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Hydrogen production from ethanol steam reforming in a micro-channel reactor

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ABSTRACT

Ethanol steam reforming was studied over a supported Ir/CeO₂ catalyst in a micro-channel structured reactor. The catalyst coating was deposited on the channel walls and showed a remarkably high homogeneity and an excellent adherence to the stainless steel substrate, leading to stable performance during long-term runs. Hydrogen yields exceeding 40 L_{H₂} g_{cat}⁻¹ h⁻¹ were achieved during testing with partial ethanol conversion of 65% and a residence time in the order of a few milliseconds. This hydrogen productivity was found significantly higher than in a comparable conventional fixed-bed reactor hence being extremely promising for hydrogen production in micro fuel cell applications.

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1. Introduction

Steam reforming of ethanol has been considered in recent studies as a possible alternative technology to supply hydrogen for PEM fuel cells, essentially for residential or industrial applications. Great interest arises from two main factors: i) the rapid development of the bio-ethanol industry with a scenario of ethanol being massively produced from biomass and directly delivered to the existing fuel distribution infrastructures [1–4] and ii) the non toxicity of ethanol compared to methanol or conventional hydrocarbon fuels for residential handling. Considerable efforts have been made in the field of ethanol reforming using conventional fixed-bed reactors [5–13]. However, those packed bed reactors can

hardly meet the process requirements for rapid and frequent load changes in small scale and mobile hydrogen production systems for powering portable computers or mobile phones.

To fulfill the miniaturization and compactness requirements, various types of micro-structured reactors have been developed in the last decade [14]. Among them, the most promising concept considers stacked systems of channeled metallic platelets, coated with active catalysts. Since the characteristic dimensions of the reaction zones are in the sub-millimeter-scale, they are generally referred to as “micro-structured reactors”, often abbreviated as “micro-channel reactors” or “micro-reactors”. In addition to compactness, the advantages of micro-reactors include i) the rapid mass and heat transfer due to high surface to volume ratio, ii) the lower

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pressure drop compared to classical packed bed reactors since micro-reactors work under laminar flow conditions, iii) the good structural and thermal stability, iv) the precise control of the process conditions leading higher product yields. Indeed, in the later case, the short characteristic time for radial diffusion in micro-reactors leads a narrower residence time distribution of the reaction gases, allowing an optimum contact time between the reactants and the catalyst and avoiding the formation of unwanted by-products. Micro-structured reactors also provide built-in safety since a large gas hold-up (reactor volume) is avoided [15–17].

Recently, considerable work has been carried out on the catalytic steam reforming of methanol in micro-channel reactors [18–20]. However, the use of micro-reactors to produce hydrogen from ethanol is relatively unexplored. Men et al. [21] investigated micro-structured systems consisting of stainless steel platelets with 14 micro-channels. The results revealed that Rh-based catalysts exhibited the highest catalytic activity, as compared to Co and Ni-based catalysts. The Rh–Ni–Ce catalyst was operated for 100 h without any noticeable degradation in activity and selectivity. Full conversion was achieved for the entire period and the H₂ selectivity was 86%. The CO content in the reformat remained constant ca. 8.2%.

Llorca et al. [22] developed a micro-channel reactor where ethanol steam reforming is performed on one side of the plate while ethanol combustion is performed on the other side in order to provide the necessary heat for the endothermic steam reforming reaction. Four different coating methods for depositing the Co/ZnO and CuMnO_x layers on the micro-channels were studied in order to guarantee a homogeneous and stable deposition and stability. At 460 °C, 3.67 mol of hydrogen were produced per mole of ethanol consumed by the system performing both reactions (steam reforming and combustion). The overall efficiency of such micro-reactor was 71%. Llorca et al. [15] also compared the ethanol steam reforming over a Co₃O₄ catalyst in a conventional monolith reactor and a micro-channel reactor. At 500 °C, ethanol conversions of 70% and 90% were measured for a monolith reactor and a micro-reactor, respectively.

