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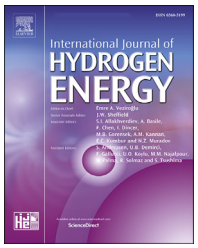

Fabrication of porous metal by selective laser melting as catalyst support for hydrogen production microreactor

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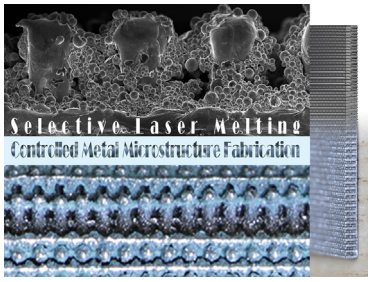
HIGHLIGHTS

- Porous metals are fabricated via SLM(Selective Laser Melting).
- Parametric modeling of controllable structure and porosity.
- Effects of structure, porosity and materials on hydrogen production performance.
- Better hydrogen production performance is obtained for porous metal with gradient porosity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 April 2019
Received in revised form
8 October 2019
Accepted 23 October 2019
Available online 21 November 2019

Keywords:
Microreactor
Porous metal
Selective laser melting
Hydrogen production
3D printing

ABSTRACT

To improve the hydrogen production performance of microreactors, the selective laser melting method was proposed to fabricate the porous metals as catalyst supports with different pore structures, porosities, and materials. The influence of the porous structures on the molecule distribution after passing through the porous metals was analyzed by molecular dynamics simulation. The developed porous metals were then used as catalyst supports in a methanol steam reforming microreactor for hydrogen production. Our results show that the porosity of the porous metal had significantly influence on the catalyst infiltration and the reaction process of hydrogen production. A lower degree of catalyst infiltration of the porous metal was obtained with lower porosity. A copper layer-coated stainless-steel porous metal with a staggered structure and gradient porosity of 80% –60% exhibited much larger methanol conversion and H_2 flow rate due to its better heat and mass transfer characteristic. Methanol conversion and H_2 flow rates could reach 97% and 0.62 mol/h, respectively. Finally, it was found that the experimental results were in good agreement with the simulation results.

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https://doi.org/10.1016/j.ijhydene.2019.10.173

Introduction

The direct hydrogen storage method is commonly used in hydrogen fuel cell vehicles; however, it has several disadvantages such as low energy storage density, high transportation cost, and large cost for hydrogenation facilities, which limit the commercial popularization of fuel cell vehicles [1,2]. Low carbon alcohol reforming is considered as one of the effective ways to solve the on-line hydrogen supply problems for fuel cells [3–5], which is a current topic of interest [6–15]. Several studies for the improvement of industrial production by microchannel reactors have been reported [16–24]. By introducing porous microchannel reactors into the on-line hydrogen supplying system, whose volume can be one or two orders of magnitude smaller than the normal fuel catalytic reforming unit, the reaction rate and hydrogen production rate have been significantly increased. At present, foam metal or porous metal fiber sintered plate, is produced by foaming or sintering process, and the catalytic catalyst support with microchannel geometry is formed by the superposition of multi-porous plates [25,26]. This kind of porous support plate structure has the advantages of high porosity, large specific surface area, effective heat conduction, good conductivity, and high temperature and corrosion resistance, which can improve the hydrogen production efficiency. However, it is difficult to achieve the active control of a multi-pore structure with gradual distribution through the porous catalyst support fabricated by foaming or sintering processes, and it is difficult to achieve the smooth transition of the pore structure by secondary splicing of two or more structures to form the gradient porous support structure due to the existence of the "ladder effect" [27]. Therefore, it is important to design and fabricate a new porous catalyst support with a gradual porous structure to improve the reaction performance of hydrogen production (see Tables 1 and 2).

For the design and fabrication of microreactors, Chen et al. [28,29] designed the disk microreactor and the tree-shaped grid plate microreactor, and thereafter verified their reaction performance by simulation. Peles [30] et al. designed and studied the heat transfer and pressure drop characteristics of a convex array microchannel. It was found that the

Table 1 – Volume, surface area, specific surface area, and porosity of the four structures.

structure	C	SA	AO	S (80%–60%)
volume (mm^3)	3146.57	3768.37	3762.59	1593.012
surface area (mm^2)	48144.25	48220.44	48108.77	21368.87
specific surface area (m^2/m^3)	15300.55	12796.1	12786.08	13414.13
porosity (%)	44	33	33	72

Table 2 – Radius, volume, surface area, and specific surface area of five porosity structures.

Stagger (S) porosity	60%	70%	80%	60%–80%	80%–60%
radius (mm)	0.31	0.26	0.2	0.31–0.2	0.2–0.31
volume (mm^3)	2240	1680	1120	1593.01	1593.01
surface area (mm^2)	28384	25990	22871	21368.87	21368.87
specific surface area (m^2/m^3)	12671.43	15470.24	20420.54	13414.13	13414.13

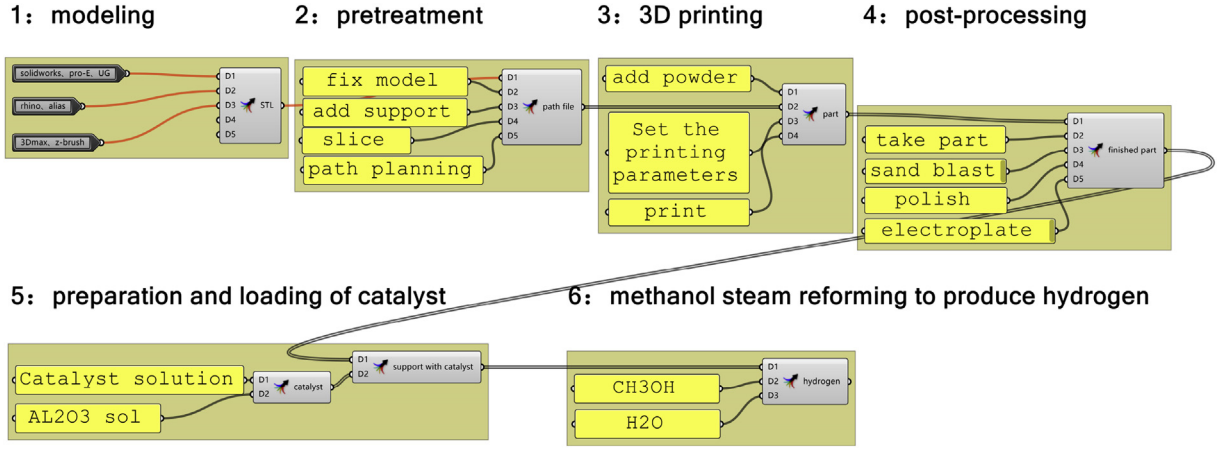

Fig. 1 – Preparation of catalyst support plate and hydrogen production process by SLM. The main process involves two stages: (1) the design and manufacture of the porous catalyst support, including modeling, slicing and path planning, 3D printing, and post-processing, as shown in Fig. 1 from step 1 to 4; (2) the hydrogen production reaction experiment, including the preparation and loading of catalysts and methanol steam reforming to produce hydrogen, as shown in Fig. 1 in steps 5 and 6. The experimental parameters are pore shape, porosity, and material. The typical procedure is to first perform the experiments in the catalyst support with different pore structures and choose the optimal structure, and thereafter vary different porosities, and choose the optimal porosity, and finally conduct the experiments in the catalyst supports with different materials, and choose the optimal material. In this manner, the most suitable parameter combination can be selected stepwise to improve the hydrogen production performance.

