the world [2]. In the near term, SMR process will continue playing an important role in the hydrogen economy [3].

In fact, many customers of modern H$_2$ plants (i.e. ammonia synthesis, methanol synthesis, petroleum hydrogenation, Fischer-Tropsch synthesis and substitute natural gas production) require the hydrogen at high pressure as the feed [4]. The industrial SMR reactors are usually operated at pressure above 2.0 MPa [5] to avoid additional compression steps. However, the main reaction of SMR process favors at low pressure and thus the industrial SMR reactor is conducted at high temperature (> 800 °C) to compensate the productivity. But limited information is available on the behavior of Ni-based catalysts at such harsh conditions. Katheria et al. [6] investigated the performance of Ni-based catalyst in SMR reaction in a fixed-bed reactor at 0.5–1.0 MPa. Their measured methane conversion was obviously lower than the industrial required level and the equilibrium conversion. Therefore the

detailed study on catalyst performance and reactor efficiency at elevated pressure is extremely important for a successful and stable running of industrial SMR process.

Compared with the traditional reactor, the high surface to volume ratio of micro-reactor offers higher heat and mass transfer rates and allows chemical reactions to be operated under more aggressive conditions [7] (i.e. higher temperature and higher pressure). Therefore the micro-channel reactor can effectively intensify the SMR process efficiency and favor the increase of space time yields to approach the industrial requirement. Thanks to the development of advanced materials and fabrication techniques, various micro-reactor types (e.g. coated wall micro-reactors, packed-bed micro-reactors, structured catalyst micro-reactors and membrane micro-reactor) have been tested and used for hydrogen production [8–15]. To date, the assembly patterns of micro-reactor with reforming channel and combustion channel have been widely discussed and optimized by experiment and simulation [16–21]. Through rational integration of multiple micro-channel units, the process intensity of Velocys methane steam reformer [22] was 60 times more than that in conventional steam reformer. The recent progress in modular integration extremely increases the capacity of micro-reactors to realize the mass-production scale of hydrogen by SMR process. However, the reactor behavior at the situation of high pressure has been always ignored in the studies above.

There is no doubt that the coated wall micro-reactor, one of the most common types of micro-reactors, has great potential for numerous reactions with strong thermal effect including SMR process [23–31].

Furthermore, the negligible pressure drop of coated wall micro-reactor makes it more suitable than other types in large scale production especially at high pressure [28]. In our previous work, a metal-ceramic complex substrate was prepared to assemble the coated wall micro-channel reactor for gas-solid catalysis. The complex substrate can simultaneously utilize the thermal conductivity of the metal for heat transfer and the porosity of the ceramics for active component loading. Subsequently, SMR process has been successfully realized in the micro-channel reactor with Ni-based catalyst supported on complex substrate at atmosphere pressure [26,30]. In the present study, we aim to investigate the behavior of Ni catalyst and performance of micro-channel reactor at high pressure (e.g. 0.1–2.0 MPa) in SMR process. The catalyst evaluations were carried out in a micro-channel reactor on-line and the properties of the catalyst before and after reaction were characterized by XRD, XPS and SEM.

2. Experiment

2.1. Catalyst preparation

Ni catalyst plates were prepared by impregnation method in this work. The metal-ceramic complex substrates were made by a thermal spray method to support the active component. Before the impregnation of Ni, alumina sol was coated on the substrate by dip-coating method to form a layer of γ-Al$_2$O$_3$ which can both increase the surface area of substrates and enhance the combination between the substrate and the catalyst as detailed below.

- Manufacture of the metal-ceramic complex substrate

Small α-Al2O3 particles was heated to half-melted and then thermally sprayed onto a FeCrAl alloy plate. Some alumina particles permeated in the metal phase during the high temperature and collision process. Finally the metal-ceramic complex substrate was manufactured and the adherence between the ceramic layer and substrate layer was greatly enhanced.

- Preparation of alumina layer

A commercial alumina sol (25 wt% Al$_2$O$_3$, Sasol Chemical Co., Ltd) was used to prepare a carrier layer of γ-Al$_2$O$_3$ on the substrate by dip-coating method. The metal-ceramics complex substrate was immersed into this alumina sol for 3 min, and then withdrawn at a constant speed of 3 cm/min to ensure the uniform coating, dried at room temperature for 60 min, then calcined at 600 °C for 6 h. This process can be repeated until the weight gain reached a desired value.

