

Process intensification of hydrogen production by steam reforming of methane over structured channel packing catalysts

Xiao-gang Kuang ^{1a*}, Li ZHANG ^{1b*}, Yan-lun REN ^{1c}, Xing-wei WANG ^{1d}

¹East China University of Science and Technology, School of Mechanical and Power Engineering, Shanghai 200237, China

Abstract—The industrial methane steam reforming reaction usually employs particulate catalyst that are easy to prepare and cost-effective, but suffer from problems such as high reactor pressure drop and low overall catalyst utilization. In this study, the Ni-Al₂CaO₄ powder prepared by the equal volume impregnation method was subjected to particle size control using a pressing method, and was made into catalyst particles of different sizes. Some of the catalysts were filled into honeycomb structures with cordierite and metal substrates, respectively, to prepare regular channel packing catalysts. The differences in methane steam reforming conversion rate, H₂/CO selectivity, and overall pressure drop among the three catalysts were compared, and the influence of particle size and regular channel on reaction performance was systematically explored. The results showed that under the same conditions, as the catalyst particle size increased, the methane conversion rate and pressure drop increased. The regular channel packing catalysts with the two substrates showed similar pressure drop levels, but the metal substrate exhibited a higher methane conversion rate due to its excellent thermal conductivity. Compared with single-particle catalysts of the same size, the pressure drop of the metal substrate regular channel packing catalysts was reduced by more than 25%. Under the conditions of a gas hourly space velocity of 2000 h⁻¹, a reaction temperature of 700 °C, and a water-to-carbon ratio of 3, the 40-60 mesh metal substrate regular packing catalysts showed a 7% increase in methane conversion rate, reaching 95.2%.

1. Introduction

Hydrogen energy as a clean and renewable energy source has a long-term prospect and a broad development space, and has an important position in chemical, petroleum, metallurgical, pharmaceutical, and aerospace industries [1-2]. Among the existing hydrogen production technologies, methane water vapor reforming (SMR) is the simplest, most economical, and most widely used hydrogen production method in industry at this stage, and the technology is relatively mature, with 50% of the annual global hydrogen production being produced by SMR [3-4]. SMR usually uses a pellet catalyst as the main catalyst, however, in a tubular reactor, the disordered accumulation of pellets causes This leads to poor catalytic performance and prevents the gas product from passing through the catalyst bed, resulting in lateral or reverse flow of the internal gas stream and re-mixing, which hinders the forward progress of the hydrogen production reaction, reduces the conversion rate and increases the energy consumption [5-6], and increases the cost of hydrogen production.

Researchers have explored various aspects of optimizing the pressure drop and catalytic capacity of particulate catalysts in tubular reactors. Among them, Pashchenko D [7] investigated the effect of the shape of the particulate catalyst on the methane conversion, Arsala [8] prepared in situ Ru/La-Al₂O₃ catalyst on Fecralloy alloy carrier for methane steam reforming. for methane steam reforming, which showed that the catalyst performance

was significantly enhanced by the carrier at low temperatures. Chang [9] et al. compared the performance of a powdered Ni/CeO₂ filled bed reactor with a Ni/porous-CeO₂ coated cordierite monolithic reactor.

The above scholars have enhanced the SMR process from two aspects: modification of particle catalysts and preparation of monolithic catalysts, but single particle catalysts suffer from high pressure drop and low overall utilization; although monolithic catalysts have high thermal conductivity, catalyst utilization and low pressure drop, there are many difficulties in the preparation of the carrier surface coating and low loading has been an important limiting factor [10-11]. In contrast, the gauge channel packed catalysts can significantly reduce the pressure drop per unit catalyst mass and enhance the catalyst efficiency and selectivity while ensuring a comparable loading to that of the particulate catalysts. This is due to the fact that gauge channel packed catalysts are filled with particulate catalysts in channels formed by a grid or woven mesh (metal or plastic) or thin vertical convoluted sheets (metal, plastic, or ceramic) stacked parallel to each other, a structure that facilitates catalyst dispersion and performance enhancement. Due to the low pressure drop requirement in chemical processes, the development and application of new structural fillers and reactors has been increasing in the last decades [12-13]. Winterberg [14] developed a model to describe the effect of effective radial thermal conductivity in a low channel to particle size ratio filled bed and extended his model to a sphere to cylinder filling. However, there is still a lack of specific experimental studies related to gauge channel

*^a17857021943@163.com, ^blzhang@ecust.edu.cn, ^crenyanlun@163.com ^dY20180064@mail.ecust.edu.cn

packed catalysts in methane water vapor reforming for hydrogen production.