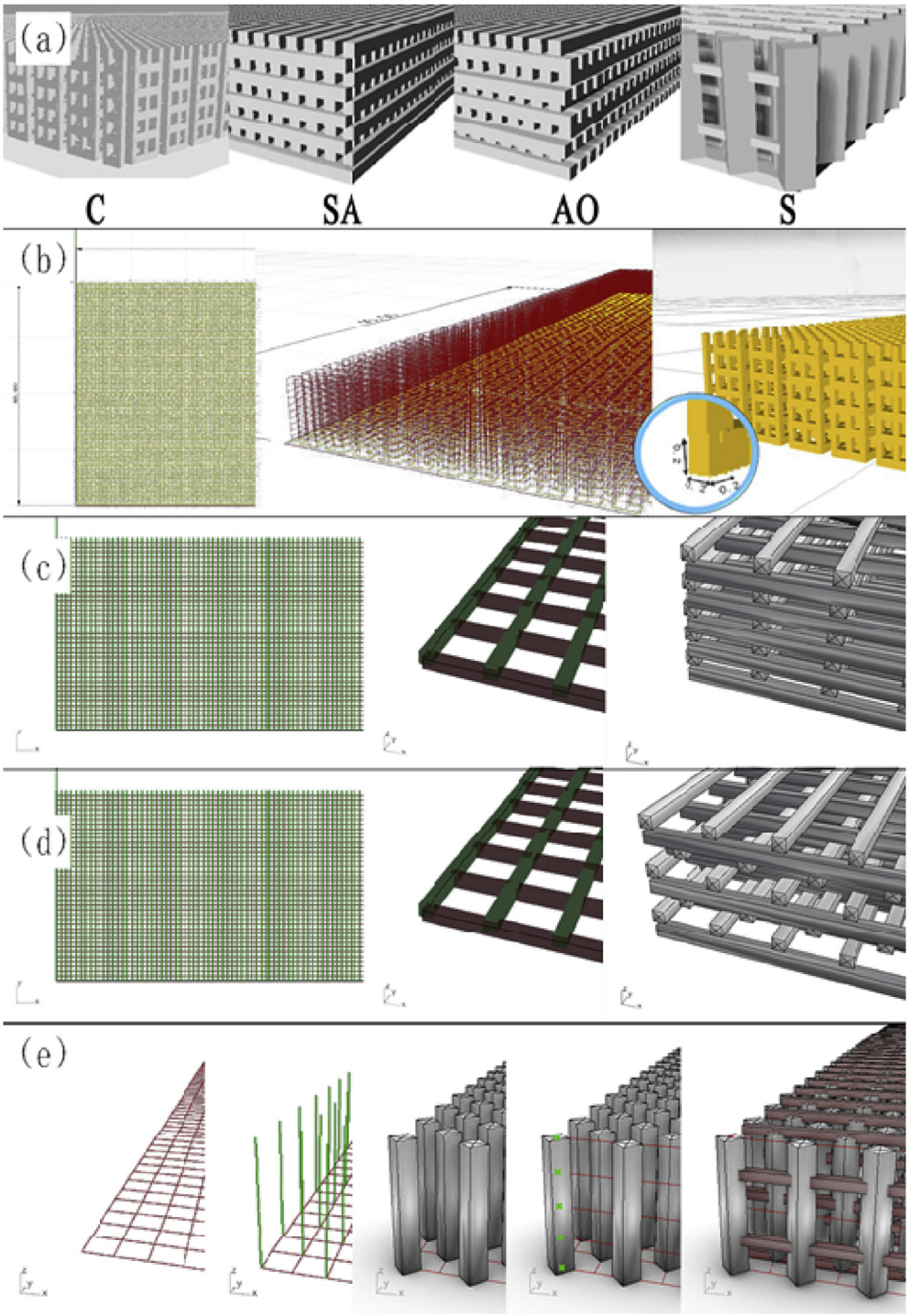

Fig. 2 – (a):Three-dimensional models; and their modeling frameworks:(b): continuous curve (C) (c):simple array (SA) (d):array offset (AO) (e):stagger (S).

structure as the main factor can affect the thermal resistance of the flow. Koga et al. [31] converted metal fiber materials into fiber pulp by wet papermaking technology, and thereafter mixed the catalyst with fiber pulp and added a promoter to enhance the loading performance of the catalyst support. High methanol conversion and catalyst stability can be achieved via this method.

Selective laser melting (SLM) is a typical additive manufacturing (AM) technique to fabricate components via point-by-point scanning, line-by-line lapping, and layer-by-layer stacking of metal materials. SLM can directly fabricate porous microchannel structures and effectively reduce the fabrication process of the microchannel catalyst support, thus improving the production efficiency. Wauthle et al. [32]

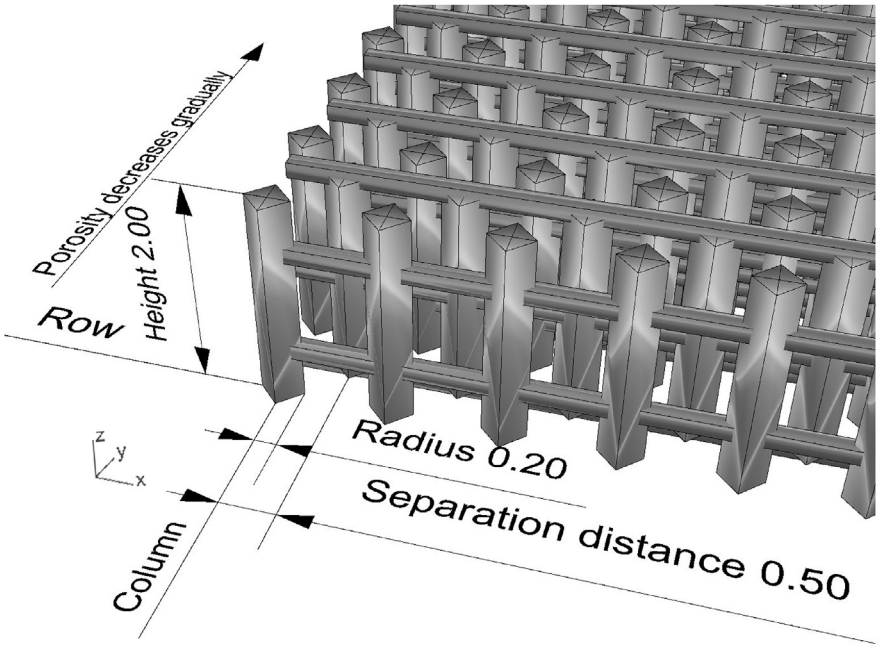

Fig. 3 – The gradual porosity structure is generated by changing the radius of each row.

prepared the dodecahedral unit structure of pure titanium by SLM and studied its mechanical properties and fatigue strength. Zhang et al. [33] fabricated CoCrMo porous parts with octahedral and hexahedral structures by SLM, and their elastic modulus was shown to meet the performance requirements of biomedicine. In addition, Dadbakhsh et al. [34] prepared Ni–Ti porous scaffolds based on the octahedral unit structure. These studies designed porous structures on the basis of an array of repeat units; nevertheless, other types of porous structures can also be explored.

