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Effect of the thermal conductivity of metallic monoliths on methanol steam reforming

Oihane Sanz[a,*], Ion Velasco[a], Inés Reyero[b], Iñigo Legorburu[a], Gurutze Arzamendi[b,c], Luis M. Gandía[b,c], Mario Montes[a]

[a] Departamento de Química Aplicada UFI 11/56, Universidad del País Vasco (UPV/EHU), 20018 San Sebastián, Spain
[b] Departamento de Química Aplicada, Edificio de los Acebos, Campus de Arrosadía, Universidad Pública de Navarra, 31006 Pamplona, Spain
[c] Institute for Advanced Materials (InaMat), Universidad Pública de Navarra, 31006 Pamplona, Spain

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ABSTRACT

We have studied the influence of cell density of two sets of metal monoliths coated with different amounts of Pd/ZnO in the methanol steam reforming (MSR). The results indicate that the conversion increases with increasing size of the channels that is accompanied by a decrease in the monoliths cell density. To explain this unexpected result, the longitudinal and radial temperature profiles were measured. It was observed that the thermal conductivity increased with increasing cell density and temperature profiles became more marked with increasing catalyst loading on the monolith. This last result was explained by the increase of the heat required for the reaction to maintain a constant space velocity. Being fixed central temperature of the monolith and being the MSR an endothermic reaction, the average temperature increases with decreasing thermal conductivity. To assess whether this increase in average temperature justifies the observed increase in conversion, a CFD modeling of the system was performed. The simulation results showed an excellent agreement with experimental values. This confirms the fundamental role of thermal conductivity, which is mainly controlled by the cell density of the monolith.

1. Introduction

The design of the reactor used for fuel processing to hydrogen production has a significant effect on reforming efficiency, system start-up time and transient response. The packed-bed reformer, the convectional reactor design, requires large pumping power to drive reactants and products and offers poor heat transfer characteristics [1,2]. Thermal conduction within the solid phase of the catalyst particles in fact is almost negligible being convection in the gas the dominating mechanism for heat transfer [3]. Hence, enhancement of heat transfer can be only done increasing the fluids velocity, but this is limited by the pressure drop, which grows with flow rate. Efficient heat transfer is particularly important in steam reforming that is an endothermic reaction, since the reaction rate in conventional reactors is usually limited by the rate of heat transfer to the reactants [4]. In the case of structured reactors made of highly conductive materials [5], heat conduction through the solid matrix can be more effective than convective heat transfer in packed-beds. This fact opened new possibilities both for the intensification of existing processes and for the development of new industrial technologies, where heat transfer is a key issue as is the case of highly exo and endothermic catalytic processes [6].

Among the fuels considered in hydrogen production, methanol reforming is an attractive option for an on-board hydrogen source due to low reforming temperature (473–573 K) and low carbon monoxide concentration in the reformate [7]. Copper-based catalysts are the most commonly used for methanol steam reforming due to their high activity and selectivity at low reforming temperature (503–573 K) [7]. Nevertheless, sintering of the metal at temperatures above 553 K and its pyrophoric character remains problematic with copper catalysts. On the other hand, Pd/ZnO catalysts exhibited comparable methanol steam reforming activity as the Cu based ones with extremely low CO selectivity upon proper pretreatment [7]. Moreover, Pd/ZnO catalysts have excellent thermal stability and are not pyrophoric, and therefore, are suitable for the development of methanol-based fuel processing technologies.

For methanol steam reforming (MSR), energy must be supplied from an external heat source because it is an endothermic reaction (ΔH°_{298} = 49.4 kJ/mol). Temperature gradients in the MSR reactor can cause hot spots which results in poor performance due to catalyst deactivation by sintering and generation of large

* Corresponding author.
E-mail address: oihane.sanz@ehu.eus (O. Sanz).

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amounts of CO which is an undesirable component [2,8,9]. To overcome this problem, metal structured substrates (foams [10,11], monoliths [9,11,12], microchannel reactors [2,13,14], etc.) have been suggested as a promising solution. The choice of the proper metallic alloy for the reformer design depends on fabrication properties (thin foil formation, capability of rolling, weldeability, etc.), catalytic coating adhesion (metallic surface roughness and chemical compatibility between catalyst coating and metallic surface) and properties related to the process (mechanical, thermal and chemical resistance under operation conditions) [5,15,16]. Different alloys have been studied for structured catalyst preparation for MSR. Among them, aluminium, stainless steel and copper are the most frequently used due to their suitable mechanical or thermal properties [10,11,14]. Therefore, in the preparation of a structured catalyst for MSR, it must be taken into account not only the intrinsic catalyst properties and the catalytic coating adhesion but also the high thermal conductivity of the structured substrate. Some authors have studied numerically the effect of the thermal conductivity of structured substrates on MSR performance [13,17]. The increase of substrate thermal conductivity by wall thickness or wall conductivity (using high conductive metallic alloys such as aluminium and copper) allows rapid heat transfer along the axial direction of the reactor by conduction through the wall, thereby reducing the temperature gradient [13]. Furthermore, Nehe and Kumar showed that the temperature difference between the channel wall and the bulk fluid increased linearly with CuZnAl catalyst thickness and both methanol conversion rate and CO concentration were higher [17].

