

Steam reforming of ethanol at moderate temperature: Multifactorial design analysis of Ni/La₂O₃-Al₂O₃, and Fe- and Mn-promoted Co/ZnO catalysts[☆]

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Abstract

Novel Co (10%) catalysts supported on ZnO and promoted with Fe and Mn (1%) were synthesized and characterized by high-resolution transmission electron microscopy (HRTEM), electron energy-loss spectroscopy (EELS), X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS). Their catalytic activity for steam reforming of ethanol was compared with that of Ni catalysts supported on La₂O₃-Al₂O₃. Experiments at 400 and 500 °C, steam to carbon ratios of 2 and 4, and a wide interval of contact time were analyzed following a multifactorial experimental design. At 500 °C and a steam to carbon molar ratio of 4, complete conversion of ethanol was achieved above a contact time of 200 g min mol⁻¹ for all catalysts. The ratio of selectivity between hydrogen and methane was around 23 mol_{H₂}/mol_{CH₄} in the Co catalysts, while it approached the thermodynamic equilibrium (5.7 mol_{H₂}/mol_{CH₄}) in the Ni catalysts. The Co catalysts do not promote methane-forming reactions like ethanol cracking and acetaldehyde decarbonylation, nor do they facilitate the reverse methane steam reforming reaction. The catalytic behavior of cobalt is enhanced by promotion with iron or manganese through the formation of bimetallic particles, which facilitates cobalt reducibility. This suggests that Co-Mn/ZnO and Co-Fe/ZnO catalysts have a good potential for their use for ethanol reforming at moderate temperature. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Developed societies face a critical need for higher efficiency in the production and consumption of energy, which is driven by the strain that the continuous rise in the demand and cost of fossil fuels is causing on the global economy, by the vulnerability and limitedness of oil and gas supplies in a mid-term future, and by global warming and environmental concerns [1–3]. In this context, fuel cells are envisaged to play a significant role as efficient devices to produce electric power, thus contributing to supply what current transformation technologies and fossil fuels alone will not be able to satisfy at an acceptable cost in the mid-term future [1,4], a context in which renewables are called to contribute significantly as a source of primary energy as well. Low

temperature fuel cells (FC) are suitable for producing electrical power in portable devices, automobiles, and small and medium stationary power plants. Among the low temperature fuel cells, polymer electrolyte membrane fuel cells (PEMFC) have the highest efficiency, reliability, favorable power-to-weight ratio, and a fast start-up time [1,5]. The PEMFC uses hydrogen as fuel, its main drawback being the sensibility towards carbon monoxide. Current electrodes in the PEMFC require hydrogen with less than 10 ppm of carbon monoxide [1,6,7]. Therefore, the use of PEMFC needs of a dependable, efficient and flexible hydrogen supply that has to rely on stand-alone processes for the production of hydrogen (fuel processors) [8], preferably directly coupled to the PEMFC unit. Current concepts for fuel processors are based either on steam reforming (SR) or partial oxidation reforming (POXR) and they can use natural gas, LPG or oxygenated fuels. Alcohols are especially appealing as primary fuels for fuel processors because they can be obtained from renewable biomass: methanol through gasification and synthesis, and ethanol through fermentation. Ethanol is easier and

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