For further research on the pore characteristics of a porous carrier system for hydrogen production, this paper presents a method based on parametric design and SLM technology to design and fabricate the porous catalyst supports with four structures, five kinds of porosity, and three kinds of materials. The hydrogen production performance was evaluated in these supports to optimize the pore structure of the reaction supports. Continuous curve (C) can increase the specific surface area and effective collision (characteristics of infinite differentiation and Angle folding of Hilbert curve). Simple Array (SA) and Array Offset (AO), two structures were compared with each other to verify the influence of flow resistance on the experimental results (simple SA structure had smaller flow resistance, while AO structure had larger flow resistance because of cross-layer). ; stagger (S) Increased accessibility during catalyst loading (structure deployable). After the extreme parameters (maximum and minimum pores) are excluded, the optimal determined parameters under structure are found. The selection of three materials is a combination of production cost (stainless steel cost is lower), thermal conductivity (copper, gold, etc., is one gradient, stainless steel aluminum, etc., is two gradient), and processing difficulty (copper is harder to process to 200 μm).

Experiments

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Porous catalyst support Design and fabricaiton of porous support

Parametric modeling of pore structure

Grasshopper is a parameterized design plug-in based on Rhinoceros [35]. By conceiving the modeling logic and drawing the connected battery diagram, four different structures, namely, continuous curve (C), simple array (SA), array offset (AO) and stagger (S) are designed as shown in Fig. 2(a). The basic modeling idea of the four structures is to generate a line from a point, scan a body from a line, and generate a single closed entity from a Boolean intersection between bodies.

The continuous structure of the curve was inspired by the Hilbert curve. The characteristic of the Hilbert curve is that by increasing the order, an infinite length curve can fill a certain size area. It is easy for the model to approach the manufacturing limit of the size. The idea of modeling is to build a high-order two-dimensional plane curve first, and then scan each layer of curve into a continuum along the z-axis array of five layers. Thereafter, the cylinder (Considering the calculation, during the manufacturing process, at a length of 200 μm, a 60-μm diameter spot and a 25-μm thickness parameter were used to form a nearly rounded rectangle when the sharp edges were swept around, even though the circle was surrounded by four straight edges.) is generated at each node of the curve and integrated with the continuum and single closed entity, as shown in Fig. 2(b).

The simple array and array offset structure were inspired by the study reported by Danaci [36] et al., on thermal

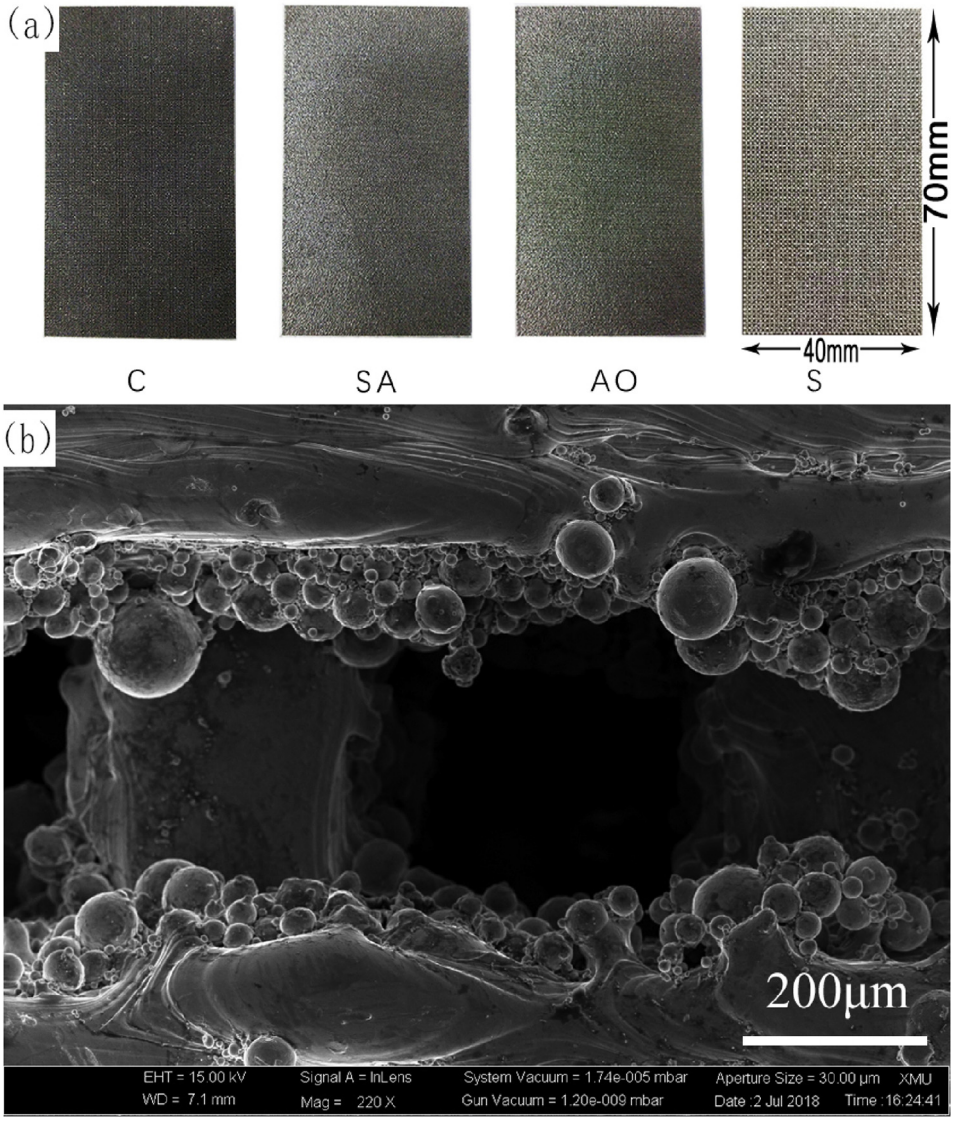

Fig. 4 – (a) Four different structural parts; (b) microstructure of the surface formed by SLM. Scale bar: 200 μm in panel b.

conductivity and pressure drop. The idea of the simple array modeling is to first establish 70 mm and 40 mm long lines along the x-axes and y-axes respectively, and then divide these curves along the y- and x-axes into multiple arrays with a certain distance between them. The number is rounded down by dividing the distance between 40 and 70. All curves are swept into entities and arrayed 5 layers upward, while the septums of 70 mm and 40 mm long cylinder are arranged in contact without overlapping. Finally, all the entitiesare integrated into a single enclosing entity, as shown in Fig. 2(c). On this basis, in array migration modeling, a certain distance should be maintained from the interval of the column of the same length, as shown in Fig. 2(d).

