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Development of Cu foam-based Ni catalyst for solar thermal reforming of methane with carbon dioxide[☆]

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ABSTRACT

Using solar energy to produce syngas via the endothermic reforming of methane has been extensively investigated at the laboratory- and pilot plant-scales as a promising method of storing solar energy. One of the challenges to scaling up this process in a tubular reformer is to improve the reactor's performance, which is limited by mass and heat transfer issues. High thermal conductivity Cu foam was therefore used as a substrate to improve the catalyst's thermal conductivity during solar reforming. We also developed a method to coat the foam with the catalytically active component $NiMg_3AlO_x$. The Cu foam-based $NiMg_3AlO_x$ performs better than catalysts supported on SiSiC foam, which is currently used as a substrate for solar-reforming catalysts, at high gas hourly space velocity ($\geq$400,000 mL/(g·h)) or at low reaction temperatures ($\leq$ 720 °C). The presence of a γ-Al_2O_3 intermediate layer improves the adhesion between the catalyst and substrate as well as the catalytic activity.

1. Introduction

Steam reforming of methane (SRM) and carbon dioxide reforming of methane (CDRM, also known as 'dry reforming'), are promising solar thermochemical processes driven by concentrated solar energy. Both reactions can store solar energy in the form of syngas (a mixture of CO and H_2) at a high storage density and with low thermal loss.

SRM (reaction 1) and CDRM (reaction 2) are reversible and highly endothermic reactions [1,2] as follows:

$$CH_4 + H_2O(g) \leftrightarrow CO + 3H_2 \qquad \Delta H^o_{25\,^\circ C} = +206\ \text{kJ/mol} \tag{1}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H^o_{25\,^\circ C} = +247\ \text{kJ/mol} \tag{2}$$

The water–gas shift reaction (reaction 3), or its reverse, can also occur in conjunction with both reactions (1) and (2).

$$CO + H_2O\,(g) \leftrightarrow H_2 + CO_2 \qquad \Delta H^o_{25\,^\circ C} = -41\ \text{kJ/mol} \tag{3}$$

Reactions (1) and (2) occur at high temperature and, in the case of conventional reforming processes, the heat is generally provided by the combustion of additional methane. In solar reforming heat is supplied by concentrated solar energy. The stored solar energy can subsequently be recovered by conducting either the reverse of the reforming reactions (i.e., by the exothermic methanation process) or by utilising the syngas, produced with lower CO_2 emissions than in conventional reforming, in any one of the many applications requiring it as a feed stock.

In certain applications CDRM has advantages over SRM due to its potential for a greater lower heating value enhancement (up to 30% relative to the input methane) as a result of increased CO production relative to hydrogen [2].

Concentrated solar radiation has the specific properties of high energy intensity, variable thermal flux distribution, and frequent thermal transients due to the fluctuating insolation. Volumetric receiver–reactors and tubular reactors have been investigated for the solar-reforming of methane. Both reactors have some disadvantages, as follows:

- A volumetric receiver–reactor is expensive and requires a quartz window, which may limit operating life and the potential for scale up.
- A tubular reactor's performance can be restricted by mass and heat transfer issues, due to the use of the reactor wall as the solar energy absorber and heat conductor to indirectly heat reactant gas and provide the heat of reaction [3].

One potential method for overcoming these limitations is to develop monolithic reforming catalysts with regular three-dimensional

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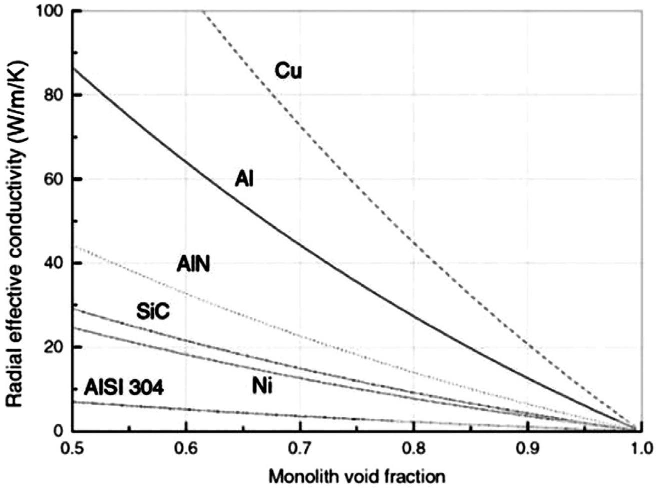

Fig. 1. Thermal conductivity of ceramic and metallic foam as a function of monolith void fraction.

structure and high thermal conductivity that can improve mass and heat transfer in a tubular reformer. This could result in a more compact reformer with shorter gas residence time, and more efficient, less costly capture of solar energy in a thermochemical form [4].

Ceramic foam (e.g., SiC, SiSiC), which has high mechanical strength and thermal conductivity [5,6], has been used as catalyst substrate for solar methane reforming in volumetric receiver-reactors. However, metallic substrates, such as Cu foam, have better thermal conductivity and are less brittle than ceramic foam. Metallic foams could therefore minimise thermal transfer limitations in solar reforming. They could also prevent cracks caused by mechanical or thermal shock resulting from the temperature variations of fluctuating insolation and the daily starting up and down of the reformer [7].

