



Hydrogen production from oxidative steam reforming of ethanol over Ir/CeO₂ catalysts in a micro-channel reactor



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HIGHLIGHTS

- Ethanol reforming over Ir/CeO₂ catalyst in a micro-reactor was investigated.
- Catalytic performance in a micro-reactor was higher compared to a fixed-bed reactor.
- The homogeneous Ir/CeO₂ layer led to a remarkable stability during 60 h test.

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ABSTRACT

Oxidative steam reforming of ethanol was investigated over a supported Ir/CeO₂ catalyst in a micro-channel structured reactor. The catalyst coating was successfully deposited on the channel and showed a remarkably high homogeneity and an excellent adherence to the stainless steel platelets leading to stable performance during long time runs. Both the activity and hydrogen selectivity in the micro-structured reactor was found higher than in a conventional fixed-bed reactor due to the rapid mass and heat transfer hence being extremely promising for hydrogen production in micro fuel cell application.

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1. Introduction

Oxidative steam reforming of ethanol has been regarded as a promising alternative technology to supply hydrogen for fuel cells [1–3]. Great interest arises mainly due to two factors: (i) the rapid development of the bio-ethanol industry and the non-toxicity of ethanol [4–7]; (ii) ethanol oxidative steam reforming, being a combination of the steam reforming and the partial oxidation reactions, possesses a reasonable balance between energy efficiency and hydrogen yield. Furthermore, the presence of oxygen in the reactant feed also facilitates the efficient removal of coke over the catalyst surface.

Enormous studies have been conducted for oxidative steam reforming of ethanol in conventional fixed-bed reactors and supported Ni, Cu, Ir, Ru or Rh catalysts were described as the active systems for this process [8–12]. However, those packed bed reactors might hardly meet the process requirements for rapid and fre-

quent load changes in small scale and mobile hydrogen production systems for powering portable computers or mobile phones [13].

Based on the above challenges, various types of micro-structured reactors have been developed in order to fulfill the miniaturization and compactness requirements in the last decade [14–17]. Among them, the most promising concept considers stacked reactors of channeled metallic platelets coated with the catalysts. For this kind of structured reactors, the characteristic dimensions of the reaction zones are in the sub-millimeter scale. Hence, they are generally referred to as “micro-structured reactors”, often abbreviated as “micro-reactors”. In addition to compactness, micro-reactor presented the advantages such as (i) the rapid heat and mass transfer coefficients due to high surface to volume ratio; (ii) the lower pressure drop compared to conventional packed bed reactors since micro-reactors work under laminar flow conditions; (iii) providing built-in safety since a large gas hold-up (reactor volume) is avoided [18].

Recently, steam reforming of methanol or natural gas in the micro-reactor has been widely investigated [19–21]. However, hydrogen production from ethanol in the micro-channel reactor is relatively unexplored [22–24]. Men et al. [25] investigated

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ethanol steam reforming over supported catalysts in a micro-structured reactor consisting of stainless steel platelets with 14 micro-channels and elucidated that Rh-based catalysts exhibited the highest catalytic activity, as compared to Co and Ni-based catalysts. Llorca and co-workers [26] 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. The overall efficiency of such micro-reactor was 71%. Peel et al. [27] also compared ethanol steam reforming over Rh/CeO₂/Al₂O₃ catalyst in a conventional fixed-bed reactor and a micro-channel reactor. The results indicated that H₂ yield obtained in the micro-reactor was ~65 Lg⁻¹ h⁻¹, as compared to 60 Lg⁻¹ h⁻¹ in the packed bed reactor. In previous studies carried out in our laboratory [28–30], we developed an efficient Ir/CeO₂ catalyst which showed the excellent activity and stability for hydrogen production from ethanol in a fixed-bed reactor even under the stoichiometric feed composition. In this work, we further extend our research to the application of an Ir/CeO₂-coated micro-channel reactor for hydrogen production from ethanol oxidative steam reforming.

2. Experimental

2.1. Micro-reactor

Fig. 1 shows the micro-reactor and one of the coated platelets used in this study. The reactor is made of stainless steel and the heating is provided by means of six cartridges of 300 W each inserted into the housing body. One of these cartridges is equipped with a thermocouple that enables temperature regulation.

