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Wall coating optimization for microchannel reactors

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Abstract

Thick and porous aluminum oxide coatings on the inner walls of a microchannel reactor have been developed as a support for catalytically active metals serving for on-board hydrogen production. These coatings must withstand extremely severe conditions in terms of temperature and mechanical shock. The developed suspension coating method uses alumina prepared from commercial powders. Optimizing the slurry preparation parameters such as particle size, viscosity, solid loading and/or binder content in tight relationship with coating properties allowed us to attain films at a desired thickness of 25 μm, with a good adhesion and reasonable uniformity. An ongoing investigation in our laboratory confirms that these coatings impregnated with an active phase can be successfully employed for hydrogen production by steam reforming of isooctane.

Keywords: Catalyst deposition; Alumina wash-coating; Microstructure; Steam reforming; Micro-structured reactors; Micro-reactors

1. Introduction

The development of catalytic microchannel reactors is today a matter of active research in catalytic reaction engineering and process intensification. A key feature of this kind of device is that mastering catalyst properties, i.e. morphology, activity, kinetics and stability, and the way to deposit and activate the catalytically active phases are inseparable from the choice of the microreactor geometry. As a matter of fact, in the global performance of the microreactor, catalyst and reactor are strongly intertwined. In consequence, the optimization must be done in an integral approach from the molecular to the reactor level. Untill now, the mainstream of studies available in open literature presents only the microreactor's catalytic performance without explicit details about the catalyst development or characteristics. The rare publications where the coatings on microchannel metallic platelets were discussed evoked no more than the preparation methods [1–6].

The most common way to deposit catalysts within the microchannel channel is the wash-coating technique. For example, the commercially available $CuO/ZnO/Al_2O_3$ catalyst is one of the most studied system for hydrogen production by methanol steam reforming (SRM) for feeding proton exchange membrane fuel cells (PEMFC) [7], or polymer electrolyte fuel cells [8]. Methods to control the thickness from 1 to 25 μm of a liquid film coating using controlled gelation of boehmite slurry have been developed. The effect of the Cu to Zn ratio, the impact of metal loading, and the effect of calcination temperature have been investigated to optimize the catalyst for the SRM reaction. Other authors [9,10] performed similar studies replacing zinc with cerium. Furthermore, Germani et al. [11] performed a systematic study on the nature of binders used for coating a Cu/Zn/Al catalyst into microchannels, and their influence on catalytic activity for the water gas shift (WGS) reaction. They concluded that binders play a major role on (i) slurry viscosity by their chemical structure but also through their molecular weight, (ii) coating adhesion and (iii) catalytic activity by redispersion of the active phase because of metal complexes formation.

Rebrov et al. [12] published a review article giving a detailed description of the procedure for preparing ZSM-5 catalysts for selective catalytic reduction of NO with ammonia. The coating thickness was adjusted varying the reaction temperature, the synthesis time, the H_2O/Si and Si/template ratios, as well as the orientation of the platelet with respect to the gravity vector. Afterwards, a ZSM-5 zeolite coating has been prepared with a zeolitic layer thickness of a single crystal, particularly suitable for the considered catalytic reaction.

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A fundamental study concerning the preparation of porous alumina wash-coats in the microchannels focused on the pre-treatment of the microstructures, properties, and adhesion of the wash-coats was performed by Zapf et al. [13]. Anodic oxidation and thermal treatment of the microstructures significantly reduced the undesirable chlorine content, which was assumed to have deleterious effects on the catalyst activity. Good adhesion of the porous catalysts, deposited by a two-step wash-coating and wet impregnation process, was demonstrated by a mechanical test. The impregnated Cr_2O_3 within alumina wash-coat was homogeneously distributed in vertical (depth of the coating) and horizontal (at the coating's surface) directions, whereas the content of CuO decreased with the wash-coat depth and islands of accumulated material were observed on the coating surface. The activity of the $CuO/Cr_2O_3/Al_2O_3$ system was investigated for methanol steam reforming.

