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The role of surface reactions on the active and selective catalyst design for bioethanol steam reforming

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ABSTRACT

In order to study the role of surface reactions involved in bioethanol steam reforming mechanism, a very active and selective catalyst for hydrogen production was analysed. The highest activity was obtained at 700 °C, temperature at which the catalyst achieved an ethanol conversion of 100% and a selectivity to hydrogen close to 70%. It also exhibited a very high hydrogen production efficiency, higher than 4.5 mol H_2 per mol of EtOH fed. The catalyst was operated at a steam to carbon ratio (S/C) of 4.8, at 700 °C and atmospheric pressure. No by-products, such as ethylene or acetaldehyde were observed. In order to consider a further application in an ethanol processor, a long-term stability test was performed under the conditions previously reported. After 750 h, the catalyst still exhibited a high stability and selectivity to hydrogen production. Based on the intermediate products detected by temperature programmed desorption and reaction (TPD and TPR) experiments, a reaction pathway was proposed. Firstly, the adsorbed ethanol is dehydrogenated to acetaldehyde producing hydrogen. Secondly, the adsorbed acetaldehyde is transformed into acetone *via* acetic acid formation. Finally, acetone is reformed to produce hydrogen and carbon dioxide, which were the final reaction products. The promotion of such reaction sequence is the key to develop an active, selective and stable catalyst, which is the technical barrier for hydrogen production by ethanol reforming.

1. Introduction

Hydrogen is a clean and free carbon energy vector that can be used directly in thermal combustion engines or converted into electrical energy using fuel cells. Nowadays, most of hydrogen is obtained from fossil fuels by reforming processes.

Natural gas or methane represents the main option for hydrogen production from fossil fuels, whose energetic efficiency is three times higher than water electrolysis when the electricity used to support the endothermic reforming process is obtained from fossil fuels [1,2]. At the moment, there are many papers published in literature concerning gasoline, diesel or jet propulsion fuel reforming, specially oriented to on-board applications [3]. From this standpoint, reforming of conventional fuels may represent an option to facilitate the transition to hydrogen economy by using the actual logistic infrastructure. Given that hydrogen is obtained from fossil fuels, what does not avoid the emission of greenhouse gases, is not possible to consider it as 'green hydrogen'. In order to avoid such emissions, the use of biomass or bio-fuels for hydrogen production may represent a very good option to partially satisfy the demand of energy. Using bioethanol for hydrogen production could be an attractive alternative to minimize negative environmental concerns and to decentralise the actual fuel market, in which few countries or geographical areas control Global Development and Economy [4,5]. Ethanol advantages as a fuel come from the fact that it can be used in internal combustion engines or transformed into hydrogen for fuel cells operation, using the actual logistic system.

On one hand, growing crops for bio-fuels is being criticized because of its direct competition for land and food production. On the other hand, the European Commission determined in 2006, that the influence of bio-fuels on corn prices was marginal and represented a 3–6% of corn price [6]. Muller et al. [7] reported that even with an expanding world population, globally there is still enough land and water to grow a substantial amount of biomass for both, food and bio-energy production.

Taking into consideration scientific aspects, many papers have been published in recent years for hydrogen production from ethanol reforming. Initial articles based on thermodynamic studies, which determined the experimental conditions to maximize

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