Minute amounts of CO in the hydrogen stream are able to poison the anode of low-temperature PEM fuel cells so reformate stream must be purified before use. This purification usually involves a first stage of water gas shift (WGS) and a second step of CO methanation or preferential oxidation (PROX). But if the CO content in the reformate is lower than 1.5%, it can be directly processed by methanation or PROX. Avoiding the WGS reaction is a significant achievement towards the intensification of the process. Process intensification can also benefit from the increasing use of advanced modeling and simulation tools during the stage of reactor design. This is the case of computational fluid dynamics (CFD) which use has expanded remarkably in the recent years, also in the case of the technologies related with the production of hydrogen as recently reviewed by Uriz et al. [18].

The aim of this work is to study both experimentally and numerically the influence of the thermal conductivity of metallic monoliths due to the increase of the cell density on the methanol steam reforming reaction. Fuel conversion, hydrogen yield and CO production in reformers made of different channel size, monolith length, catalyst thickness and catalyst mass are studied.

2. Experimental and numerical parts

2.1. Preparation of structured substrates

Homemade parallel channel monoliths (3 × 1.6 cm) consisting of 50 μm Fecralloy® sheets (FeCr22Al5, Goodfellow) corrugated using rollers producing different channel sizes (see Table 1) were fabricated. Before the pre-treatment, monoliths were cleaned with water and soap, thoroughly rinsed with water and acetone, and finally dried at 393 K. After that, structured substrates were submitted to a pre-treatment (in air at 1173 K during 22 h) to create an alumina oxide layer on the base alloy with the adequate physical parameters (roughness, homogeneity and adherence, see Fig. 1) for anchoring the washcoated catalyst [19].

To analyze the thermal transport properties of monoliths the effective axial and radial conductivity was calculated as proposed

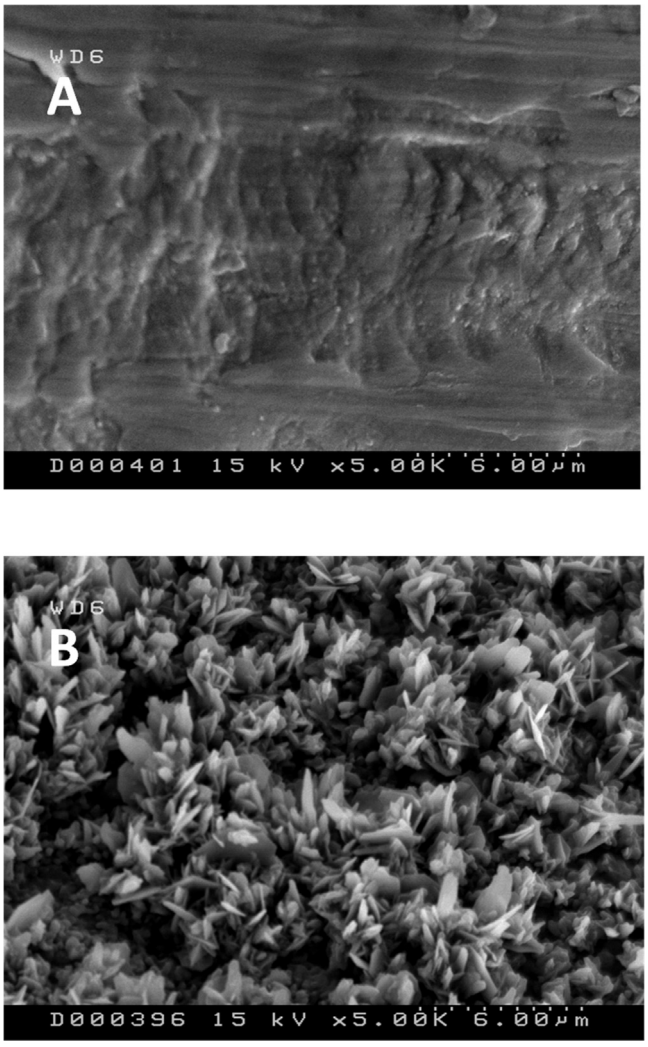

Fig. 1. Fecralloy metallic surface before (A) and after calcination at 1173 K (B).

for honeycomb monoliths by Tronconi et al. [20,21]. Considering the parallel flow pattern along the channels of the monolith structure, axial and radial effective conductivities, $k_{e,a}$ and $k_{e,r}$, respectively, have been calculated. It is important to note, that the expression proposed by these authors was developed for square cell monoliths that are different from our monoliths of corrugated sheets. However, the dependence of the main parameters as the void fraction and the thermal conductivity of the substrate alloy should be similar thus allowing to show the general trends.

2.2. Washcoating

The catalyst (2.5 wt.% Pd-ZnO) was deposited on the monoliths by the washcoating method proposed in a previous work [19]. The catalyst slurry (pH 4.3) was prepared with 22.5 wt.% of synthesized ZnO, 2.5 wt.% of colloidal ZnO dispersion (NYACOL® DP5370) and the required amount of $Pd(NO_3)_2$ solution (Johnson Matthey) to obtain 2.5 wt.% Pd-ZnO. The monoliths were dipped into the catalyst slurry for 60 s, and withdrawn at constant speed of 3 cm min^{-1}. Then, elimination of the slurry excess was made by centrifugation (1 min, 400 rpm). The washcoating was repeated several times with an intermediate drying step at 393 K for 30 min between coatings until the desired catalyst load was obtained. Finally, calcination in air of the coated monoliths was done at 623 K for 1 h. The solid obtained by drying and calcination under the same conditions of