- Preparation of the catalyst layer

The metal-ceramic complex substrate coated with γ-Al$_2$O$_3$ layer was impregnated into the prepared solution of Ni(NO$_3$)$_2$ (28 wt%) for 6 h at 80 °C, followed by a drying process at 120 °C for 6 h and a calcination process at 600 °C for 6 h.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of samples were recorded on a Bruker D8 Advance equipment with Cu Kα radiation in the 2θ range of 20–90°. Phase identification of the catalysts was carried out by comparing the collected spectra with those listed in the JCPDS database (Joint Committee of Powder Diffraction Standards) and the ICSD database (Inorganic Crystal Structure Database).

The morphology and particle size distribution were characterized using a scanning electron microscopy (SEM, JEOL, JSM-7401F) and a JEOL JEM2010 high-resolution transmission electron microscopy (HR-TEM). SEM samples were prepared by cutting the catalyst plates before

Fig. 1. Scheme of micro-channel reactor and catalyst plate in SMR reaction.

and after reaction into 5 mm × 5 mm pieces. TEM samples were prepared as follows: scraped the catalyst powder from catalyst plate surface, dispersed the powder in ethanol by ultrasonic agitation, and then dropped the suspension on a carbon-coated copper grid and finally dried in air. An energy dispersive X-ray spectroscopy (EDS) was coupled with SEM and TEM to analyze the element composition of selected points or areas.

X-ray photoelectron spectra (XPS) was acquired using a PHI Quantera SXM system, equipped with Al Kα X-ray source. The binding energy data of reference material were obtained from NIST X-ray Photoelectron Spectroscopy Database. Survey scans (0–1200 eV) and high-resolution Ni (2p) spectra were then achieved. The uncertainty of the peak positions was estimated to be 0.2 eV for all spectra and the binding energy (BE) scale was calibrated by setting the C (1s) transition to 284.8 eV. The analysis of the measured high-resolution spectra was performed using XPSPEAK4.1 software.

2.3. Catalyst testing

The dimensions and assembly of the reactors used in the SMR process are illustrated in Fig. 1. To facilitate the reaction in the micro-channel reactor, the catalyst plate was first cut into the size of 2 cm × 4 cm. Then two sheets of the catalyst plates were inserted into the slits of micro-channel reactor separately. As a result the space between the plates formed a channel, with the size of 1.6 cm × 4.0 cm × 0.08 cm. The channel size has been demonstrated to maintain a uniform temperature profile in the reaction zone by numerical analysis [32,33].

Before the catalyst evaluation, the catalysts were reduced in situ under a flow stream of dilute hydrogen (10% H$_2$/Ar) with the total flow rate of 50 NmL/min at 900 °C for 120 min. After reduction, CH$_4$/H$_2$O mixture with determined flow rate (varying from 346 to 2076 mL/min) and S/C (steam to methane, varying from 3.0 to 5.0) ratio was introduced into the system. At these conditions, the GHSV based on channel volume changed from 40,000 h^{-1} to 240,000 h^{-1}. The reaction temperature was varied between 800 °C and 900 °C and the reaction pressure was varied in the range of 0.1–2.0 MPa. A HPLC (High Performance Liquid Chromatography) pump (Series II, Scientific Systems, Inc.) was used in the feeding system to guarantee the precision and accuracy of water delivery under high pressure.

The outlet gases were analyzed after water condensation and separation with an on-line GC (GC-2014, Shimadzu Co., Ltd.) equipped with a TCD and a TDX-01 column. The conversion and selectivity for SMR process are defined as follows:

$$X_{CH_4} = \left(1 - \frac{f_{CH_4}}{f_{CH_4} + f_{CO} + f_{CO_2}}\right) \times 100\% \tag{1}$$

$$S_{CO} = \frac{f_{CO}}{f_{CO} + f_{CO_2}} \times 100\% \tag{2}$$

where, X is the conversion, S is the selectivity to a certain product, and f is the molar fraction in the effluent gas.