In this paper, we combine the idea of regularized channel with the original pellet catalyst in SMR tubular reactor to optimize the catalyst disordered packing form while enhancing the internal heat transfer to reduce the overall pressure drop and improve the conversion rate. In order to systematically illustrate the effects of particle size and regulation channel on SMR reactor performance, a comprehensive comparison of methane conversion and, H_2/CO selectivity and overall pressure drop between single particle catalysts, cordierite-based and metal-based regulated channel-filled bed catalysts is presented.

2. Experimental tests

2.1 Experimental materials

Metal honeycomb carrier, provided by Shandong Hongzun Auto Parts Co. Cordierite carrier was provided by Tianma Industrial Ceramics Co. The proposed thin alumina was provided by Sasol with a specific surface area

of 267 m^2/g . Calcium aluminate (Shanghai Zonghe Chemical Technology Co. purity 99.0% or more) was used as dispersant. Nickel nitrate (Shanghai Aladdin Biochemical Technology Co.) was used as an additive.

2.2 Catalyst preparation

The 20 wt% $Ni/CaAl_2O_4$ powder was prepared by the impregnation method. A certain amount of calcium aluminate powder was weighed and the catalyst was prepared by the equal volume impregnation method. The weighed powder was impregnated with 1 M nickel nitrate solution for 2 h, dried at 100 °C for 12 h, and then heated up to 250 °C for 2 h at a rate of 1 °C/min. After cooling, the catalyst was prepared in different mesh sizes by the pressing method.

The packed catalysts were prepared by using honeycomb cordierite material and honeycomb metal material as the substrates of the gauge channels, and filling the catalyst particles with particle size of 40-60 mesh into these two gauge channels in equal amounts, and naming them as shown in Table 1

Table 1 Names of catalysts required for experiments

Catalyst Naming	Particle size	Substrate
KL-4	40-60mesh	-
JQ-4	40-60mesh	Cordierite 200 mesh
JS-4	40-60 mesh	Metal 200 mesh

2.3 Catalyst characterization and evaluation

The surface morphology of the catalyst was analyzed using Gemini SEM 500 equipment from Germany, and the

macroscopic morphology of the catalyst carrier coating was obtained using a BX51 optical microscope manufactured by Olympus. U-tube was used to test the pressure drop, as shown in Figure 1.

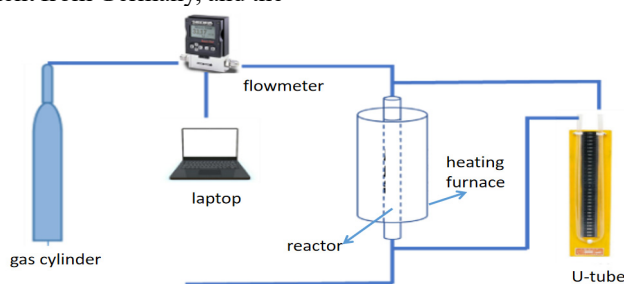


Fig.1 Catalyst pressure drop evaluation device

A laboratory-built catalyst evaluation equipment as shown in Figure 2 was used for catalyst evaluation. The experimental system mainly includes liquid and gas

transport modules, heating and insulation modules, reaction modules, gas handling and collection modules, and gas analysis modules.

