



# Dynamic modeling of a three-stage low-temperature ethanol reformer for fuel cell application

Vanesa M. García<sup>a,\*</sup>, Eduardo López<sup>b</sup>, Maria Serra<sup>a</sup>, Jordi Llorca<sup>b</sup>

<sup>a</sup> Institut de Robòtica i Informàtica Industrial (CSIC-UPC), Llorens i Artigas 4-6, 08028 Barcelona, Spain

<sup>b</sup> Institut de Tècniques Energètiques, Universitat Politècnica de Catalunya, Diagonal 647, ed. ETSEIB, 08028 Barcelona, Spain

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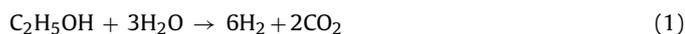
## ABSTRACT

A low-temperature ethanol reformer based on a cobalt catalyst for the production of hydrogen has been designed aiming the feed of a fuel cell for an autonomous low-scale power production unit. The reformer comprises three stages: ethanol dehydrogenation to acetaldehyde and hydrogen over SnO<sub>2</sub> followed by acetaldehyde steam reforming over Co(Fe)/ZnO catalyst and water gas shift reaction. Kinetic data have been obtained under different experimental conditions and a dynamic model has been developed for a tubular reformer loaded with catalytic monoliths for the production of the hydrogen required to feed a 1 kW PEMFC.

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## 1. Introduction

Fuel cells are attractive power sources largely because they can achieve efficiencies much greater than conventional engines. However, among the most daunting challenges limiting the implementation of fuel cells is the development of a sustainable source of hydrogen. Ethanol is a promising source of hydrogen as it is a renewable source when obtained from biomass, and hence, catalytic steam reforming of ethanol to produce hydrogen for fuel cells is acquiring increasing interest (Eq. (1)). The reaction has been extensively studied over catalysts based on Ni, Ni/Cu, Co, and noble metals (Pd, Pt, Rh and Ru) [1,2]. The reaction is highly endothermic  $\Delta H_{298}^{\circ} = 347.4 \text{ kJ mol}^{-1}$ , which accounts for the requirement of reforming temperatures usually above 873 K. At such high temperatures ethanol is mainly reformed into a mixture of H<sub>2</sub> and CO (Eq. (2)), and it is necessary to pass the reformate through a water gas shift reactor in order to generate further hydrogen and eliminate CO (Eq. (3)), which is a strong fuel cell poison. However, cobalt-based catalysts are particularly effective for ethanol steam reforming at lower temperature, 623–673 K [3–6], where the water gas shift reaction is also operative. For this reason, increasing attention is being focused on developing low-temperature catalytic processes with cobalt catalysts.



Among different supported cobalt catalysts already tested for low-temperature ethanol steam reforming, the best performance in terms of hydrogen generation, CO<sub>2</sub>/CO ratio, and long-term stability is ZnO-supported cobalt [3]. At 673 K, 5.3–5.4 mol H<sub>2</sub> per mol of reacted ethanol is obtained and almost no CO is present in the reformate when a bioethanol-like mixture (C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O~13 mol) is reacted at 5000 h<sup>-1</sup> [4]. The main undesired product obtained over Co/ZnO is methane (<3% on a dry basis). Methane may be formed during ethanol steam reforming by ethanol decomposition (Eq. (4)) or methanation of CO or CO<sub>2</sub> (Eq. (5)):



Methanation is a very costly side reaction for the production of hydrogen because it consumes between 3 and 4 mol of hydrogen for each mol of methane formed. In addition, the reaction is thermodynamically favored at low temperature. Following a survey addressed to improve the catalytic performance of the Co/ZnO system for real ethanol steam reforming application, it has been recently reported that the addition of iron has a positive effect in decreasing methane formation [7]. Under the same experimental conditions tested for Co/ZnO, a Co(Fe)/ZnO catalyst with a molar ratio of Co:Fe~10:1 yields up to 30 times less methane. The enrichment in iron that occurs on the surface of cobalt particles in Co(Fe)/ZnO as determined by X-ray photoelectron spectroscopy [7]

\* Corresponding author. Tel.: +34 93 401 57 89.

E-mail address: [vgarcia@iri.upc.edu](mailto:vgarcia@iri.upc.edu) (V.M. García).