Interest is hence growing in using metallic foams as a catalyst substrate for solar reforming [8,9]. Roh et al. [10] investigated 2% Ru/Al_2O_3 catalyst-coated FeCr alloy metal monolith for SRM in a tubular reactor at a temperature range of 577–727 °C. The monolithic catalyst had a higher bed thermal conductivity and greater heat transfer than Ru/Al_2O_3 pellet catalyst. They concluded that using a highly porous structured support with high thermal conductivity for these catalysts can improve heat exchange inside the reactor. Cybulski and Moulijn [11] modelled heat transfer in a FeCr alloy monolith at a density of 62 cells/cm^2 and air flow rate of 0.2–0.7 kg/m^2/s, as well as in a packed bed of 3.5-mm diameter pellets at the same flow rates and tube size. The overall heat transfer coefficients for the monolith were increased by about 15%.

However, it is more difficult to coat catalysts onto metallic substrates than onto ceramic substrates. This is because both the smooth metallic surface and the difference in thermal expansion coefficient between the metal substrate and catalyst result in weak adhesion between them [12]. Hence, more research is required to improve the thermal conductivity of monolithic metallic supports, as well as the adhesion between substrate and catalyst, to improve heat transfer in monolithic catalysts.

Lotus-type, porous Cu foams have recently attracted a great deal of attention. Their unique features include: (i) high thermal conductivity, (ii) controllable pore size and porosity, and (iii) high mechanical shock resistance. These metallic monoliths are expected to find uses in lightweight materials, catalyst supports, electrodes, vibration and acoustic energy damping materials, and impact energy absorption materials [13,14]. Fig. 1 illustrates that Cu foam has the highest thermal conductivity among ceramic and metallic foams [15]. However, few studies to date have reported the use of Cu foam as a catalyst support.

Ni-based catalysts are used in catalysing a wide range of reactions which includes dry reforming of methane [16], steam reforming of toluene [17] and water gas shift reaction [18].

Ni/Mg/Al catalysts prepared by co-precipitation show higher activity and stability for CDRM than catalysts prepared by conventional impregnation methods [19,20]. This is because the strong interaction between Ni and Mg-Al support improves Ni dispersion and inhibits Ni sintering, thereby increasing catalyst activity and stability.

The objective of the paper is to investigate the catalyst Ni/Mg/Al metal oxide coated onto lotus-type porous Cu foam for solar CDRM applications. As part of this study, we developed an effective method to coat Ni/Mg/Al catalyst onto the Cu foam.

2. Experimental

2.1. Foam catalyst preparation

2.1.1. Catalyst substrates

Lotus-type porous Cu foam with a pore size of 420 μm was selected as a monolithic catalyst substrate. Substrates were fabricated using a unidirectional solidification method described in our previous work [21]. In a standard preparation, high-purity copper (99.99 wt%) was melted in a crucible by middle-frequency heating after the chamber was evacuated to 5.0 Pa. When the temperature reached 1250 °C, which was monitored by a W-5Re/W-26Re thermocouple, certain pressure high-purity hydrogen and argon were introduced into the chamber respectively. To dissolve the hydrogen uniformly in the liquid copper, the pressure was maintained at 5.0 Pa for 1800 s at the selected temperature. Finally, the melt was poured into the mould and solidified under the same pressure.

SiSiC foam (pore size of 1000 μm, provided by Erbicol SA) was used as a reference to evaluate the performance of the Cu foam-based catalysts. To eliminate traces of grease and other contaminants, all substrates were degreased using an ultrasonicator in acetone for 20 min, and then washed with distilled water three times. The Cu foam was washed further using an inorganic acid solution to improve its surface roughness and coating adhesion. Preparation of the acid solution and the pre-treatment method are described in a US patent [22]. Briefly, the Cu foam was dipped into a mixed acid aqueous solution containing 40 g/L H_2O_2, 90 g/L H_2SO_4 and 4 g/L 5-aminotetrazole and etched for 3 min at room temperature. The surface of the Cu foam then became roughened.

As an alternative approach to improving adhesion between the catalyst powder and metallic substrate [23], a γ-Al_2O_3 layer was first coated on the substrate before coating it with the active catalyst phase. The γ-Al_2O_3 layer was prepared as follows: a boehmite γ-AlO(OH) mineral) solution was first prepared by dispersing 10% (*w*/*w*) of commercial, high-purity, dispersible alumina (Disperal23N4-80, Sasol) in a 0.4% (*w*/*w*) HNO_3 solution. After 10 min of mixing, a stable dispersion of boehmite was obtained. The substrate was then dipped into the boehmite solution and removed at a controlled speed of 3 cm/min, and dried at room temperature for 30 min. A well-adhered layer formed on the substrate surface. The catalyst powder was then washcoated on the γ-Al_2O_3 layer coated substrate described above.

2.1.2. Ni-containing foam catalysts

$NiMg_3AlO_x$ was selected as a CDRM catalyst in this work, because the catalyst formulation showed the highest performance among a series of $NiMg_bAl_cO_x$ catalysts in our previous work [24]. $NiMg_3AlO_x$ powder was prepared by the co-precipitation method reported [22].

Ni-containing monolithic catalysts were prepared by depositing $NiMg_3AlO_x$ catalyst powder onto substrates by the following washcoat technique. The $NiMg_3AlO_x$ catalyst powders were first wet-milled in a laboratory vibration mill (typical milling condition: 10 g catalyst powder +100 g and 800 μm of ZrO_2 milling media +70 g deionised water, milled for 2 h. The pre-treated catalyst substrate