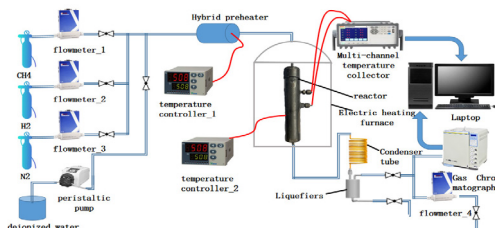
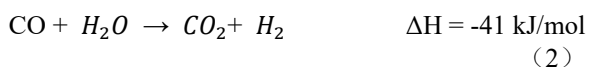
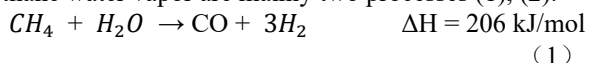


Fig. 2 Flow chart of methane steam plant

The main reactions for hydrogen reforming from methane water vapor are mainly two processes (1), (2).



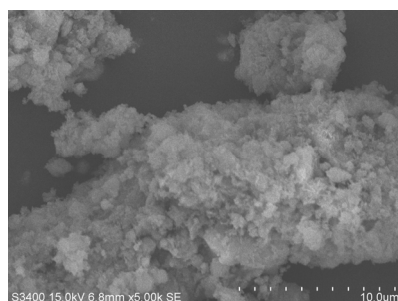
The conversion rate of methane with the selectivity of each gas is calculated and used to evaluate the activity of the catalyst for hydrogen production from methane water vapor. The calculation equation is as follows.

Methane conversion rate:

$$X_{\text{CH}_4} = \frac{[\text{CO}] + [\text{CO}_2]}{[\text{CH}_4] + [\text{CO}] + [\text{CO}_2]} * 100\% \quad (3)$$

$$\text{Gas selectivity: } X_{\text{H}_2} = \frac{[\text{H}_2]}{[\text{H}_2] + [\text{CO}] + [\text{CO}_2]} * 100\% \quad (4)$$

$$X_{\text{CO}} = \frac{[\text{CO}]}{[\text{H}_2] + [\text{CO}] + [\text{CO}_2]} * 100\% \quad (5)$$

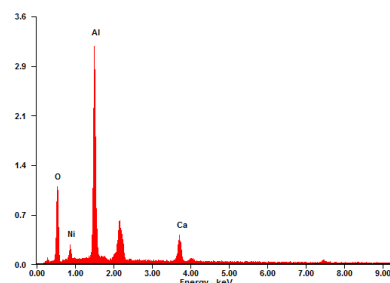


(a) SEM characterization of catalysts

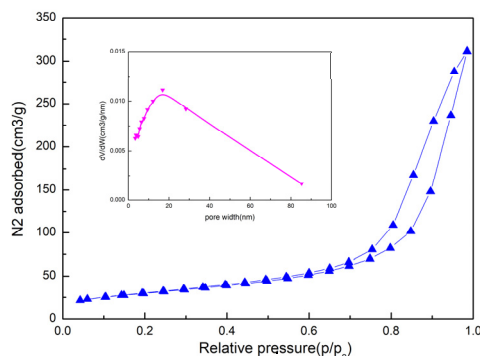
3. Results and Discussion

3.1 Catalyst characterization

The scanning electron microscopy results of the prepared catalysts are shown in Fig. 3(a), it can be seen that the prepared catalysts have high surface porosity and the catalyst particles are less than 1 μm in diameter, there is some agglomeration on the catalyst surface, but the particles are not agglomerated catalysts are consistent in size and uniform in particle size. From Fig. 3(b), it can be seen that the catalyst elements are mainly Al, Ca, Ni, elements and preparation are consistent and no other impurities are generated. From Fig. 3(c), it can be seen that the catalyst is a cylindrical uniform mesoporous material with narrow pore size distribution, an H1-type hysteresis loop with a steep and narrow hysteresis loop and an obvious delayed coalescence of adsorption branches. The pore size distribution is uniform, with a size of mainly 20 nm.



