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Methanol steam reforming on catalyst coating by cold gas dynamic spray

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ABSTRACT

Catalytic hydrogen production by methanol steam reforming is considered to be an attractive H_2 source option. However, performance of conventional packed beds of methanol steam reforming is limited by heat transfer, which results in a low effective factor of the catalyst. In this work, $CuO/ZnO/Al_2O_3$ catalyst coating has been generated by an innovate method named cold gas dynamic spray. Performance of the catalyst coating is investigated in a plate-type reactor after its characterization. SEM results of the catalyst coating show that it is rough and porous. Methanol steam reforming results of the coating are compared to that of the same catalyst in a packed bed of tubular reactor. Catalytic coating activity is superior to that of the packed bed due to more effective heat transfer. The highest methanol conversion of 90.45% is achieved at the temperature of 543 K when the space velocity is 1.09 h^{-1} on the coating. And the highest hydrogen production rate is 30.05 ml/min at the temperature of 543 K when the space velocity is 1.56 h^{-1} on the coating.

Introduction

Hydrogen has been considered as a power source in the future for a long time because of its low pollutant emissions [1]. However, difficulties in storage of hydrogen persist. Methanol provides easier and safer storage compared to hydrogen [2–4]. And it can be reformed to produce hydrogen by steam reforming at low temperature with very small amount of CO in the products. As a result, methanol is considered as a primary liquid fuel to generate hydrogen [5]. And methanol steam reforming (MSR) is generally considered as an attractive approach to producing hydrogen [6].

However, the traditional packed bed reactors which are widely used in industry suffer from axial temperature gradients. This leads to the problems such as the occurrence of cold spots in the catalyst bed [7]. Axial temperature gradients will result in thermal stresses in the reactor channels. These disadvantages are usually caused by mass and heat transfer limitations in the catalyst bed. Catalyst performance is also significantly affected by the thermal stress [8–11]. Therefore, due to the transfer resistance, traditional MSR reformers are limited to a low effective factor of the catalyst [11]. Moreover, when the catalyst sinters in the packed bed, the pressure drop will increase because the void fraction is reduced. When reactor scale is reduced, traditional reactors may not be

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efficient because of large pressure drop [12,13]. The reactor diameter also affects the cold spot temperature difference in MSR. It was found that the cold spot temperature difference was 22 K in the packed bed reactor with 1 mm in diameter [14,15]. The equivalent diameter should be reduced as small as 300 μm in order to remove the cold spot temperature difference [14]. However, such size scale is unavailable in industrial applications for MSR. Also, when the micro-reactors are used, it is difficult to introduce catalyst particles into the microchannel. Random packing will result in a high-pressure drop, so each channel should be packed identically [16]. The pressure drop is lower in a coated catalyst bed, because the coating catalyst provides the advantage of superior geometry [13]. The activity of the coated catalyst was also found to be superior to that of the same catalyst in a packed bed for MSR [14].

There are a number of methods to generate catalyst coating, such as anodic oxidation of aluminum surfaces through electrolysis or thermal oxidation of aluminum rich in steel. Cold gas dynamic spray (CGDS) is a technology based on gas dynamics. It is composed of spray gun, powder feeding, heating, gas regulating, high-pressure gas source and powder recovering. Fig. 1 presents a schematic representation of CGDS and a picture of CGDS system. Gas is preheated to accelerate the particle in the cold spray. Feedstock and substrate will little be affected because of low preheating temperature and short heating time in the process [17–19]. Therefore, many materials can be used as feedstock in the cold spray, such as