The present study is exclusively dedicated to catalyst/carrier coatings in a microreactor designed for on-board steam-reforming production of hydrogen for PEMFC powered vehicles. These catalysts must withstand extremely severe conditions: the system must be fully operational within a minute, i.e. reaching its operating temperature (800 °C) after a cold-start, and must respond rapidly to varying loads. Significant load transients occur frequently as a result of acceleration, hills, highway cruising, etc. not to mention the mechanical shocks that the catalyst undergoes during its utilization.

The purpose of the present work is to optimize all the relevant coating parameters for getting a thick, porous and stable (adherent) support layer for the active catalysts. To evaluate these properties, various descriptors or criteria like the resistance to mechanical and thermal shocks and the surface enhancement factor will be defined and used. The next steps of the active phase deposition, activation, and the catalytic performance of the optimized system will be presented in upcoming papers.

2. Experimental

2.1. Synthesis of the wash-coat

For the preparation of the alumina slurries, commercial materials were employed. The so-called ''solids'' are gamma-alumina (γ-Al_2O_3, 99.97%/Alfa Aesar Johnson Matthey; particle size 3 μm; surface area 85 $m^2\,g^{-1}$), and boehmite (AlOOH-Disperal S/Condea Chemie GmbH; particle size 25 μm, nano-sized in dispersed phase; surface area 180 $m^2\,g^{-1}$). The liquids used are distilled water (DI) and the ''binders'' acetic acid (CH_3CO_2H, glacial, 99+%/Alfa Aesar GmbH & Co KG) and acrylic acid ($C_3H_4O_2$, 99%/Aldrich). Water and acids were mixed at first, followed by the powders, which were added under vigorous stirring. The suspension was kept under stirring for 24 h prior to deposition at room temperature. Several samples were prepared by varying the solid loading (more solid = Solid(+) sample; less solid = Solid(−) sample) or the binder content (less binder = Binder(−) sample; even less binder = Binder(− −) sample) when compared to reference sample (Table 1).

2.2. Coating of microchannel platelets

The proposed wash-coating method consists of: (i) a chemical and thermal treatment of the microchannel platelets and (ii) the coating deposition.

2.2.1. Support pre-treatment

The Aluchrom microchannel platelets having the following dimensions: 70 mm × 50 mm × 1.5 mm were used as the support for alumina coating. There are 40 microchannels on each platelet having: 70 mm length × 500 μm width × 550 μm depth.

In order to eliminate impurities as well as organic compounds, a three-step treatment was applied [14] using acetone (CH_3COCH_3, 99+%, Aldrich), acetic acid (CH_3CO_2H, glacial, 99+%/Alfa Aesar GmbH & Co KG), ammonium hydroxide (NH_4OH, 1.0N Standardized Solution, Aldrich), phosphoric acid (H_3PO_4, 85 wt.%, Aldrich), and hydrogen peroxide (H_2O_2, 29–32%, Alfa Aesar GmbH & Co KG). First, the platelets were washed with acetone (Treatment I). Next they were immersed in a bath of 5:1:1 DI water:H_2O_2:NH_4OH and rinsed in DI water (Treatment II) followed by immersion in a solution of 5:1:1:1 DI water:H_2O_2:H_3PO_4:CH_3CO_2H in an ultrasonic bath and DI rinsing with this second stage being repeated twice (Treatment III). The XPS analysis confirms a three-fold reduction of the carbon compounds after the chemical treatment (Treatment III) compared to a regular washing with acetone (Treatment I) (Table 2).

Subsequently, the microchannel platelets were annealed at 1200 °C for 1 h at a heating rate of 5 °C/min. This thermal treatment triggered the segregation of an alumina layer on the metallic surface. The XRD patterns clearly showed the peaks associated to α-alumina. Prior to starting the coating procedure,

Table 1
Composition of tested slurries in wt.%

	Water (wt.%)	Acrylic acid (wt.%)	Acetic acid (wt.%)	Boehmite (wt.%)	γ-Alumina (wt.%)	Solid loading (wt.%)	Binder[a] content (wt.%)
Reference	78	5	2	11	5	16	5
Binder(−)	79	3	2	11	5	16	3
Binder(− −)	81	2	2	11	5	16	2
Solid(−)	82	5	2	8	3	11	5
Solid(+)	67	5	2	19	8	27	5

[a] Binder used in these slurries is acrylic acid because no adherence is observed for samples without acrylic acid.