(b) Catalyst EDS characterization



(c) Characterization of nitrogen adsorption and desorption from catalysts

Fig. 3 Analysis of catalyst physical properties

3.2 Comparison of the performance of pellet catalyst and gauge channel packing catalyst

Figure 4(a) shows the comparison of methane conversion between 40-60 mesh pellet catalysts and two regular channel catalysts of the same size. Under the same reaction conditions, when cordierite-based and metal-based channel carriers are used, the methane conversion rates of both regular channel filler catalysts are significantly higher than that of the single particle catalyst. It can be observed that the methane conversion of JS-4 at 700 °C is already higher than that of KL-4 at 750 °C, indicating that the introduction of regular channels into the particulate catalysts has a significant effect on improving their overall catalytic capacity. It is also noted that the

difference in methane conversion between the particulate catalyst and the metal-based channel catalyst is 7% at 650 °C, and the difference narrows to 4.5% when the temperature is increased to 750 °C. It is not difficult to find that the performance enhancement brought by the gauge channel is weakened under the high temperature environment. As shown in Fig. 4(b), the H₂ selectivity of the two gauge channel packed catalysts is always better than that of the pellet catalysts and has lower CO concentration, but the difference between H₂/CO concentration of the three catalysts decreases with the increase of the reaction temperature, which is also due to the weakening of the gauge channel by the high temperature environment.

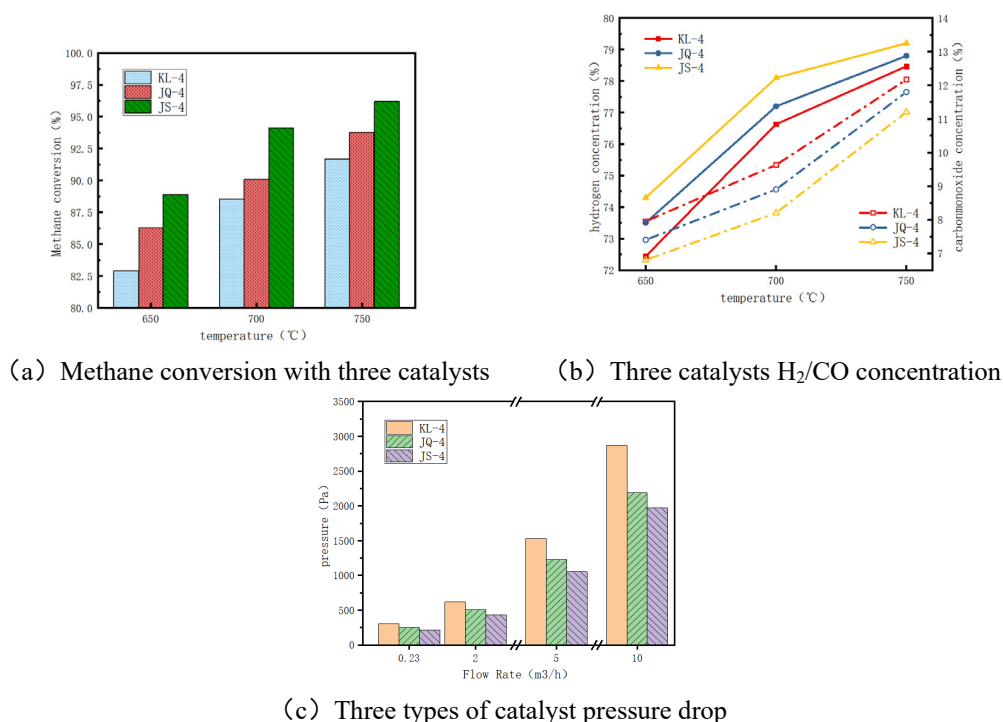


Fig.4 Comparison of methane conversion rate, H₂/CO concentration and pressure drop of three catalysts

It can be observed from Figure 4(c) that both metal-based and cordierite-based gauge channel packed catalyst structures have lower pressure drop values than the particulate catalysts at different flow rates. At 0.23 m³/h flow rate, the overall pressure drop is reduced by nearly 21% using metal-based as the channel matrix compared to a single 40-60 mesh pellet catalyst, while it is reduced by about 32% at 10 m³/h flow rate, indicating that the gauge channel structure is indeed effective in reducing the overall pressure drop, and the pressure reduction effect brought by the gauge channel becomes more obvious as the gas flow rate increases, and the choice of cordierite-based The choice of cordierite-based or metal-based as the channel matrix is of great significance to reduce the overall pressure drop.

