



Design and testing of a microchannel reactor for the PROX reaction

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ABSTRACT

The different steps for manufacturing a microchannel reactor for the PROX reaction are discussed. Transient Liquid Phase bonding (TLP) using a Ni–B–Si amorphous melt spun is used for joining micromilled Al-alloyed ferritic stainless steel plates followed by recrystallization at 1200 °C for 5 h. A CuO_x–CeO₂ catalyst synthesized by the coprecipitation method was washcoated on the microchannel block resulting in a homogenous 20–30 μm thick layer. The catalytic activity for CO-PROX reaction is similar in both the powder catalyst and the microchannel coated reactor but the selectivity is higher in the microchannel reactor.

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1. Introduction

The widespread use of portable electric and electronic devices increases the need for efficient autonomous power supplies that replace the currently predominant battery technology. The use of common fuels/chemicals (hydrocarbons or alcohols) as energy sources is a promising alternative when combined with the recent developments in microchannel reactor technology. The high power density, rapid start-up time, and low-temperature operation of PEMFC make these devices as the most promising for powering up electric or electronic devices. However, an essential requirement for the reformat-fed PEMFC is the removal of CO from the H₂ stream after the reforming and water–gas shift (WGS) reactions. After the WGS units the CO content of the hydrogen streams may vary between ca. 0.5 and 2 vol.% being, therefore, mandatory clean-up units for the removal of CO to trace level. Preferential CO oxidation (CO-PROX) is among the preferred technologies for small-scale fuel processor applications [1]. CO-PROX reactions allow reducing CO contents from 1% in the feed to the ppm level.

When using PEMFCs for portable or automotive applications packed-bed reactors have several drawbacks such as pressure drop within catalyst layer, temperature gradients, and hot spot due to the high exothermicity of the oxidations of CO and H₂. Microreactors have the advantages of fast response time, easy integration,

and small footprint, which are ideal for portable power systems. In addition, enhanced mass and heat transport properties are also widely recognized as advantages of microreactors [2–6]. In addition to this, recent studies of simulated CO-PROX reactions have shown that the reverse water–gas-shift side reaction is favoured in the case of packed bed reactors with respect to thin catalytic films deposited on microchannel walls [4]. Therefore, CO-PROX units based on microchannel reactors have been reported as part of integrated fuel processors in a wide power range [6–9].

Different catalytic systems and reactor designs have been proposed for the CO-PROX reaction. In a recent study Bion et al. [10] review the performances of noble metals (including Pt, Ru, Rh, Pd and Au) and transition metal oxides catalysts and compare the advantages and drawbacks for each type of catalysts in terms of activity and selectivity including the influence of the presence of CO₂ and H₂O in the reactants flow. They conclude that CuO–CeO₂ catalysts are very attractive for industrial applications since their excellent performances, stability and low cost compared to noble metal-based catalysts.

Dudfield et al. [11,12] operated a compact fin heat-exchanger reactor containing 2.5% Pt–Ru catalyst in the CO-PROX reaction. Using a two-stage configuration this unit allowed reductions in the CO concentrations down to 15 ppm. Silicon wafers [13] or austenitic stainless steel plates [14,15] were used for building microchannel reactors for the PROX reaction. Hwang et al. [16] studied the reaction over a silicon-based microreactor coated with a Pt/Al₂O₃ catalyst, yielding 99.4% CO conversion. Kim et al. [15,17] obtained CO outlet concentration below 50 ppm at O₂/CO ratio of

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2.5 by using a 13-layered micro-channel reactor built by stacking chemically etched stainless steel plates coated with a Pt-Co/Al₂O₃ catalyst. Despite most of the work on CO-PROX in microreactors has been carried out using noble metal based catalysts a few insights on copper based catalysts have been reported. Snytnikov et al. [18] compared a 5 wt.% Cu/CeO₂ catalyst in both fixed bed and microchannel reactors with the latter exhibiting higher conversion and selectivity. This catalyst allowed the reduction of the CO concentration from 1 vol.% to 10 ppm. Kim et al. [15] compared a CuO/CeO₂ coated microreactor with a Pt-Co coated microreactor showing better selectivities in the CO-PROX reaction for the copper-based catalyst.

In the present work, we provide a description of the different steps required for manufacturing a microchannel reactor for the CO-PROX reaction. The reactor is tested using conventional Cu_x/CeO₂ catalysts and the results compared with those obtained for powdered catalysts.

2. Materials and methods

2.1. Catalyst preparation

The Cu_x-CeO₂ catalyst was prepared by the coprecipitation method. The amount necessary for preparing a 0.5 M solution of Cu(NO₃)₂·3H₂O and Ce(NO₃)₃·6H₂O were mixed, under vigorous stirring, to get a 9:1 Ce(OH)₃:Cu(OH)₂ weight ratio. After homogenizing the system, a NaOH solution (2 M) was added dropwise until a stable pH of 9. The precipitate was filtered and washed with distilled water in order to remove the Na⁺ and NO₃⁻ ions. Finally, the obtained solid was dried overnight at 60 °C and finally, calcined 2 h at 300 °C.

2.2. Catalysts characterization

BET specific surface areas were measured by nitrogen adsorption at liquid nitrogen temperature in a Micromeritics ASAP 2000 apparatus. Before analysis, the samples were degassed 2 h at 150 °C in vacuum.

