Metallic structured catalysts: Influence of the substrate on the catalytic activity

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A B S T R A C T

In order to study the influence of the metallic substrate on the catalytic activity of structured micromonolithic catalysts, a CuO_x/CeO_2 catalyst was deposited on different oxidized or enameled metallic micromonoliths and tested in the PROX reaction under ideal and realistic conditions. The obtained results show as both activity and selectivity depend on the nature of the alloy and the nature of the interphase between the metal substrate and the catalyst layer. In oxidized micromonoliths, diffusion of Cr and Fe has been observed. For enameled micromonoliths, together with that diffusion, the interaction of the glass–ceramic interphase with the reactive gas streams resulted in the partial hydrolysis of this layer leading to diffusion toward the catalyst surface of the hydrolysis products, namely Na, Ca and Si cations. In some cases, the alteration of the surface composition favors the spreading of the copper active phase. As a result, it must be concluded that the metallic substrates are not spectators, at least in the PROX reaction, playing a fundamental role in the performances of the catalytic devices.

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1. Introduction

The management of the heat of reaction is a key issue in all the processes that may be involved in the production and clean-up of the H_2-rich reformate gases. Catalytic wall microchannel reactors seem to be a well-suited solution for solving the practical problems in heat management. Moreover, these catalytic devices allow low pressure drops, high catalyst loading per reactor volume, high external mass transfer rate from bulk fluid onto catalyst surface and high internal mass transfer rate from catalyst surface to the catalysts inside. In this scenario, metallic materials, which have inherent high thermal conductivities, fulfill most heat management criteria, providing an optimal heat control during exothermic and endothermic reaction [1,2].

Between metallic alloys, Al_2O_3 forming stainless steels have usually a brittle behavior upon thermal treatment. Therefore, austenitic chromia-forming stainless steel with high Ni contents, as the EN 1.4301 (AISI 304) [3] or the EN 1.4571 (AISI 316Ti) [4], or even nickel base alloys, as Incoloy 800H [5], are preferred for manufacturing microreactor devices and fuel processors. However, in atmospheres with carbon activities above unity those alloys suffer corrosion phenomena of metal dusting, MD, the catastrophic form

of carburization. The carburization thermodynamics of metals in these atmospheres depends on temperature, pressure and metal nature, Ni and Fe behaving differently [6]. While in 10% CH_4/H_2 at 1 atm, Fe can be carburized in excess of 735 °C, Ni is carburized only beyond 975 °C. However, for 10% $CO—CO_2$ (or $CO—H_2—H_2O$) at 1 atm the opposite behavior is observed, Fe is carburized only below 490 °C (510 °C) while Ni can be carburized at temperatures lower than 400 °C (380 °C). Thus, carburizing phenomena, though severe, are less catastrophic in CH_4/H_2 mixtures than in $CO/H_2O/H_2$ ones in the case of alloys with high Ni contents as Haynes 556 [7], AISI 310SS [8] or Incoloy 800HT [9]. Carburization phenomenon is frequent in the chemical industry, occurring in reforming and synthesis gas plants [10,11] compromising the microreactor performances. Moreover, catalytic processes leading to coke formation considerably decrease the induction period of the MD phenomena [12].

To overcome these corrosion problems, complex surface protection procedures using aluminide coatings have been proposed [13]. Metal aluminide coatings form inert alumina layers on the metallic surface that protects the high nickel alloy from corrosion [13,14]. Oxide layers formed on chromia- or alumina-forming stainless steels also protect the base alloy against MD being more effective the alumina former ones [15–17].

However, it has been reported that catalyst deposition on metallic surfaces can result in modifications of the catalyst, the oxide scale and the oxide scale/alloy interface through the interaction

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Table 1
Stainless steel chemical compositions (wt.%).

Metal	Fe	Cr	Ni	Si	Al	Mn	C	Cu	Mo	Co	Others
AISI 304	70.40	18.40	8.11	0.44	–	1.45	0.06	0.23	0.25	0.20	<0.32
FeCrAl	72.28	22.00	–	0.30	5.00	0.20	0.02	–	–	–	<0.20

between the coating and the metal oxidation layer [18–20]. The base alloy oxidation has also been described [18].

One recently proposed solution to avoid MD and the modification of the catalyst by the influence of the substrate is the formation of an enamel barrier between the substrate and the catalyst [21]. An enameled stainless steel surface can prevent corrosion phenomena and unwanted and uncontrolled catalytic effects that may occur at the contact surface of the alloy with the reaction mixture in equipment for the chemical industry [22]. This corrosion resistance and barrier effect against the release of metal provided by the enamel could be very useful in the case of devices that use metal as catalyst support, especially when applied to catalytic processes working at high temperatures and/or in aggressive atmospheres [21].