The platelets used for oxidative steam reforming of ethanol have the following dimensions: 50 mm length × 50 mm width × 5 mm height and each platelet contained 46 micro-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 treatment was applied [31]. Agents used are acetone, acetic acid, ammonium hydroxide, phosphoric acid, and hydrogen peroxide. The platelets were firstly washed with acetone (Treatment 1) followed by immersion into a bath of 5:1:1 deionized (DI) water:H₂O₂:NH₄OH and rinsed in DI water (Treatment 2). After that, they were immersed into a solution of 5:1:1:1 DI water:H₂O₂:H₃PO₄:CH₃COOH in an ultrasonic bath and deionized water rinsing (Treatment 3). 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. Prior to starting the coating procedure, all platelets were

ultrasonically washed with ethanol to remove any superficial impurities caused by manipulation.

2.2. Coating of micro-channel platelets

CeO₂ support was prepared by precipitation of ammonia cerium nitrate with urea in an aqueous solution. First, 6 g of (NH₄)₂Ce(NO₃)₆ and 20 g of urea were dissolved into 200 mL deionized water and the mixture was heated gradually to 90 °C under stirring and kept at this temperature for 5 h. After filtration and thorough washing with water, the precipitate was dried at 100 °C for 12 h, and then calcined at 400 °C for 5 h in air. Ir/CeO₂ catalyst with an Ir nominal loading of 2 wt.% was prepared by a deposition-precipitation method. CeO₂ powders were suspended in aqueous solution containing appropriate amounts of Ir precursor (H₂IrCl₆·6H₂O), and the mixture was heated to 75 °C under stirring. A 0.1 M Na₂CO₃ aqueous solution was gradually added until the pH value of the mixture reached 9, followed by further aging at 75 °C for 1 h during which the precipitate was exclusively deposited on the ceria surface. After filtration and washing with water, the solid obtained was dried at 100 °C overnight and finally calcined at 400 °C for 5 h in air.

To prepare the slurry before coating, Ir/CeO₂ powder was initially milled down to particle size <5 μm using a wet ball-milling method. According to a procedure previously described [32], the powder (2 g) 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 prepared slurry was then 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 for 5 h. Before reaction, two platelets were assembled in the reactor housings. Then the reactors were closed, tested for leaks tightness, eventually tightened until being leak-free.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-RB diffractor with Cu Kα radiation source operated at 40 kV and 100 mA. The mean crystallite sizes of catalysts before and after reaction were calculated using Scherrer equation [33].

TEM images were obtained using a Philips Tecnai G220 transmission electron microscope. Specimens were prepared by ultrasonically suspending the sample in ethanol. A drop of the suspension was deposited onto a thin carbon film supported on a standard copper grid and dried in air.

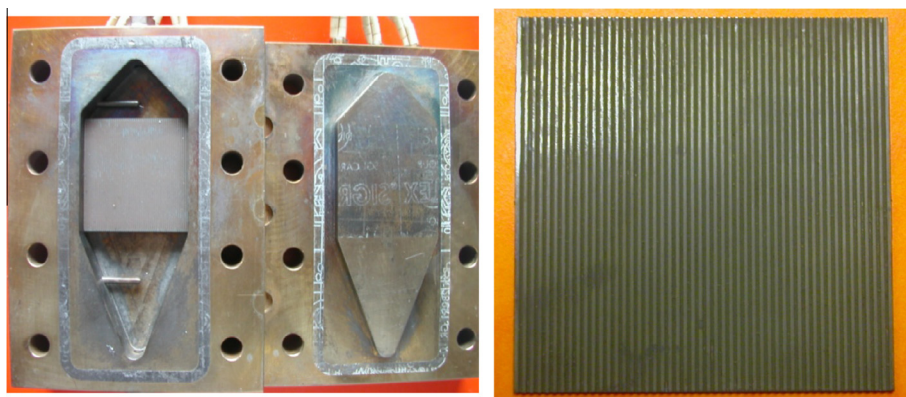


Fig. 1. Photographs of the micro-reactor (left), one coated platelet (right).

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