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Performance of a catalytic micro-combustor based on $Pt/Al_2O_3/Ni$ for methanol fuel cell application

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HIGHLIGHTS

- A catalytic micro-combustor is designed for methanol fuel cells.
- The combustor uses $Pt/Al_2O_3/Ni$ to provide catalysis for methanol combustion.
- The effects of Pt and Al_2O_3 loadings and methanol feeding mode are evaluated.
- The feasibility of self-combustion based on heat recirculation is validated.

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ABSTRACT

This work focuses on the performance of a catalytic micro-combustor to be used as a heat source for a direct methanol fuel cell. This combustor uses $Pt/Al_2O_3/Ni$ to provide catalysis for methanol combustion. It is proved that the use of a higher catalyst loading mostly promotes a higher methanol conversion rate. The catalyst distribution has a dominant effect on the reaction performance. Results also verify the necessity of optimizing the amount of Al_2O_3 loading. Three models based on different structural design and operating mechanism are evaluated. It is shown that adding a preheating layer helps gain a uniform temperature distribution in the combustion chamber. Compared with methanol injection, the bubbling method for methanol supply promotes a faster start-up of the combustion reaction. Besides, the feasibility of using a heat recirculation layer to realize self-combustion at room temperature is also validated. All these issues are of practical significance to the combination of combustor and fuel cell.

1. Introduction

With the rapid development of laptop computers, mobile phones, implantable medical devices and the like, people are more eager to explore alternative power production technology for portable applications. Although traditional lithium batteries are still widely viable, they cannot meet the increasing power demand because of its short life, long charging time and low energy density. As a potential candidate, the hydrocarbon feedstock equipment shows many advantages such as rapid charging and discharging process, longer duration and higher energy density [1]. Especially, the emergence of micro-reaction technology enables high-efficient production in a more compact system with a highly reduced volume [2–5]. In this field, the micro-combustor can be regarded as a miniaturized power generation plant for micro-engines [6–8], which also possibly combines with thermoelectric elements to produce electricity [9,10]. Besides, it can be also used as a heat source to serve the chemical reactors like fuel cells and reformers in order to enhance their reactions [11–15].

As for a polymer electrolyte membrane (PEM) fuel cell, hydrogen gas is mostly used as the anode fuel. However, considering the production cost and storage safety, many researchers preferred to use aqueous fuel rather than pressurized hydrogen. As an attractive choice, methanol can be reformed into hydrogen or be directly fed into a PEM fuel cell which could receive additional thermal energy from a catalytic combustor. The combustor may share the same fuel source or partially use the recycled residual methanol from the fuel cell anode. This design not only maximizes the fuel utilization efficiency but also helps more quickly vaporize the methanol for the fuel cell so as to realize faster start-up and lower methanol crossover [14,15].

The open literatures have provided plenty of technical information regarding the micro-combustion and with it the design, operation and performance of dedicated combustors [16,17].

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However, we have to face the challenge that it is quite difficult to ignite the fuel in the limited space of a micro-combustion chamber which owns a larger ratio of surface area to volume because the diffusion and residence time of reactants significantly decrease so as to increase the heat loss under this condition. As a result, the reaction is greatly depressed due to flame instability and even instant quenching. To overcome such obstacles, a certain kind of catalyst is usually added into the microscale chamber to assist combustion reaction which can be greatly improved by optimizing both the structural design and operating conditions of the combustor.

Many research findings have been reported toward the catalytic methanol combustion based on platinum (Pt) catalysts. Hu et al. [18] made an early study on the spontaneous ignition of methanol/air mixtures over Pt nanoparticles. They used quartz fibers to carry Pt particles and fed the air flow saturated with methanol vapor into the combustor. In order to actively control the reaction process, the stoichiometric ratios of methanol and oxygen were regulated achieving a controllable combustor temperature. Results suggested that the catalytic activity was related closely to its particle size and surface morphology. Moreover, the adiabatic catalyst bed was also proved conducive to the ignition of methanol on account of the slower heat release process and higher local temperature. Ma et al. [19] investigated the effects of particle size, catalyst loading and flow residence time on the combustion reaction of methanol/air premixtures. The authors prepared different Pt particles (2–5 nm, 200 nm, 500 nm) attached to the quartz fibers, and found that the smaller particles produced a higher catalytic performance due to enhanced reactivity caused by a higher surface area. They also proved that an extremely high loading of Pt catalyst possibly lead to a decrease in steady-state temperature, while a higher air flow rate could carry more methanol vapor yielding a higher temperature. Applegate et al. [20] evaluated the high-temperature catalysis of methanol/air mixtures by using Pt nanoparticles dispersed on a cordierite substrate. Results indicated that the overall catalytic activity had less sensitivity to the effect of restructuring and sintering of catalyst nanoparticles. They further validated the mechanisms of room-temperature ignition of stoichiometric methanol/air mixture and also discussed a series of engineering aspects related to the operation and management of a catalytic microreactor for methanol combustion [21].