In previous studies carried out in our laboratory [23–26], we developed a reforming catalyst, Ir/CeO₂, which demonstrated high efficiency and stable in the hydrogen production from ethanol in a fixed-bed reactor even under stoichiometric reaction conditions. In this work, we further investigated the application of an Ir/CeO₂-coated micro-channel reactor for the production of hydrogen via ethanol steam reforming.

2. Experimental

2.1. Micro-channel reactor design

Fig. 1 shows the micro-reactor and one of the platelets used in this study. The reactor is made of stainless steel and has been designed in collaboration with IMM (Mainz, Germany). A graphite gasket insured the gas tightness between the end-standing flanges with welded-in gas connections and the platelet housing. The heating is provided by means of four cartridges of 300 W each inserted into the housing body. One

of these cartridges is equipped with a thermocouple that enables temperature regulation. The pressure drop over the reactor was recorded using a heated electronic pressure transducer connected to the feed line at reactor entrance.

The platelets had the following dimensions: 100 mm length × 30 mm width × 2 mm height, each platelet having 28 channels: 50 mm length × 0.5 mm width × 0.5 mm depth. They are made of the metal alloy (20%Cr, 30Ni, 4%Al, 46%Fe). In order to eliminate impurities such as organic compounds, a three-step pre-treatment was applied [27]. Agents used were acetone, acetic acid, ammonium hydroxide, phosphoric acid, and hydrogen peroxide. First, the platelets were washed with acetone (Treatment I). Next they were immersed in a bath of 5:1:1 deionized water: H₂O₂: NH₄OH and rinsed in deionized water (Treatment II) followed by immersion in a solution of 5:1:1:1 deionized water: H₂O₂: H₃PO₄: H₃COOH in an ultrasonic bath and deionized water rinsing (Treatment III). Subsequently, the micro-channel platelets were annealed at 1000 °C for 10 h at a heating rate of 5 °C/min. This thermal treatment triggered the segregation of an alumina layer on the metallic surface.

2.2. Coating of micro-channel platelets

The Ir/CeO₂ catalyst was prepared via deposition-precipitation, as described elsewhere [23], leading to an iridium loading of 2.1% and a surface area of 153 m²/g. 2 g of the Ir/CeO₂ catalyst (as a powder) were initially milled down to particle size below 5 μm using the wet ball-milling method. Adapted from a procedure previously described [28] the powder was then dispersed into 8 g of water under vigorous stirring and 0.12 g of methylhydroxyethyl cellulose (Tylose MH 300 P2) was added to serve as a binder (mass ratio Ir/CeO₂:H₂O = 1:4, binder:H₂O = 1:67) before the slurry was kept under stirring for 12 h at room temperature.

The slurry was injected into the micro-channels of the platelets using a syringe and the excess suspension was wiped off with chip knife. The platelets were further dried at ambient temperature in air for 3 h, before calcination in static air at 400 °C (temperature ramp rate: 5 °C/min) for 5 h. The catalyst loading was about 0.05 g per plate. Two coated platelets were then stacked and inserted in the dedicated housing.

2.3. Catalyst characterization (SEM)

The microstructure and morphology of coating layers were studied both before and after reaction using a JEOL 5800 Scanning Electron Microscope operated at 15 kV. Prior observation, the samples were covered with a thin Au–Pd film to avoid any charge accumulation on the sample surface and to improve the image contrast.

2.4. Ethanol steam reforming (ESR)

Before testing, the catalyst deposited in the micro-channels was reduced in situ under 5 vol% H₂/He (30 mL min⁻¹) at 400 °C for 1 h. Subsequently, a mixture of ethanol and water (1:3, molar ratio) was injected using a liquid pump (LC-10AD, SHIMADZU) and further vaporized in the feeding line which was heated at 180 °C. The effluent was finally analyzed online

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