4. Conclusion

In this paper, to investigate the effects of gauge channel and particle size on the performance of SMR reactors, the differences in methane conversion, H₂/CO selectivity and overall pressure drop between a single particle catalyst and two different matrixes of gauge channel packed catalysts were compared and the following conclusions were drawn.

(1) The introduction of regular channels significantly improves the heat transfer performance and reduces the overall pressure drop inside the reactor. When a single 40-60 mesh particle catalyst was introduced into the metal-based gauge channel, the pressure drop was reduced from 2780 Pa to 1970 Pa at a flow rate of 10 m³/h, and the methane conversion was increased from 87.2% to 95% at an experimental condition of 2000 h⁻¹ air speed, S/C=3, and 700 °C.

(2) Both cordierite-based and metal-based channels

can effectively improve the methane conversion and reduce the pressure drop, with both improving the methane conversion by more than 7% and reducing the pressure drop by more than 25%. The metal-based channel is more advantageous than the cordierite-based channel in improving the catalytic capacity and reducing the pressure drop.

Reference

1. Baykara SZ. Hydrogen: a brief overview on its sources, production and environmental impact. *Int J Hydrogen Energy* 2018;43:10605-14.
2. Andrews J, Shabani B. Where does hydrogen fit in a sustainable energy economy? *Procedia Eng* 2012;49:15-25.
3. Suleman F . Environmental impact assessment and comparison of some hydrogen production options[J]. *International Journal of Hydrogen Energy*, 2015, 40(21):6976-6987.
4. Bartholomew C H , Farrauto R J . Fundamentals of Industrial Catalytic Processes (Bartholomew/Fundamentals) || Homogeneous, Enzyme, and Polymerization Catalysis[M]. 2005.
5. Wismann, Sebastian T , Engbaek, et al. Electrified methane reforming: A compact approach to greener industrial hydrogen production.
6. Wahid, Abdul M , Hosseini, et al. Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development[J]. *Renewable & sustainable energy reviews*, 2016.
7. Pashchenko D . Experimental investigation of reforming and flow characteristics of a steam methane reformer filled with nickel catalyst of

- various shapes[J]. *Energy Conversion & Management*, 2019, 185(APR.):465-472.
8. Ashraf M A , Sanz O , Montes M , et al. Insights into the effect of catalyst loading on methane steam reforming and controlling regime for metallic catalytic monoliths[J]. *International Journal of Hydrogen Energy*, 2018, 43(26):11778-11792.
 9. Chang AC, Lee KY. Biogas reforming by the honeycomb reactor for hydrogen production. *Int J Hydrogen Energy*
 10. Singh S, Nguyen TD, Siang TJ, Phuong PT, Huy Phuc NH, Truong QD, Lam SS, Vo DVN. Boron-doped Ni/SBA-15 catalysts with enhanced coke resistance and catalytic performance for dry reforming of methane. *J Energy Inst* 2020;93(1):31e42.
 11. Sun Y, Zhang G, Xu Y, Zhang R. Dry reforming of methane over Co-Ce-M/AC-N catalyst: effect of promoters (Ca and Mg) and preparation method on catalytic activity and stability. *Int J Hydrogen Energy* 2019;44(41):22972e82.
 12. Maurice I. Stewart Jr. PhD, PE, in *Surface Production Operations (Third Edition)*, Volume 2, 2014
 13. H.P.A. Calis, J. Nijenhuis, B. Paikert, F.M. Dautzenberg, C.M. Vaden, CFD modelling and experimental validation of pressure drop and flow profile in a novel structured catalyst packing, *Chem. Eng. Sci.* 56 (2001) 1713–1720.
 14. M. Winterberg, E. Tsotsas, Correlations for effective heat transport coefficients in beds packed with cylindrical particles, *Chem. Eng. Sci.* 55 (2000) 5937–5943.