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Spin coating deposition on complex geometry substrates: Influence of operative parameters

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ABSTRACT

An industrial spin coater was used to coat complex substrates for catalytic applications. Metallic open cell foams (20, 30 and 40 pores per inch, PPI) were coated for times up to 120 s using a range of spinning velocities (from 1000 to 3000 rpm). Water/glycerol solutions of different viscosities were used as model liquids to assess the influence of operating parameters on the deposition process. Coating weight (i.e., load) was found to decrease with rotation speed and spinning time, while higher coating loads were measured with an increase of viscosity and geometrical support PPI. Moreover, a process to spin coat acid-free cerium oxide slurries was developed to create a catalyst carrier on the three-dimensional substrates. Excellent control of deposited load and good adhesion performance were obtained.

1. Introduction

Current progress in chemical reaction engineering development is connected to process intensification. In many cases, process performance can be increased by using complex geometry substrates, such as monoliths or open cell foams, in structured reactor designs. Depending on the nature of the process, different substrate materials, including metals and ceramics, can be used. Regardless the nature of structured support material, geometrical support activation is needed [1]. Several methods are available to create coatings for activation, including plasma spraying [2], suspension and sol-gel deposition, electrophoretic deposition and chemical vapor deposition [3].

In many cases, thin ceramic layers are deposited on structured supports surfaces to serve as primers [4,5], catalyst carriers [6,7] or catalytic active powders [8]. To create these layers, one approach is to deposit particulate ceramic slurries. This 'slurry coating' method, which is also referred to as washcoating, has been widely applied in catalyst production [9]. To deposit washcoats on substrates with complex geometries, dip-coating is considered a good compromise between technique complexity and coating results [3,4]. In this technique, the support is dipped into slurry and then withdrawn at controlled speed. During this withdrawal, a thin liquid layer is deposited based on the balance of gravitational, viscous and surface tension forces. The effect of these forces on the coating thickness is well-understood for dense, flat substrates [10,11]. Unfortunately, less is known about the control of coating thickness on complex supports, such as open cell foams and high cell density monoliths. In particular, slurry entrapment in support macropores, leading to pore clogging, is a major concern for catalytic applications. Thus, a technique to remove excess slurry after dip coating is needed. Several methods are cited in literature; blowing gas (usually air or nitrogen) is one of the most frequently used procedures [6,12,13].

Spin coating is another method to consider for catalyst deposition. Like dip coating, this technique produces thin, reproducible layers when employed mainly to coat flat, dense substrates [14] for a wide variety of applications [15–17]. Only a few publications have addressed the use of spin coating for deposition of coatings on complex substrates. For example, a few authors focused on the use of spin coating for washcoat deposition on open cell foams [18–20] or monoliths [21–26] for catalytic application. Most references report a fixed rotation speed (from 400 to 1000 rpm) for a certain time (from 30 s to 10 min), in order to remove excess slurry from support pores. By contrast, Zhang et al. [20] focused on the relationships among deposition conditions and deposited washcoat thickness on open cell carbon foams. They found that when foams were spun at sufficiently high speeds, the final thickness of coatings was independent of the initial quantity of liquid loaded into the foam by dip coating, and that consistent with spin coating on flat substrates, the coating thickness decreased with increasing spinning speed and decreasing coating liquid viscosity. Their results, however, were limited to carbon foams and did not include effects of foam shape and dimension. Moreover, no evidence of cerium

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oxide depositions on open cell foams by spin coating was found in literature.

In this work, the influence of spin coating parameters, such as spinning speed, spinning time and liquid viscosity, on washcoat deposition was investigated. Aqueous glycerol solutions were used as model liquids, and metallic and ceramic open cell foams of various shapes, dimensions and porosities were used as complex substrates. In addition, thin cerium oxide layers were deposited on foams to demonstrate the utility of the method for creating catalytic active phase carriers.

2. Experimental

2.1. Materials

FeCrAlY alloy metallic open cell foams were provided by Selee Corporation (Hendersonville, NC, US). Samples of different porosities (20, 30 and 40 pores per inch, PPI) were tested. Both cylindrical and parallelepiped supports were used. In the first case, support dimensions were set at 1 cm and 1.5 cm for external diameter and length, respectively. In the second case, dimensions were tuned to produce samples with an apparent volume in the 2–16 cm^3 range. In Fig. 1, optical microscope images of the bare cylindrical supports are reported, both in terms of side and cross section views.

To improve washcoat adhesion, metallic supports were heated at 900 °C in air for 10 h (2 °C·min^{-1} heating and cooling ramps) to allow α-Al_2O_3 formation at the surface [4,5,27–29]. To clean support surfaces, samples were sonicated for 30 min in distilled water before any deposition and then dried overnight.

2.2. Procedures

The experimental part of the work was carried out using two different coating liquids: water/glycerol solutions and cerium oxide slurry. In the first, coating liquid was obtained by mixing pure glycerol with distilled water at room temperature until a uniform solution was obtained. Pure glycerol, as well as 80 %wt. glycerol (20 %wt. water) and 50 %wt. glycerol (50 %wt. water) solutions were used. These solutions were used to test the effect of process variables and tune operating parameters.