The staggered structure is a structure proposed after considering the flow direction of experimental gas for hydrogen production. This structure is characterized by the observation that the molecules can bump into the solid surface of the latter lines after flowing out of the former rows of pores. The modeling idea was to form an array of rectangles and obtain array points. For each odd row, the points with odd numbers were considered, and for each even row, the points with even numbers were considered, and both were stretched 2 mm along the z-axis to form lines. The lines were swept into entities. Then, the 4 equidistant points of the 2 mm line at the origin were considered. In the five equidistant points, three odd points were arrayed to the even rows, and two even points were arrayed to the odd rows. The lines were stretched 70 mm along the x-axis to form a body, which was then combined with the above body to integrate multiple closed entities, as shown in Fig. 2(e). The porosity could be adjusted by changing the radius (circumcircle of parallelogram), and the gradual porosity model could be generated by changing the radius of each row by the gradient along the y-axis, as shown in Fig. 3.

Catalyst support additive manufacturing

The experimental materials used for catalyst supports with four different structures and five different porosities were made of 316L stainless steel, and the printing machine used

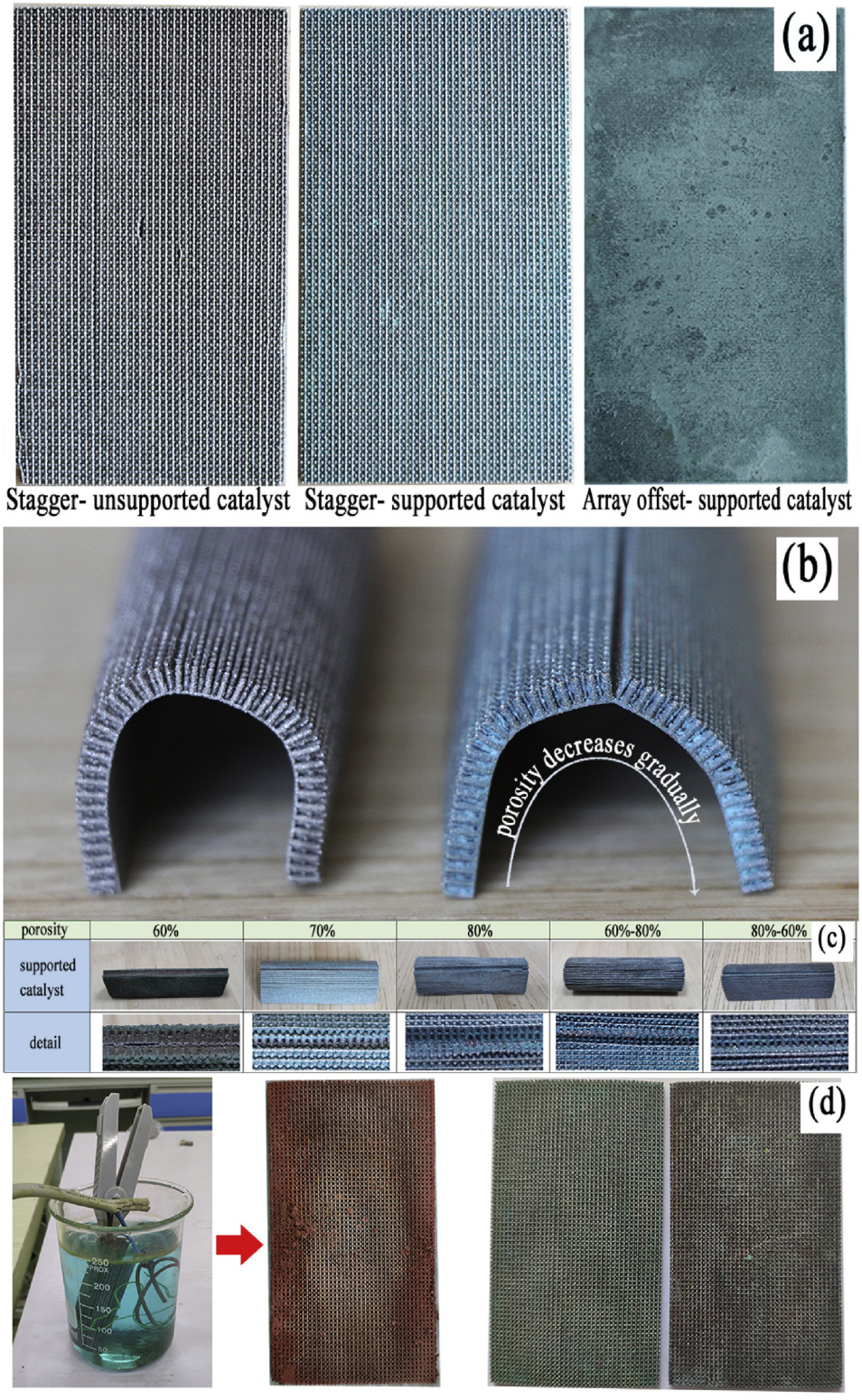

Fig. 5 – (a) Staggered structure-supported catalysts and array offset structure-supported catalysts; (b) staggered structure-supported catalysts bent to facilitate powder shedding and catalyst loading; (c) five kinds of porosity-supported catalysts; (d) The copper layer plating process (left) as well as porous support before and after electroplating (right).