Enamel is a glass obtained by fusion at high temperature (1000–1300 °C) whose main component is SiO_2. Enamels of different compositions could be used, depending on the substrate to be enameled and its intended use. In any case, the enamel must have suitable physical, chemical and mechanical properties and good adhesion to the substrate [23]. At first place, the coefficient of thermal expansion (CTE) of the enamel must be compatible with the substrate. Austenitic steels are difficult to be enameled because of its high CTE, which could produce stress in the enamel coating, causing it to peel off. According to several studies [23,24], the pretreatment of the substrate before the enameling process plays an essential role for the good adhesion of the enamel to the substrate. These works agree that the adhesion of the enamel to the substrate is controlled by a mechanical interlocking mechanism, which will be facilitated by the surface roughness of the metal. This roughness can be achieved by mechanical, chemical or electrochemical methods. However, other works support the chemical theories [25,26], considering that chemical bonding is the key factor for having strong adherence. The chemical bonding needs a transition from the metallic structure of the metal substrate to the covalent structure of the enamel [27]. In these sense, some authors relate good adhesion with the presence at the steel/enamel interface of a phase, fayalite, which forms Fe—O—Si bonds [28]. Finally, the enameling temperature should also be compatible with the substrate. For example, in the case of steels, phase transitions have to be avoided.

The enameling of metallic surfaces can be carried out by dry or simple wet processes, such as painting, dipping or spraying. However, in the case of micromonoliths or microchannel blocks, it is necessary to mill the enamel powder and the development of a formulation suitable for the preparation of stable suspensions of enamel with the adequate rheological properties to ascend across the microchannels.

Within this scenario, the aim of this work is to study the effect that different steel substrates and different treatment, previous to the catalyst coating, could have in the activity of a set of catalytic devices. With this purpose, a well-known CuO_x/CeO_2 catalyst has been washcoated on both AISI 304 and FeCrAl stainless steels metallic micromonoliths, previously enameled or oxidized at high temperature [29]. The catalytic devices have been tested in the preferential CO oxidation reaction (PROX), of interest from an environmental and energetic point of view and having atmospheres with high carbon activities.

2. Experimental

2.1. Preparation of the stainless steel micromonoliths

The chemical composition of two different 50 μm thick foils (Goodfellow) used to prepare the metallic micromonoliths, a commercial AISI 304 austenitic stainless steel and a FeCrAl ferritic stainless steel, is presented in Table 1. Cylindrical micromonoliths are built by rolling together around an axis, as described elsewhere [30], a flat and a corrugated sheet (1.180 cells per square inch, $L = 30$ mm and $\phi = 17$ mm). The metallic substrate is submitted to an oxidation pretreatment to create an oxide scale on the alloy that allows anchoring either the enamel or the catalyst with adequate physical parameters (roughness, homogeneity and adherence). By modifying the oxidation treatment, two sets of micromonoliths were prepared. The first one (to be enameled before the catalysts washcoating) is prepared at low temperatures, 500 °C, in stagnant air and short oxidation times, 1 h, in order to generate a thin oxide layer that may improve the adherence of the enamel to steel through redox reactions [31] that can take place at the metal/enamel interface. Since the thermal expansion coefficient of the oxide is more similar to that of the enamel than to the metal one, an excessively thick oxide layer may cause the detachment of the layer by the metal/oxide interface. That is why a treatment of mild oxidation (low temperatures and short times) is applied, in order to generate a thin layer that promotes adhesion of the enamel without the risk of detachment.

The second set of micromonoliths (to be directly washcoated with the catalyst slurry) was oxidized at 900 °C, during 22 h in stagnant air in the case of FeCrAl micromonoliths and during 1 h in a 10 ml min^{-1} synthetic air flow for AISI 304 micromonoliths. These treatments are optimized for every substrate [32–34] generating oxide scales (mainly Cr_2O_3 and $Mn_{1+x}Cr_{2rx}O_{4rx}$ spinel for AISI 304 and Al_2O_3 for FeCrAl) that favor further anchoring of the catalytic layer.

2.2. Enameling process

In this work commercial enamel supplied by Ferro Spain has been used. The enamel chemical composition is presented in Table 2.

Prior to its use, the enamel was milled to an average particle size of *ca.* 5 μm (D [4,3] = 5,3 μm, D (v,0.9) = 15,4 μm). Stable slurries were prepared in water with this enamel, colloidal alumina (Nyacol S20), polyvinyl alcohol (PVOH) and polyethylene glycol (PEG). The detailed composition of the enamel slurries is showed

Table 2
Main components of enamel composition (Ferro Spain) (wt.%).

Na₂O	K₂O	CaO	Al₂O₃	B₂O₃	Fe₂O₃	BaO	Co₃O₄	CuO	P₂O₅	SiO₂
10–15%	0–3%	6–9%	4–7%	12–18%	2–5%	<2%	<2%	<1%	<1%	46–58%