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Inkjet printing of porous nanoparticle-based catalyst layers in microchannel reactors

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ABSTRACT

Inkjet printing technology was applied for the precise deposition of alumina nanoparticles in microchannels as a catalyst support layer. Several alumina nanoparticle containing inks were prepared and tested for inkjet printability. It could be shown that additives such as ethylene glycol and polyethylene glycol are needed for aqueous inks up to a concentration of 50 wt.% for continuous drop generation. The printing was conducted both in semicircular and rectangular microchannels. The coating thickness was controlled by repetitive printing of each channel, and the generated layers were uniform in thickness throughout the microchannel foil. The printed alumina layers were impregnated with rhodium nitrate after calcination. A high metal loading of 15 wt.% was applied to enable a high reaction rate per coated area despite the low thickness of the layer, and the catalytic activity was demonstrated for methane steam reforming (MSR). The prepared catalyst layers were highly active, and conversions exceeding 98% were obtained at 973 K and a W/F (catalyst weight/CH_4 feed rate) ratio of 19.7 (kgcat s)/mol_{CH_4}.

1. Introduction

Microchannel reactor technology has been demonstrated as a successful approach for chemical process intensification and efficient heat integration [1,2]. The activity and selectivity of the catalyst in complex reaction media (such as reaction mixtures in Fischer–Tropsch synthesis, dimethyl ether synthesis, steam reforming, etc.) can be tuned effectively by exploiting the inherent advantages of microchannels such as high surface to volume ratio and small diffusional length scales giving rise to high heat and mass transfer coefficients [3,4]. The catalytic performance of surface-coated microchannel foils is largely influenced by the quality of the catalyst layers. Non-uniform catalyst layers in microchannels may lead to reactant flow maldistribution and a drop in reactor performance [5]. Different coating techniques (flow coating, filling and drying, and anodic oxidation) have been demonstrated in the literature for laboratory microchannel reactors [5–8]. However, these methods show certain limitations such as poor uniformity and reproducibility when coating a multitude of channels as well as undesired coating on the fins and side bands when coating open structures. The latter creates problems during stacking and joining of coated foils and eventually also during integration of metallic membranes, e.g., for in situ hydrogen separation in membrane reactors [9,10]. Therefore, research activities were started recently at the Institute for Micro Process Engineering aiming at a precise and highly reproducible preparation of uniform catalyst layers in up side open microchannels on planar substrates through inkjet printing of catalyst nanoparticle suspensions. The method is believed to be broadly applicable to a variety of different catalyst systems. The thickness of the coating should be variable without affecting other important properties to be able to take care of the needs of different applications with respect to catalyst loading per volume. The rationale is that catalyst layers should be as thick as possible as long as there is no major influence of heat and mass transport limitations on its performance. Coverage of the sidewalls in addition to the bottom of the channels is desirable as well in order to increase the amount of catalyst.

Inkjet printing is well known in the paper printing industry. The ability to generate picoliter scale droplets and to deposit them in specific patterns facilitates that inkjet printing technology is applied in various industrial fields such as electronics, life sciences, and chemistry [11–13]. In general, there are two different mechanisms to generate droplets with an inkjet printer: continuous drop formation and drop-on-demand (DOD) [14]. In the former, a liquid stream is continuously pumped through a small orifice and small droplets are generated by Rayleigh instability. The latter generates droplets by pressure waves in a liquid-filled cavity using a piezoelectric transducer. The DOD printing technique is preferred for the deposition of ceramic or metallic particle suspensions acting as support or catalytically active materials.

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The inkjet printer can cope with the demand for selective deposition in confined spaces. By controlling drop size and printing pitch, the coating amount and thickness on substrates can be regulated. Therefore, inkjet printing can also be used to obtain a precise deposition of catalyst in confined geometries, such as microchannel reactors. The catalysts are only deposited in the void volume of the microchannels, not on the fins or side bands of the microchannel foil.

The inkjet printing technology has already been adopted in catalysis research, e.g. for photocatalysis and fuel cell technology. Arin et al. printed a transparent 85 nm thin TiO_2 film on a glass substrate by inkjet printing and tested its photocatalytic activity [15]. Taylor et al. demonstrated layer by layer deposition of platinum catalysts for fuel cell applications [16]. These benefits, thin film and multilayer deposition, can also be utilized for catalyst coatings in microstructured reactors.

The physical properties of the ink such as density, surface tension, and viscosity do have a large influence on the drop formation mechanism in DOD printers and the resulting inkjet drop characteristics such as drop size, drop ejection velocity, satellite drop formation and drop relaxation time. The printability of an ink is connected with the Z number, which is a dimensionless grouping of fluid properties equivalent to the inverse of the Ohnesorge number Oh [17]:

$$Z = \frac{1}{\mathrm{Oh}} = \frac{Re}{\sqrt{\mathrm{We}}} = \frac{(\gamma\rho\alpha)^{1/2}}{\eta} \tag{1}$$

In this equation η, γ, ρ, and α are the dynamic viscosity, surface tension, density and nozzle diameter. The Z number describes the ratio of the surface forces to the inertial forces during drop formation in DOD print heads. The region $4 < Z < 14$ has been reported as the printable range for various systems [18]. If the Z value is too low or too high, satellite droplets may be generated during printing operation. This shows that the ink formulation is a crucial step for the successful application of inkjet printing.