Cerium oxide slurry was used to deposit a solid carrier layer on support surfaces. Slurries were produced according to a procedure reported in literature [30]. In a typical experiment, polyvinyl alcohol (Mowiol 88-8, Sigma-Aldrich, St. Louis, MO, US) - in the following labeled as P - was dissolved in water (H) at 85 °C, using a magnetic stir bar. Then, an aqueous glycerol solution (G, 87 %wt. water, Sigma-Aldrich, St. Louis, MO, US) was added to form the liquid medium, which will be referred to as HGP. Then, low surface area cerium oxide (CeO_2, Sigma-Aldrich, St. Louis, MO, US) was added to the HGP solution to produce a suspension with a solids loading of 25 %wt. Slurry was poured in a polyethylene jar and ball milled at 50 rpm for 24 h, using zirconia spheres as grinding medium. After ball milling, the resulting slurry was sonicated for 30 min in order to reduce foaming [31].

Liquid deposition was performed by coupling a dip coating and a spin coating procedure. In a typical procedure, supports are dipped in the liquid medium. As reported in a previous work [20], immersion and withdrawal velocities do not affect sample washcoat load after spin treatment. For this reason, dipping procedure in liquid medium was performed by hand. Then, a commercial spin-coater (CB15PL spinner with PWM320 controller by Headway Research Inc., Austin, TX, US) was used to remove the excess liquid that was entrapped in support porosity. The spinning device was properly modified for complex geometry substrates spinning. Due to the device modification and to support dimensions, a maximum of 3000 rpm in rotation speed was set for safety reasons. Spin time, speed and acceleration were precisely controlled. Washcoat load was tuned by performing multiple depositions.

In the case of cerium oxide slurry, samples were heat treated after each spin coating deposition, in order to consolidate the solid coating with a flash drying step (350 °C for 6 min in a pre-heat oven). Then, a calcination step was carried out at 800 °C for 10 h, with 2 °C·min^{-1} heating and cooling ramps.

2.3. Characterization

The rheological behavior of the cerium oxide suspensions was characterized by means of rotational rheometer measurements. A DSR 200 device (Rheometrics, New Castle, DE, US) with parallel disk plates (40 mm diameter) was used to assess viscosity in the 1–1000 s^{-1} shear rate range. The viscosities, surface tensions and densities of the glycerol-water solutions at 20 °C are reported in the literature [20,32]. The viscosities of these solutions vary considerably. For pure glycerol, 80 %wt. glycerol and 50 %wt. glycerol, the viscosities are approximately 1400 mPa·s, 60 mPa·s and 6 mPa·s, respectively. The surface tensions and densities, however, are less variable. Surface tension is on the order

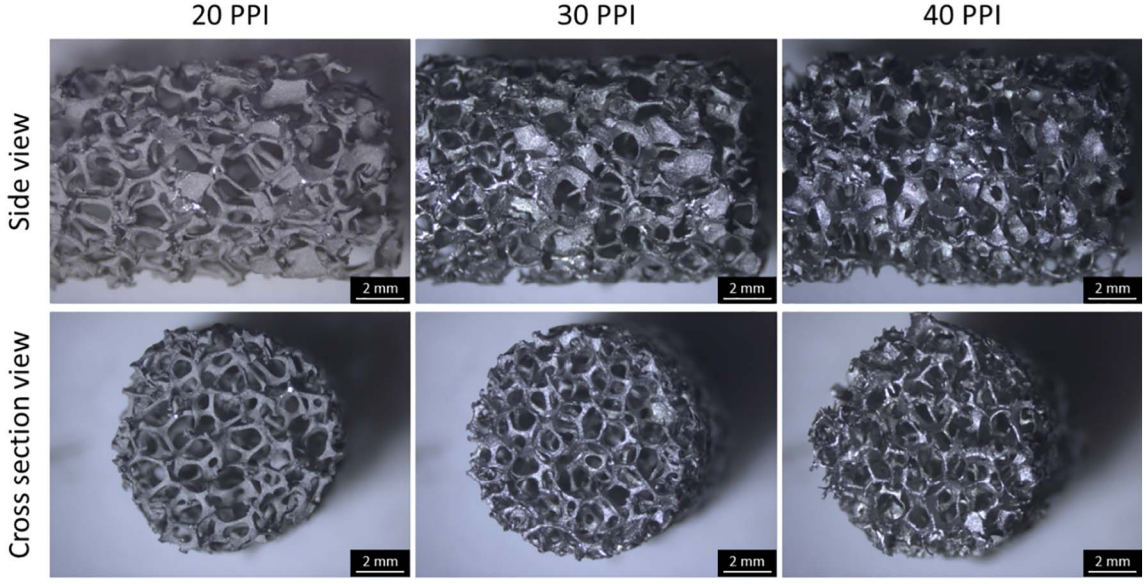

Fig. 1. Optical microscope images of the metal supports at different pore density values.