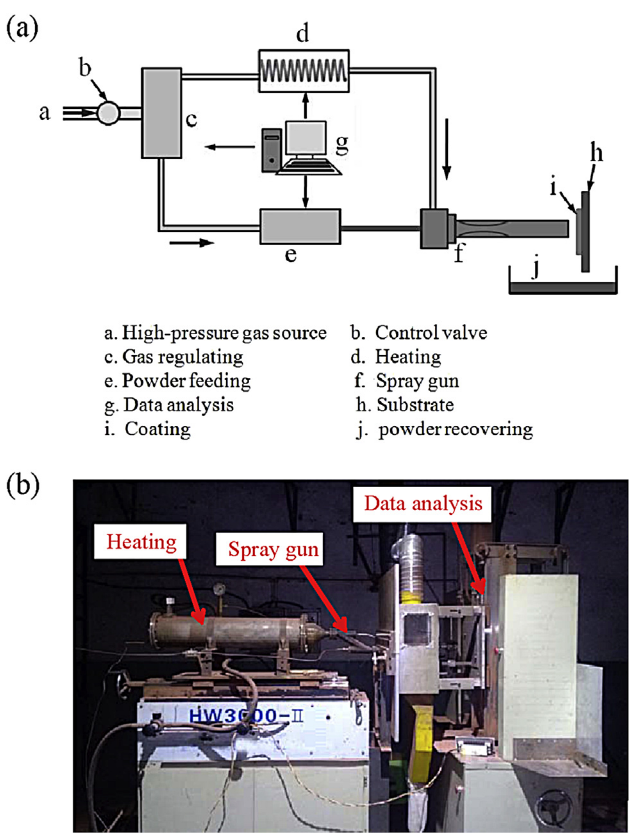

Fig. 1 – (a) Schematic representation of CGDS and (b) Picture of CGDS system.

metal, alloy, even plastics. High pressure gas (nitrogen, helium, air or mixed gas) carries the particles through the spraying gun to impact the substrate at the solid state with high speed. Severe plastic deformation of particle takes place on the substrate surface, and then the coating is formed [20,21].

Functional coatings can also be manufactured by this technology, such as corrosion-resistant coating, thermal-resistant coating, conductive coating and catalyst coating. Stolenhof manufactured Cu coating by cold spray and thermal spray [22]. It was found that the oxygen content of the cold sprayed coating was lower than that manufactured by thermal spray. The coating prepared by cold spray also had good electric and thermal conductive performance. Kuemmel successively deposited the aluminum and Cu on the ceramics surfaces [23]. The coating combined closely with the ceramic substrate, and it also had a good heat conduction performance.

In our past research, we have successively prepared Cu coating, Cu–Al_2O_3 coating and NiO/Al_2O_3 catalyst coating by cold spray. Particle deposition characteristic and coating microstructure have been studied [24,25]. Cu–Al_2O_3 coating with high porosity has been found and no phase transition has been observed. In the cold spray coating, particles are found to be combined with the substrate through metal bonding. This can intensify thermal conductivity from substrate to the coating due to the decreased thermal contact resistance.

In this study, CuO/ZnO/Al_2O_3 catalyst coatings were deposited on the aluminum substrates by cold spray method. Coating catalytic performance of MSR was investigated in a plate-type reactor. And activity of the coating was compared to that of the same type catalyst in a packed bed of tubular reactor.

Experimental apparatus

Catalyst coating preparation by cold spray

Aluminum slabs which exhibit no catalysis for MSR were used as substrates in the cold spray. Dimensions of the substrate were 20 mm × 6 mm in length and width and 1 mm in height. The slabs were polished and then cleaned by the acetone and deionized water before the cold spray in order to remove its oxide surface and increase surface roughness. This pretreatment would be beneficial for catalyst particles depositing onto the substrate surface. Substrates were weighed after dried in an oven before cold spray process. The sprayed catalyst (CuO/ZnO/Al_2O_3, CB-7, Chuanhua Co. Ltd.) was grinded to size less than 50 μm in diameter. Composition of the CuO/ZnO/Al_2O_3 catalyst was shown in Table 1. And catalyst coating weight was obtained from the substrate weight

Table 1 – Composition of the CuO/ZnO/Al_2O_3 catalyst.

Technology parameters	Wt.%
CuO	≥65.0
ZnO	≥8.0
Al_2O_3	≥8.0
Other additives	≥2.0

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