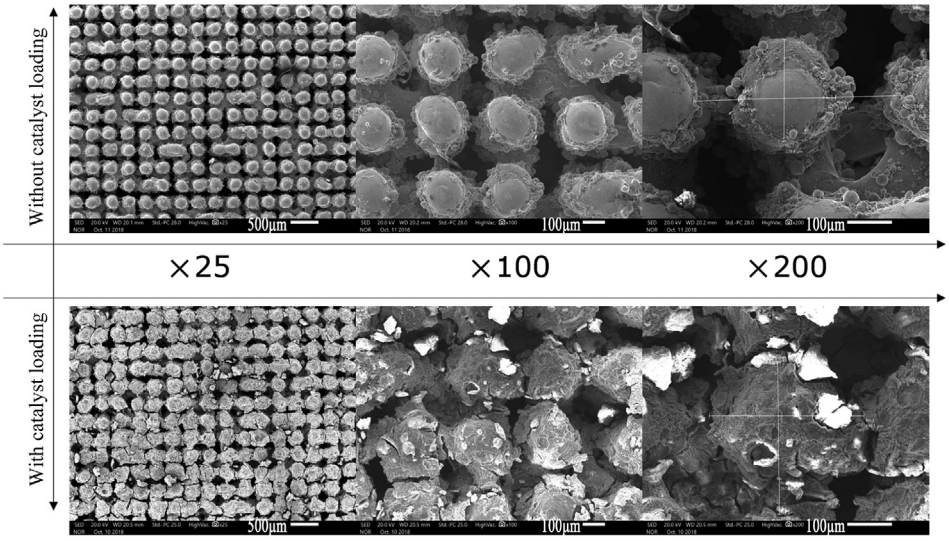

Fig. 6 – SEM images of continuous curve structure without catalyst loading and with catalyst loading.

was the HBD 280 SLM rapid prototyping equipment. The particle size of spherical 316L stainless steel powder prepared by the aerosol method was 15–35 μm. Stainless steel 316L, copper layer-coated stainless steel 316L, and aluminum alloy AlSi10Mg were selected to evaluate the influence of materials on the hydrogen production performance. Printing parameters were listed as follows: layer thickness of 0.025 mm, 65% contour power, scanning speed of 1200 mm/s, spot size of 0.06 mm; 65% solid power, scanning speed of 1200 mm/s, and spot size of 0.07 mm. The optical image of printed parts as catalyst supports are shown in Fig. 4(a). Scanning electron microscopy (SEM) images are shown in Fig. 4(b). The copper layer-coated stainless steel was obtained by electroplating copper on 316L stainless steel material. After printing, the printed parts should be placed into the ultrasonic cleaning machine in order to remove the unbonded powder. A large amount of metal powder was still attached to the surface of the model after shock, which was beneficial to further increase the surface area and the catalyst loading performance.

Hydrogen production performance of catalyst support

Catalyst loading was required before the hydrogen production experiment. In this process, the support plate was first fully impregnated in the mixture of the precursors of the catalyst (Al_2O_3 sol and nitrate solution), and then dried in the oven. This process was repeated until the catalyst was loaded and the two-layer catalyst structure with Cu/Zn/Al/Zr catalyst was obtained [37]. The catalyst load of each support plate was 0.5 g. After the catalyst loading experiments for the first three structures, it was found that a low porosity makes soaking with the catalyst solution difficult, as shown in Fig. 5(a) toward the right, which is not conducive to catalyst loading. At the same time, considering the separation of powder in the pores after printing, a fourth kind of staggered structure model was designed. The staggered structure after bending can expose internal pores and facilitate the shedding of metal powders and the loading of catalysts, as shown in Fig. 5(b).

The staggered structure support plates were designed and printed with five porosity parameters, i.e., 60%, 70%, 80%, 60%–80%, and 80%–60%. By observing the infiltration degree of the single-row catalyst, as shown in Fig. 5(c), it can be seen that it was difficult to infiltrate the catalyst solution into the support with a 60% porosity due to its dense pore structure. A clear boundary can be seen. The infiltration degree is small, which significantly affects the hydrogen production efficiency. The support plate with a porosity of 70% has medium infiltration degree, those with a gradual porosity of 60%–80% and 80%–60% have higher infiltration degree, and that with the porosity of 80% has the highest infiltration degree. The experimental process of copper plating is shown in Fig. 5(d). In the solution of copper nitrate, under the voltage of 5 V of DC power supply, the negative pole was connected to the bent support plate, and the positive pole was connected to the copper wire. The support plate was rotated at 10–15° every 10 min, and a layer of copper was slowly plated. As shown in Fig. 6, the surface thickness increased by 0.125 mm on average according to the SEM images of the continuous structure without catalyst loading. Many of the cylinders are adhered to each other, which significantly reduces the effective surface area.

The hydrogen production reaction from methanol steam reforming uses the experimental system as shown in Fig. 7(a). The specific hydrogen production process was carried out in the reactor shown in Fig. 7(b). Methanol steam was first gasified through the evaporation chamber and thereafter entered the reaction chamber for reforming to produce hydrogen [18].

Methanol conversion X_{MeOH} and hydrogen flow rate υH_2 were calculated as follows [27]:

$$X_{MeOH} = \frac{F\left(y_{CO} + y_{CO_2}\right)}{22.4 + \upsilon_{MeOH,in}} \times 100\% \quad (1)$$

$$\upsilon_{H_2} = F \times y_{H_2} \quad (2)$$

where F is the velocity of reforming gas, y represents the volume fraction, and $\upsilon_{MeOH,in}$ is the molar rate of the gas entering the microreactor.