In the present work, DOD inkjet printing was used to generate thin alumina films in microchannels of different geometries and materials. Distinct aqueous alumina inks were formulated, and the printable ranges of the inks were determined. The printed alumina supports were calcined and subsequently impregnated with rhodium and applied in methane steam reforming to demonstrate the activity of the catalyst layers.

2. Experiment

2.1. Ink preparation

The alumina-based inks were prepared from a commercial stable aqueous colloidal nano-suspension of aluminum oxide having a particle size (d_{90}) of 100 nm (Alfa Aesar GmbH & Co KG), which exists at pH 4 as pseudo-Boehmite (AlO(OH)), CAS No. 1344-28-1). This colloidal suspension was either used directly as ink (Ink-1) or further modified with water (Ink-2) and ethylene glycol (Ink-3) to adjust the alumina particle concentration. Ink-4 was formulated with ethylene glycol and polyethylene glycol-600. The density of the inks was measured using the pycnometer method. The surface tension of the inks was measured using the pendant drop technique with the help of a liquid dosing nozzle, an optical cell (both from SITEC AG, Maur/Zurich) and a CCD camera (Sony AVC-D5CE). The viscosity of the inks was measured at a shear rate of $100\,s^{-1}$, using a Thermo Scientific HAAKE rheometer having a plate and cone arrangement. The physical properties such as density, surface tension, and viscosity of inks used in this work, and corresponding Z values are given in Table 1.

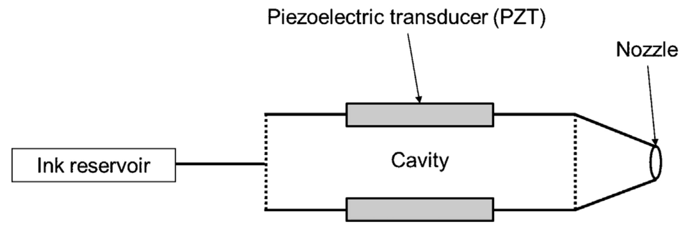

Fig. 1. A schematic diagram of the piezoelectric print head.

2.2. Inkjet printing

Inkjet printing was conducted with a commercial printer (microdrop Technology GmbH). The inkjet printer was equipped with a print head (MD-K-140) containing a 100 μm diameter nozzle. The ink reservoir (5 ml) supplies the ink to the print head. The print head was filled with the ink from the ink reservoir, and a negative holding pressure (−10 mbar) was applied to keep the ink in the print head cavity. A schematic diagram of a piezoelectric print head used in DOD inkjet printing is shown in Fig. 1. The print head cavity is surrounded by a piezoelectric transducer operated by a particular applied voltage and pulse width. The piezoelectric transducer contracts or expands itself depending on the type of voltage (positive or negative). This movement generates a pressure wave that is a driving force of the ejection of the ink through the nozzle. The produced ink drops fall in the microchannel. Finally, drying and calcination forms a porous solid layer on the surface of the microchannel.

In the present work, two different types of pulse modes, single and bi-polar pulse, were applied to generate the droplets. In single pulse mode, only positive voltages were used. In bi-polar pulse mode, both a positive and a negative voltage are applied sequentially. Positive voltage ejects the ink fluid, and then the negative voltage breaks off the drop and withdraws the rest of the ejected fluid.

The printing studies were conducted both in semicircular and rectangular microchannels which differ also in terms of aspect ratio (depth versus width) and surface roughness. The semicircular microchannels were fabricated in stainless steel foils (Material No. 1.4301) (300 μm in width and 90 μm in depth, 105 channels/foil) by wet chemical etching (Herz Ätztechnik, Germany). This method leads to a roughness level of the structured surface in the range of several microns (typically < 5 μm) resulting in a matt appearance.

The rectangular microchannels were fabricated by micro milling with a hard metal tool in high temperature resistant Nicrofer® foils (Material No. 1.4876, Thyssen-Krupp VDM, Germany). These foils were used for reaction tests. They contained 100 channels/foil with a channel geometry of width × depth × length of 200 μm × 200 μm × 8 cm. The roughness level for micro milling is usually well below 1 μm giving the structured surface a shiny appearance.

The foils were oxidized in air (stainless steel 1.4301 at 823K & Nicrofer® 1.4876 at 1073 K) prior to inkjet printing to form an oxide layer on the surface for increased adhesion of the coating [19,20]. After printing, the alumina layers were dried at 343 K in an oven for 24 h and subsequently calcined in air at 823 K (1.4301) or 1023 K (1.4876) for 6 h. The temperature ramp was set to 2 K/min. At 653 K the temperature was held for 6 h to reduce crack formation of the coating layer during transition from AlO(OH) to γ-Al_2O_3.

2.3. Characterization of the catalyst layers

The catalyst layer's cross-sections were analyzed for the distribution of Rh. After metallographic preparation, the samples were cleaned in an ultrasonic bath and then coated with a conductive carbon layer by evaporation deposition from a heated carbon filament.