The cerium and copper contents of the samples were determined by X-ray fluorescence spectrometry (XRF) in a Panalytical AXIOS PW4400 sequential spectrophotometer with a rhodium tube as the source of radiation.

X-ray diffraction (XRD) analysis was performed on a Siemens D 500 diffractometer. Diffraction patterns were recorded with Cu K α radiation (40 mA, 40 kV) over a 10–80° 2 θ range using a position-sensitive detector with a step size of 0.01° and a step time of 7 s.

The Raman spectra were recorded in a dispersive Horiva Jobin Yvon LabRam HR800 microscope, with a 20 mW He–Ne green laser (532.14 nm), without filter, and with a 600 g mm⁻¹ grating. The microscope used a 50 \times objective and a confocal pinhole of 100 μ m. The Raman spectrometer is calibrated using a silicon wafer.

The reducibility studies were carried out on a pilot plant built by PID Eng&Tech in TPR mode equipped with a VINCI thermal conductivity detector. The experiments were done by a thermo-programmed reduction (TPR) of 50 mg of catalyst, in a H₂ flow of 5% diluted in Ar (total flow = 50 mL/min), using a temperature ramp of 10 °C/min from room temperature to 900 °C.

The Zeta Potential was measured by using a MALVERN Zetasizer 2000 instrument. The solids were dispersed in an aqueous solution of 0.003 M NaCl. The pHs of the solutions were adjusted with HNO₃ or NaOH solutions.

Rheological properties of the slurries were measured in a rotational viscosimeter HAAKE, model VT 500, geometry NV.

The adherence of the catalytic layer deposited onto the substrates was evaluated using an ultrasonic technique. The weight

loss caused by the exposure of the sample to ultrasound is measured. The structured supports immersed in petroleum ether were submitted to an ultrasonic treatment for 30 min at room temperature. After that, the samples were dried and calcined. The weight loss was determined by the difference in the mass of the samples before and after the ultrasonic test. The results are presented in terms of the retained amount of coating on the monolith, expressed as percentage.

2.3. Catalytic activity measurements

The CO-PROX reaction was carried out at atmospheric pressure in a PID Eng&Tech Microactivity set-up, employing a stainless steel tubular reactor with internal diameter of 9 mm and a constant feed stream flow rate of 100 cm³ min⁻¹ (STP). The catalyst (100 mg, particle size in the 100–200 μ m range) was diluted with crushed glass particles in the same particle size range forming a bed of about 5 mm in length. The experimental runs were carried out in a flow containing 50 vol.% H₂, 2 vol.% CO and 1 vol. % O₂ concentrations using N₂ as balance. The reaction temperature was increased from 50–60 to 190–250 °C in steps of 10 °C. For each step the temperature was stabilized and data were recorded at steady-state conditions. Fresh catalyst was loaded into the reactor after each complete run. Some experiments carried out at the same space-time but at varying gas linear velocities confirmed the absence of external mass transfer effects. On-line analyses of the feed and products streams were performed on an Agilent 7890 gas chromatograph equipped with a Porapak Q, two Molecular Sieve 5A and two Hayesep Q columns and two TCD detectors and a FID detector.

The same computerized PID Eng&Tech Microactivity set-up was used to study the reaction in the microchannel reactor, replacing the tubular stainless steel reactor for the built microchannel reactor the same compositions were chosen but 300 cm³ min⁻¹ (STP) feed stream flow rate since 300 mg catalyst was loaded in the microchannel block. To study the effect of CO₂ and H₂O, a series of experiments keeping constant the H₂ content of the feed stream set at 50 vol.%, and both the CO and O₂ concentrations fixed at 1 vol.% were carried out. The CO₂ and H₂O concentrations in the feed were varied within the 2–10 vol.% and 0–20 vol.% ranges, respectively, using N₂ as balance. The microactivity reference hot box controlled the reaction temperature. For each step the temperature was stabilized and data were recorded at steady-state conditions.

3. Microchannel reactor

The metallic microchannel reactor was manufactured using Al-alloyed ferritic stainless steel (for instance, Fecralloy[®]), since ferritic alloys containing 3–5% of aluminium produce by thermal treatment an Al₂O₃ layer that favours the interaction with the catalytic coating [19–22]. The Fecralloy consisted of Cr 22%, Al 4.8%, Si 0.3%, Y 0.3%, and Fe balance [21].

Characterization of the joined steel plates were carried out by optical and electron microscopy. Specimens were extracted from the samples, grinded with SiC paper of #240, #400, #600 and #1200 grain size and mirror polished with 0.3 and 0.1 μ m Al₂O₃ powder. Etching with Vilella's reagent developed the microstructure. Sample observation in the as polished and etched conditions was done in a Leica-DM-IRM optical microscope equipped with a digital camera (Leica DC300). In order to identify metallic and non-metallic inclusions as well as to determine local compositions, the as-polished samples were also observed by SEM using a JEOL 5400 system equipped with secondary and backscattered electron and X-ray detectors.

Microchannels were fabricated by micro-milling 1 mm thick ferritic stainless steel plates. Each plate has 10 square chan-

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