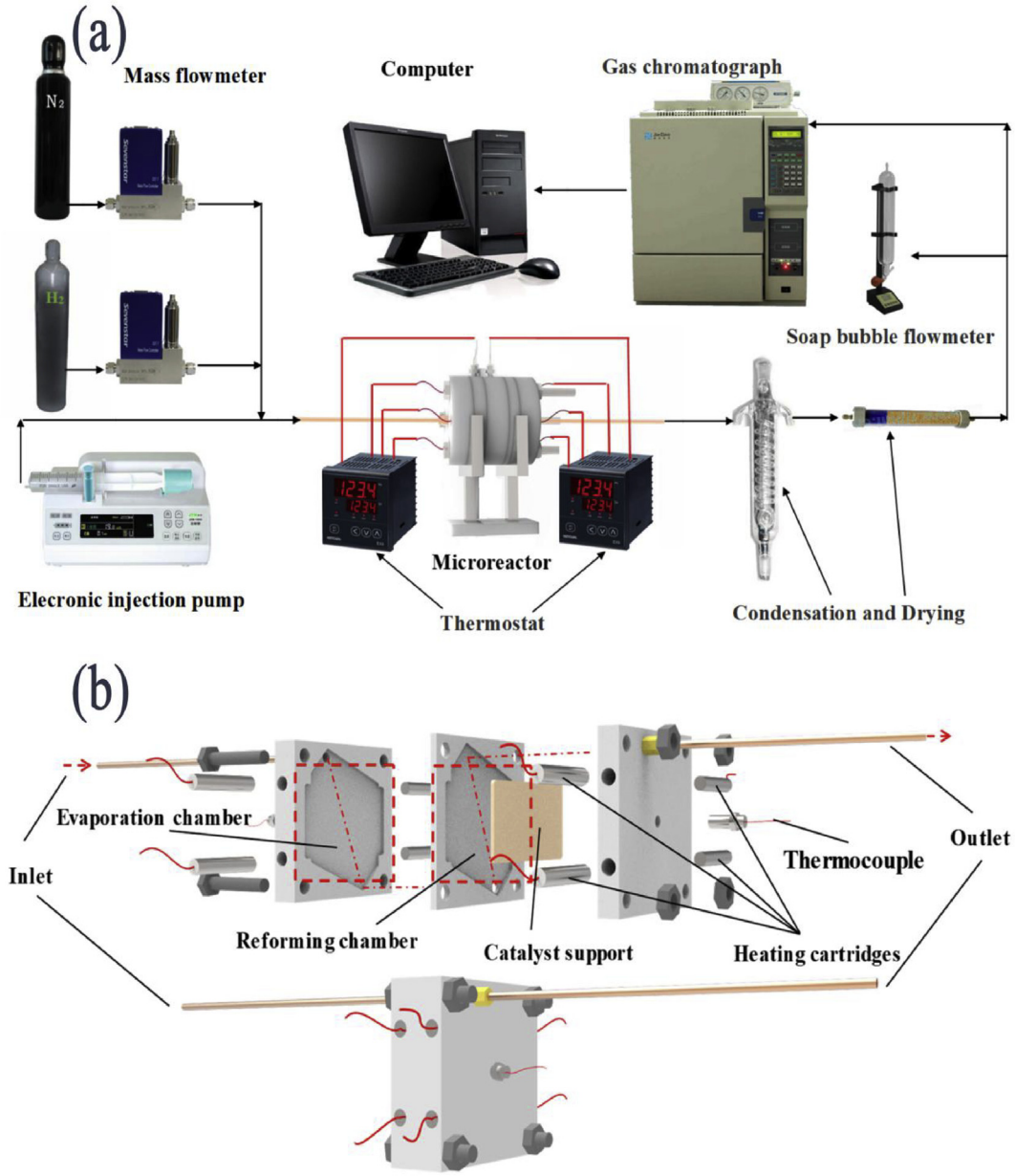

Fig. 7 – (a) Test system of hydrogen production and (b) Laminated plate microreactor for hydrogen production.

Results and discussions

Simulation test analysis

Particle flow simulation in complex porous structures remains a difficult problem. In this paper, molecular dynamics theory was used to explain and discuss the hydrogen production performance of support plate with different gradual porosities by ignoring chemical reaction, simplifying the geometric model, and observing only the collision and free diffusion process of particles in the reactor. The modeling process was established using Rhinoceros and Grasshopper software, and the simulation process was performed in C4D and RealFlow software. The overall size of the porous support was 70 × 40 × 2 mm (L × W × H), the porosity was 70%, and the velocity of reaction molecules at the inlet was 0.08 m/s. The initial color was red, and gradually turned white with the increase of time frames.

The residence time is the time from the moment the material enters the porous support to the moment it leaves the porous support. The change of residence time can directly affect the reactor performance by influencing the reactions efficiency. This time should be as long as possible to ensure the complete reaction of the material [38]. As shown in Fig. 8(a), when the simulation animation reaches 580 frames, it can be observed that a large number of molecules have passed through the porous reaction support region with uniform porosity structure, which indicates that the molecules in the uniform porosity structure have the shortest residence

time and relatively less chance of collision. On the other hand, less molecules exit from the two kinds of structures with the porosity values from 60% to 80% and from 80% to 60%, and the difference is inconspicuous, which illustrates that the residence times are longer in these two kinds of structures, thus, these structures could provide better performances.

Chaos and diffusion uniformity are used to characterize the degree of molecular diffusion in microchannels. When the diffusion is more uniform, the effective collision area becomes larger, which leads to better heat transfer and hydrogen production performance. When the simulation animation reaches 2000 frames, it can be observed that molecules form strands and flow out of the outlet of the structure with 60%–80% porosity, and a large number of cavity areas appear, as shown in green in Fig. 8(b), which means the molecules are diffused unevenly. On the contrary, there is no cavity at the bottom exit of the structure with 80%–60% porosity. The molecular diffusion is uniform and the chaotic phenomenon is relatively obvious, indicating that the molecular heat energy obtained from the microreactor is more and the heat transfer performance is better, therefore, the hydrogen production performance is better.

In addition, by observing the motion of molecules, it can be seen that the channel with a 45° oblique angle is narrower in the structure with 80%–60% porosity. The movement of molecules in the channel is similar to that in the funnel, i.e., the closer they are to the exit, the more severe collision is observed, as shown in Fig. 8(c). This further increases the probability of molecular collisions. Combined with the above three points, the structure with 80%–60% porosity shows the

