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Simultaneous production of hydrogen and carbon nanostructured materials from ethanol over $LaNiO_3$ and $LaFeO_3$ perovskites as catalyst precursors

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ABSTRACT

The simultaneous production of hydrogen and carbon materials from ethanol was studied using the perovskites $LaNiO_3$ and $LaFeO_3$ as catalyst precursors. The reaction was performed at temperatures between 700 °C and 900 °C with ethanol concentration of 50 vol%. Using $LaNiO_3$, the yield of carbon materials is maximum at low temperature due to the presence of dense carbon like nanofibers while at higher temperatures, multiwalled carbon nanotubes are produced. A reaction temperature of 900 °C is necessary to obtain hydrogen and carbon materials with $LaFeO_3$. The hydrogen yield reaches 16.2 L per hour and per gram of catalyst, hydrogen representing 70% in volume of the products in gas phase while methane is only 3.6%. We show that the perovskite $LaFeO_3$ is reduced in situ under ethanol leading to the formation of Fe^0 and Fe_3C responsible for the carbon growth. A scheme is proposed for the growth of carbon material from the species obtained by $LaFeO_3$ reduction. The morphology of carbon materials depends on the nature of the catalyst, MWCNTs are produced from $LaNiO_3$ as catalyst precursor while twisted nanofibers are obtained from $LaFeO_3$ at 900 °C.

1. Introduction

Energy sources environmentally friendly have received much attention in recent years as alternatives to fossil resources [1]. Biomass represents a big reservoir of available carbon still little used for energy applications – except for the heat produced from wood combustion.

Among the biomass feedstock issued from biomass, ethanol is a particular interesting source of carbon due to its low toxicity, low production cost and the possibility of production in large amount by first and second generation processes [2].

Ethanol produced from biomass, often referred in the scientific literature as “bio-ethanol”, can be used as additive in gasoline but it cannot be incorporated directly in diesel fuels due to a low cetane number and a poor miscibility with diesel blends. In order to valorize ethanol differently, many researchers developed steam reforming of ethanol, which is a process for hydrogen production from renewable resources instead of the fossil gas: methane (natural gas) [3,4].

Maruyama et al. [5] reported first, the use of ethanol as carbon source for CNTs production by chemical vapor deposition (CVD). The particular interest in carbon nanotubes results from their outstanding mechanical, thermal and optical properties leading to many potential applications. The quality of carbon nanostructured materials can be correlated with electronic properties, a nanoscale circuits can be produced by the direct growth of single-walled carbon nanotubes (SWNTs) on substrates [6]. It has been reported that almost any Fe containing compound can be used to produce forest SWCNT when the catalyst is supported on AlOx [7]. Most of the studies have focused on the quality of nanotubes, consequently drastic experimental conditions were used such as low pressure [5] or in the presence of hydrogen in feed gas [8]. However, multi-walled carbon nanotubes (MWCNTs) and carbon nanofibers (CNFs) possess also interesting properties and can be produced with higher yields than SWCNTs by CVD methods.

The interest of a simultaneous production of CNTs and hydrogen from ethanol was reported by Wang and co-workers [9]. The catalyst used was Fe/Al_2O_3, the maximum yield of CNTs obtained at 800 °C was 1.41 g per gram of catalyst after 40 min, while the hydrogen production reaches 80%.

In a previous study [10] we showed that the perovskite $LaNiO_3$ was an interesting catalyst precursor to produce simultaneously hydrogen and MWCNTs in high yields from ethanol. The perovskite structure allows to obtain, after a reduction step, good dispersion of nano-sized metal particles at the surface of the support, which is one of the key factors for the growth of carbon nanotube. The use of

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