Research paper

Tailoring structured WGS catalysts: Impact of multilayered concept on the water surface interactions

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A B S T R A C T

A novel multilayer approach for designing structured WGS catalyst is employed in this study as a response to the lack of new strategies in the literature. The approach proposes the use of two successive layers with different functionalities on metallic micromonolith substrate. The WGS catalyst behavior is modulated by the nature of the inner layer which determines the active species surface population by acting on the water activation step. The catalytic promotion attained by introducing inner ceria containing solids with increasing number of oxygen defects is intensely analyzed through FT-IR and H_2O-TPD. Several evidences about the participation of the oxygen vacancies, as key sites, for water absorption processes are established. Besides, remarkable relationships between the water absorption strengths and the water splitting processes within their influence on the catalyst performance are also discussed.

1. Introduction

Among the new green energies, H_2 appears as a promising vector. However, its success relies on the removal of CO coproduced with H_2 in the reformate process in order to avoid the poisoning of the Pt-based anode of the Polymeric Exchange Membranes Fuel Cells (PEMFC). The water gas shift (WGS, $CO + H_2O \rightarrow CO_2 + H_2$) reaction allows CO removal at the same time that increases the H_2 concentration. The reaction is also moderately exothermic and equilibrium limited, therefore, the control of the temperature is a crucial task [1]. Moreover, WGS reaction is characterized by high contact times and as a result, high reactor volume are necessary to achieve good catalytic performances [2].

The industrially established WGS process is not well suited for small-scale applications, such as residential fuel cells or on-board hydrogen generators, for which reduced volume and weight catalytic beds are required. In fact, on-board portable applications intrinsically demand long lasting and highly active catalytic systems which should also support fast start-up and shutdown conditions. Attending to the mobile device power requirements, the drawbacks presented by the traditional WGS catalysts, e.g. slow response to transient operation of flow rate and temperature, could be overpassed applying noble metal (NM) based catalysts [1,3]. Within the reported NM catalysts, those based on Pt formulations appear as the best solutions especially when coupled with

ceria containing support [4–7]. The use of ceria presumably intensifies the rate of WGS CO conversion by increasing the water activation rate due to its advantageous electronic properties which are, in turn, intimately associated to its structural defects, i.e. oxygen vacancies (Ov) [8,9]. So, the attention received by the oxygen defects lies on its capacity for dissociating water species and on the concomitant enhancement of the WGS catalyst' reaction rates [10,11]. A possible way to control and increase the number of oxygen defect sites within ceria matrix is its doping with trivalent metal in proportion where the formation of solid solution is observed [12–18].

Nevertheless, not only the catalyst but also the reactor design is of crucial importance for the WGS process on-board applications [2]. An optimal structured reactor design should solve practical problems arising from WGS reaction particularities. The desired performance criteria for catalysts bed are low pressure drop, high catalyst loading per reactor volume, high external fluid to catalyst mass and heat transfer rates and high internal mass transfer rate within the catalyst [19–22]. In this context, parallel channel metallic micromonoliths appear as an attractive alternative from their inherent high thermal conductivities which assure enhanced heat transfer managements and allow shorter contact times, reduced transport limitations and higher catalyst surface-to-volume ratios. As a result, metallic micromonoliths should lead to compact catalytic beds and, then, to increased overall process efficiencies.

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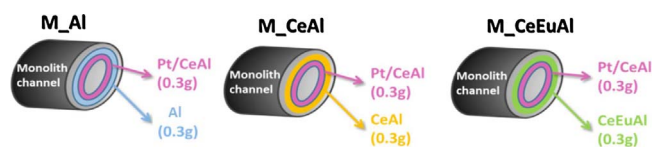
Fig. 1. Schematical representation of the prepared structured catalysts.

In a previous work [20], the oxygen vacancies and metallic micromonoliths benefits were merged on the development of a novel structured catalyst composed by two consecutives layers with different tasks: an inner layer of material able to absorb water and release activated water species in continuous manner and an outer catalyst layer where the WGS reaction should occur. The greater WGS overall reaction rate in presence of the inner layer was related to superior apparent H_2O partial kinetic orders and consequently, to higher H/OH species population in the vicinity of the Pt active sites.

From the introduction of the multilayered concept, this work provides an intense analysis of the role of the buffer layer as a function of its water splitting capacity. The studied structured catalytic systems are schematically presented in Fig. 1. For that purpose, Pt(2%)/CeO$_2$/Al$_2$O$_3$ was maintained as catalyst for the all structured catalyst outer layers meanwhile the nature of the inner layer, named buffer layer, was varied. Three buffer materials differing on their water splitting capacity were chosen:

i) γ-Al$_2$O$_3$ chosen for its chemical similarity to oxidized stainless steel monolith surface and more importantly because of low available number of oxygen defect sites for water activation. In fact, this material is generally considered as inactive support for WGS reaction [32,33];

ii) CeO$_2$/Al$_2$O$_3$ chosen as material with similar textural properties to that of γ-Al$_2$O$_3$ but with increased number of oxygen defect sites due to the presence of CeO$_2$ surface layer;

iii) Ce$_{0.9}$Eu$_{0.1}$O$_2$/Al$_2$O$_3$ chosen for its expected intensification of the oxygen vacancies concentration due to Eu^{3+} to Ce^{4+} substitution and solid solution formation accompanied by oxygen defects formation via charge compensation mechanism [18]. In addition, Eu$_2$O$_3$ do not possess by itself any intrinsic activity for the WGS reaction.