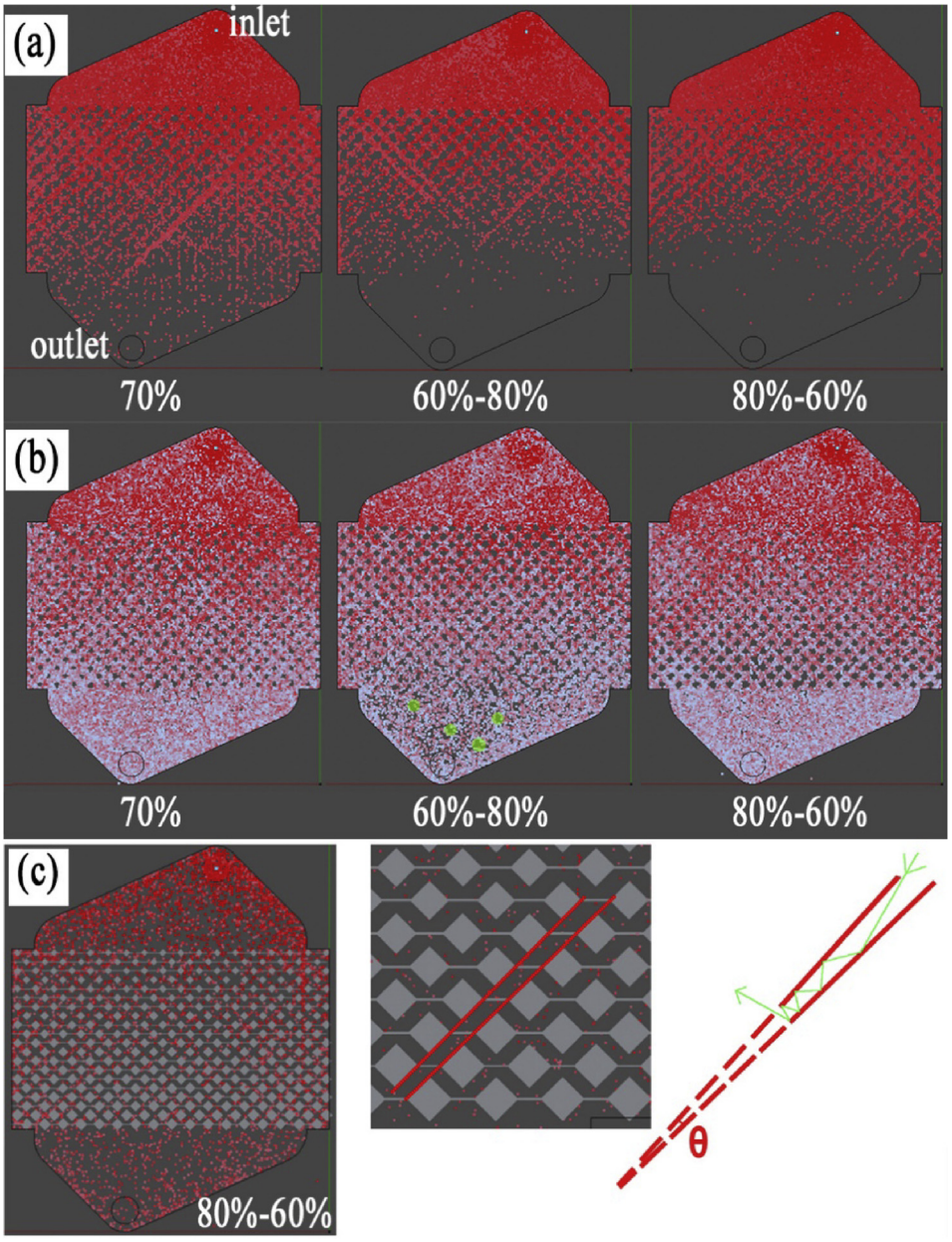

Fig. 8 – (a) Simulation diagram of three kinds of porosity structure at the 580 frame and (b) 2000 frame. (c) The image showing that the closer the structural molecules are to the exit, the more severe collision is observed.

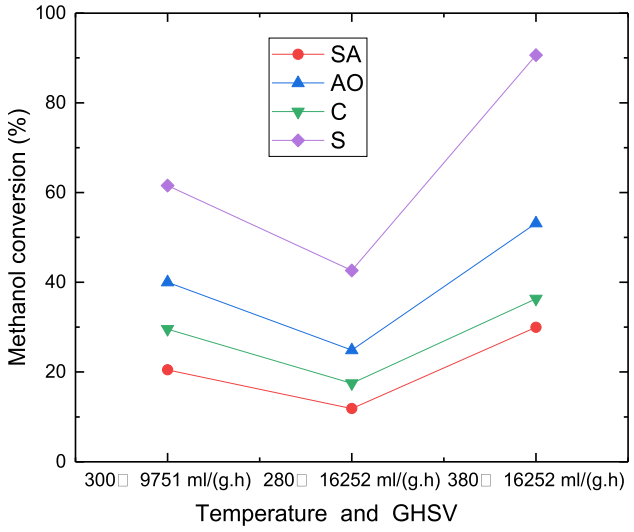

Fig. 9 – Comparison of the methanol conversion in reactors with curve of continuous (C), simple array (SA), array offset (AO), and staggered structure (S) methanol conversion.

best performance in terms of mass and heat transfer; consequently, the hydrogen production efficiency is the best in this case.

Effect of different porous structures on the methanol conversion

The effects of different porous structures on the methanol conversion at different reaction conditions are shown in Fig. 9. The plot shows that the methanol conversion in the catalyst support with staggered structure (S) is highest because the bending structure exposes its internal surface, which is beneficial for the loading of catalyst. Therefore, its effective surface area is the highest. Due to the low porosity, a large number of catalysts are only attached to the surface layer, decreasing the effective reaction area in the reaction support SA and AO structures. Therefore, the methanol conversions are relatively low in these catalyst supports. Compared with the methanol conversion in the catalyst support with SA structure, that in the catalyst support with AO structure is higher, because of the easy diffusion of the reaction gas and contact with the surface catalyst due to its interlaced layers. For the catalyst support with continuous curve structure (C), because the vertical holes are clogged, the reaction gases are silted up in a large amount of space, leading to the cavity in the reactor. The gases flow through the shortest path, shortening the residence time and reducing the effective reaction area. Therefore, the methanol conversion in the catalyst support with C structure is relatively low.

Effect of porosity on the methanol conversion

Figs. 10 and 11 show the methanol conversion rate and hydrogen flow rate at different flow rates and temperatures, respectively. From these plots, it is inferred that due to the low porosity, the methanol conversion ratio in the porous carrier with 60% porosity is the lowest. Since the catalyst only adheres to the upper layer, the reaction gases have less contact with the catalyst, leading to the lower efficiency of hydrogen production. Therefore, compared with other samples, the performance of 60% porosity support is the worst. Although the geometric surface area of 80% porosity support is smaller than that of 70% porosity support, the effective surface area may be slightly higher than that of 70% porosity support because of the higher loading degree of the catalyst. Therefore, the methanol conversion in 80% porosity support is slightly higher than that in 70% porosity support in the varied flow rate experiments, therefore, the methanol conversion is slightly higher than that of 80% porosity support in the varied temperature experiments. Among the results of catalyst supports with uniform 70% porosity structure, gradient 60%–80% porosity structure, and gradient 80%–60% porosity structure, the catalyst support with gradient 80%–60% porosity structure shows the best performance in hydrogen production, which is in accordance with the results of previous simulation and analysis.

Effect of different materials on the methanol conversion

Staggered structure with a porosity of 80%–60% was selected, and the catalyst 0.5 g was evenly loaded on three supports of different materials using the same loading process. The hydrogen production performance in catalyst supports made out of stainless steel, copper plated stainless steel, and

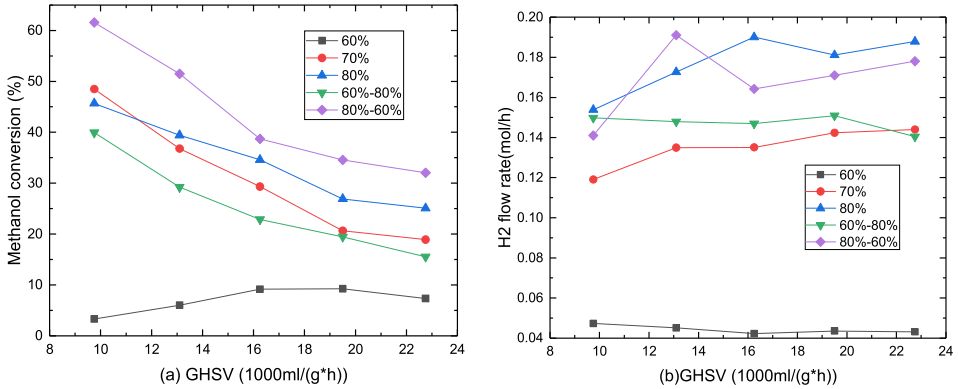

Fig. 10 – Comparison of five kinds of porosity with different GHSV at 300 °C: (a) Methanol conversion; (b) hydrogen flow rate.