Lindström and Pettersson [22] used nozzles to atomize the liquid methanol and successfully ignited the methanol/air mixture at room temperature. They claimed that replacing a large portion of the catalyst bed with base metal catalysts yielded a more homogeneous temperature distribution. The increase of Pt loading resulted in higher activity whereas increased the risk of hot spot formation. They also recommended mixing manganese (Mn) into the catalyst so as to improve the catalytic reaction. Pavlov and Qiao [23] developed a catalytic combustion unit for a micropropulsion device. They successfully achieved self-initiated and self-supported catalytic conversion of methanol/air mixtures in the absence of an external heat source. Results indicated that the temperatures at different locations of the reactor varied with the change of air flow rate. Some of other publications were more devoted to the effects of catalyst fabrication and catalyst support. Additionally, optimization of the reactor design and the testing system has also attracted extensive attention [24–28]. Although the technology of catalytic combustion has ever been used for the PEM fuel cell combined with a methanol reformer, there is barely information oriented to the direct methanol fuel cell (DMFC) applications. With this background, this work focuses primarily on a catalytic micro-combustor based on the Pt–Al_2O_3–Ni catalyst system. This device is intended to be used to provide additional heat for a methanol-feed fuel cell.

2. Experimental

2.1. Catalyst preparation

In this work, we used nickel (Ni) foam (40 mm × 40 mm × 1 mm) as the catalyst backing since it owns higher mechanical strength and thermal conductivity. Another reason is that, its higher porosity helps avoid agglomeration of Pt particles on its surface, which improves the catalyst utilization. Furthermore, we used the alumina (Al_2O_3) sol to enhance the effective surface area and adhesive ability of the catalyst support. The detailed process for fabricating the catalyst system can be described as follows. The Al_2O_3 sol and 0.02 g mL^{-1} chloroplatinic acid solution were prepared in advance. Subsequently, the Ni foam was dipped into the Al_2O_3 suspension, then removed from the sol and dried. The above step was repeated until the amount of the Al_2O_3 sol reached the required level. To form the catalyst support, the pretreated Ni foam was placed in a muffle furnace and calcined at 500 °C for 2 h. Afterward, a certain amount of diluted chloroplatinic acid solution was uniformly dispersed onto the Ni foam and again treated in the furnace. Finally, the catalyzed sample was sintered in a reductive atmosphere with 20% H_2/N_2 in a tubular furnace conditioned at 500 °C for 2.5 h. Fig. 1 compares the appearance of Ni foams in each processing stage. The catalyst morphology was also characterized by scanning electron microscope (SEM) showing that the Al_2O_3 sol is spread onto the porous skeleton of Ni foam (see Fig. 2). It is also found that the produced dendritic Pt nanoparticles were uniformly distributed on the sol surface. Different catalyst compositions in the form of $Pt_a(Al_2O_3)_b$ were prescribed in this experiment. The footnote letters a and b respectively denote the mass percentage of Pt and Al_2O_3 loadings in the catalyst.

2.2. Combustor design and testing setup

Fig. 3 shows a schematic view of the testing setup. In this work, bottled oxygen was used as the oxidant while a syringe pump was used to control the flow rate of methanol. The methanol mixed with oxygen in the combustion chamber and reacted under the influence of Pt catalyst. The operational temperature could be acquired by the embedded K-type thermocouples and controlled by a programmable controller. The exhaust gas flow rate was measured through the soap bubble flowmeter. The composition of reaction products was detected by a commercial gas chromatograph (Agilent 6820). In this study, we designed three models of micro-combustor consisting of different laminated components, as shown in Fig. 4. For the model I, the methanol and oxygen were mixed in the combustion chamber and then directly exhausted after reaction. A heat block was used to heat the combustor. Based on this structure, the model II added a preheating layer before the methanol/oxygen mixture entered the reaction chamber. An exploded view of its configuration is displayed in Fig. 5 in which the geometric dimensions of the preheating and reaction plates are also included. A serpentine single channel with a depth of 3 mm was machined in the preheating plate. For the model III, a heat recirculation layer was sandwiched between the reaction chamber and back-up block. The whole assembly was housed with insulation material, e.g. quartz wool. This embodiment got rid of the external heater, relying on self-regulation of the combustor temperature. For all the models, the hexagonal combustion chamber had the same thickness of 1.5 mm. A gasket made of flexible graphite felt was used to seal the gap between the adjacent components. In order to better integrate the combustor with the methanol-feed fuel cell, we used compatibles design parameters for these two devices.