Hence, as an initial hypothesis, one could expect that the WGS activity sequence should correlate directly to buffer's ability to activate water, presumably in the following descending activity order Ce$_{0.9}$Eu$_{0.1}$O$_2$/Al$_2$O$_3$ > CeO$_2$/Al$_2$O$_3$ > γ-Al$_2$O$_3$. The use of Pt(2%)/CeO$_2$/Al$_2$O$_3$ catalyst prepared in one unique batch with equivalent properties (chemical composition, metal dispersion etc.) consent ascribing the observed changes uniquely to the buffer layer role.

Therefore, this study offers a tuning procedure for enhanced WGS structured catalysts at the same time as it delivers a comprehensive analysis of the water ceria surface interactions which, depending on defect surface population, tailor the WGS catalytic behaviors. In fact, the application of the multilayer approach pretends to prove the design suitability and to highlight it as a potential strategy for achieving advanced structured WGS catalysts.

2. Materials and methods

2.1. Preparation of metallic micromonolith substrates

The micromonoliths were prepared by rolling up flat and corrugated ferritic stainless steel a foil (Fecralloy) around a spindle. The resulting structures are cylinders of 1.6 cm diameter, 3 cm height and 540 cm^2 geometric surface area with cell density of 2067 cpsi. The micromonoliths were thermally pretreated during 22 h at 900 °C in order to generate α-Al$_2$O$_3$ oxidized surface layer for better catalyst adhesion during the deposition assured by roughness increase for physical anchorage and chemical compatibility [23,24].

2.2. Catalyst and buffer synthesis

The CeO$_2$/Al$_2$O$_3$ and the Ce$_{0.9}$Eu$_{0.1}$O$_2$/Al$_2$O$_3$ buffer materials were prepared by wet impregnation of their respective nitrates over a commercial γ-Al$_2$O$_3$ (Sasol). The CeO$_2$(Ce$_{0.9}$Eu$_{0.1}$O$_2$):Al$_2$O$_3$ ratio was fixed to 20:80 (wt.%). For each solid, the adequate precursor amounts were dissolved into ethanol solution and added over the commercial γ-Al$_2$O$_3$ under stirring for ensuring the solution homogeneity. Some ethanol was added until the γ-Al$_2$O$_3$ powder was completely covered. The resulting suspension was concentrated (almost dry) by evaporating the ethanol under reduced pressure. The obtained dry solid was treated with diluted NH$_3$ (10 M) solution during 30 min, filtered and rinsed with deionized water. The resulting powder is dry during 12 h at 120 °C, grinded and calcined at 450 °C for 4 h at 10 °C/min heating rate. The as prepared buffers are denominated Al, CeAl and CeEuAl for Al$_2$O$_3$, CeO$_2$/Al$_2$O$_3$ and Ce$_{0.9}$Eu$_{0.1}$O$_2$/Al$_2$O$_3$ respectively.

The platinum catalyst was prepared in a similar way by wetness impregnation of the targeted Pt loading of 2 wt.% and using tetrammoniun nitrate platinate (Johnson Mattey) as metal precursor. As catalyst support a commercial Puralox CeO$_2$/Al$_2$O$_3$ (Sasol) was used. After impregnation, the catalyst was dried and calcined at 350 °C during 8 h with a heating rate of 5 °C min^{-1}. The obtained catalyst was labelled Pt/CeAl.

2.3. Preparation of the structured catalysts

The washcoating method was used to cover the metallic substrate surface with buffer and catalyst layer successively. For this, slurries with adjusted rheological properties were prepared. For all employed solids, prepared suspensions contain 18.14 wt.% of solid, 1.96 wt.% of polyvinylalcohol (PVA) solution (1.5 wt.% in water), 17.65 wt.% of colloidal Al$_2$O$_3$ suspension (Nyacol, 20 wt.% in water) and 62.25 wt.% of H$_2$O. Prior use, all solids were grinded and sieved to particle size lower than 10 μm. During the coating process the PVA, was used to facilitate the suspension impregnation by capillarity within the channels meanwhile Al$_2$O$_3$ Nyacol helped the stabilization of the catalyst particles in the resulting suspension [23].

The micromonoliths were immersed for 1 min and then removed from suspensions always at a constant rate of 3 cm min^{-1}. Centrifugation combined with air flushing was employed to remove the excess suspension and to avoid the channels obstruction. For the buffer layer the procedure was repeated several times till the desired amount of 300 mg approx. was deposited. The micromonoliths were calcined at 450 °C during 4 h at 2 °C min^{-1} heating ramp. The remaining suspensions after layer deposition were dried and calcined in the same conditions as micromonoliths and used for comparison with the powder catalysts. The chosen nomenclature for the suspensions were S_Al, S_CeAl and S_CeEuAl, for the suspensions resulting from the buffers based on Al, CeAl and CeEuAl solids, respectively.

Once a homogeneous buffer layer obtained, the catalyst layer was coated in the same proportions and conditions of deposition used for the buffers. Finally, the micromonoliths were calcined at 350 °C for 8 h at 2 °C min^{-1} heating ramp. The structured catalysts constituted by two layers, buffer and catalyst ones are labelled M_Al, M_CeAl and M_CeEuAl, while the buffer only deposited monoliths are labelled Mb_Al, Mb_CeAl and Mb_CeEuAl ("b" reffering to buffer only), respectively. The targeted quantity of catalyst of approx. 300 mg was achieved after successive washcoating steps. The actual achieved amounts are shown in Table 1.

For all layered systems, both buffer and external catalyst layers are maintained constant, the only variation being the chemical composition of the buffer layer. Both layers present similar densities and textural properties (all having at least 80% of γ − alumina) and, for the similar