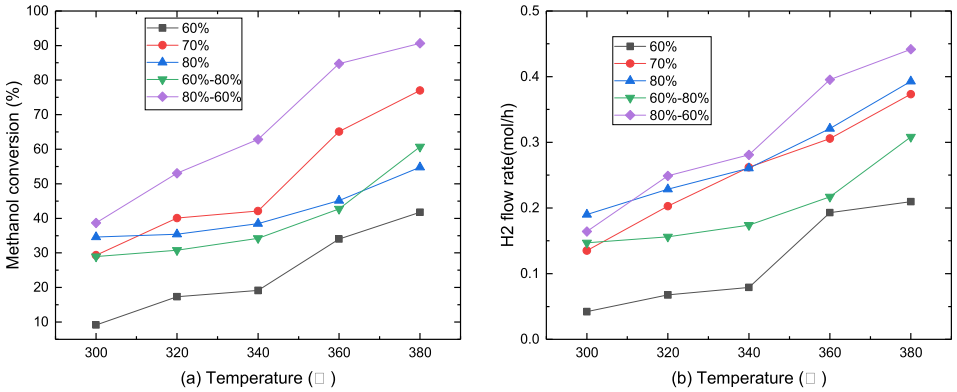

Fig. 11 – Comparison of five kinds of porosity with different temperature at 16252 (ml/(g*h)): (a) Methanol conversion; (b) hydrogen flow rate.

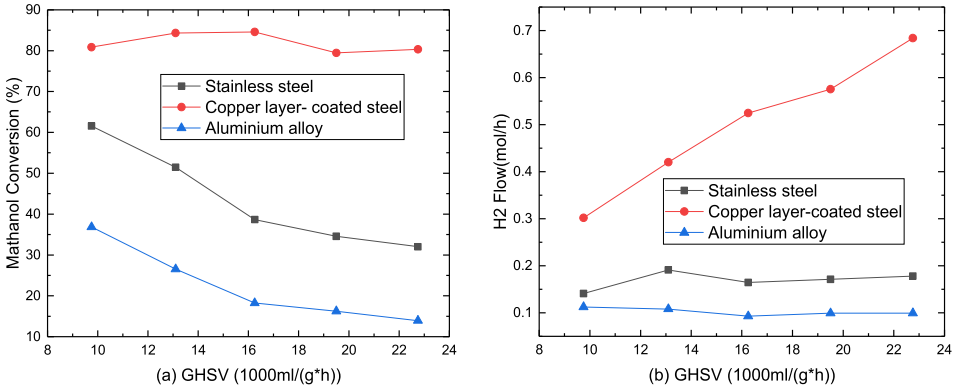

Fig. 12 – Comparison of three kinds of materials with different GHSV at 300 °C: (a) Methanol conversion; (b) Hydrogen flow rate.

aluminum alloy was tested, and it was found that the hydrogen production performances in catalyst supports made out of different materials varied significantly, and the performances ranked from high to low were observed for copper plated stainless steel catalyst support, stainless steel catalyst support, and aluminum alloy catalyst support, as shown in Figs. 12 and 13. Compared with stainless steel catalyst support, the copper layer-coated stainless steel catalyst support shows better hydrogen production performance. This is due to the better heat transfer performance of copper than that of stainless steel and since the copper element on the surface can prevent the reaction between the stainless steel and the catalyst to avoid severe catalyst deactivation. Although the thermal conductivity of aluminum alloy is much higher than that of stainless steel, the intensity of replacement reaction with the catalyst is stronger than that of stainless steel with the catalyst, resulting in catalyst deactivation and low hydrogen production performance. The highest hydrogen production performance in all experiments is observed in the copper coated stainless steel catalyst support and the

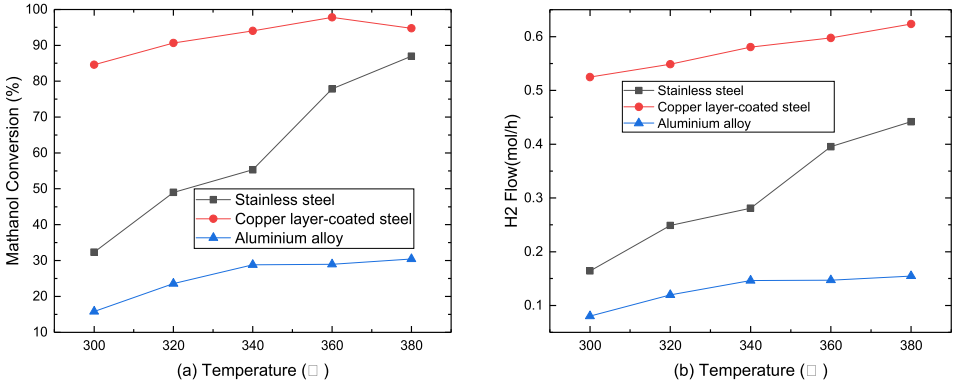

Fig. 13 – Comparison of three kinds of materials with different temperature at 16252 (ml/(g*h)): (a) Methanol conversion; (b) Hydrogen flow rate.

methanol conversion in all test conditions can reach more than 79% at 360 °C, and with the highest value of 97%.

Conclusions

In this study, a novel fabrication method of porous support with controllable structure and porosity by parameterized modeling and selective laser melting additive was proposed, and it was successfully applied to a methanol steam reforming microreactor as catalyst support for hydrogen production, providing a new idea for the design and fabrication of porous catalyst support. Three experiments were designed and conducted, and the results showed that the stagger structure copper layer-coated stainless steel with porosity from 80% to 60% exhibited the highest the methanol conversion rate, up to 97%.The main conclusions are listed as follows:

1 Many metal particles are adhered to the surface of porous carrier fabricated by selective laser melting process, which increases the surface roughness and is beneficial to the catalyst loading process.
2 For the hydrogen production experiment of porous catalyst support with four different structures, the staggered structure has the higher hydrogen production performance. The main reason is that the flexible feature of the staggered structure makes the internal surface more easily exposed, which is conducive to the catalytic adhesion in the internal pores and increases the effective surface area.
3 For the hydrogen production experiment of catalyst support with five kinds of porosity, the higher hydrogen production is obtained for the from sparse to dense porosity from 80% to 60% pres, which is in good agreement with the simulation results. In combination with simulation experiments, the reason lies in the best comprehensive performance of retention time, diffusion uniformity and specific molecular motion path.
4 For the hydrogen production experiment of porous catalyst support with three different materials, the copper layer-coated stainless steel exhibite the better hydrogen production performance. The reason is that after copper plating, copper separates the catalyst from stainless steel, effectively preventing the reaction between catalyst and stainless steel from reducing the activity.

The experimental results show that the porosity of catalyst support has a great influence on the hydrogen production performance. Too high porosity of more than 90% will result in a printing failure, and too low porosity will cause the catalyst solution to be difficult to penetrate. Further research is required to explore the optimal structure of the porous support for hydrogen production and reveal the internal molecular motion law so as to realize low-cost fabrication.

Acknowledgments

The work is financially supported by the National Natural Science Foundation of China (Grant No. 51405082, 51922092), the Natural Science Foundation of Guangdong Province (Grant No. 2019A1515011961), and the Science and Technology Innovation Platform of Foshan City, Guangdong Province, China. (Grant No. 2016AG100341). In addition, the supports from the Hunan Provincial Support Plan for Outstanding Young Investigators (Grant No. 2017RS3072) is also acknowledged.

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