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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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perovskites as oxide precursors for CNTs synthesis has already been investigated with different carbon sources such as La_2NiO_4 with CO [11,12], $LaCoO_3$ with ethylene and methane [13]. Substituted iron based perovskite: $LaCu_{1-x}Ni_xO_3$ [14] and $LaFe_xMo_yMnO_3$ [15] were used for the synthesis of multi-walled carbon nanotubes from methane between 900 °C and 1100 °C at short contact time.

It is known that the reduction of iron in a perovskite structure is not easy and requires high temperature and/or pressure under hydrogen to obtain metallic iron [16]. However, Liu et al. [17] showed that the unsubstituted iron perovskite: $LaFeO_3$ was active for the synthesis of single-walled carbon nanotubes, at 1010 °C from methane in mixture with hydrogen.

In the present work, we have investigated the use of the perovskite $LaFeO_3$ as catalyst precursor for the simultaneous production of carbon materials and hydrogen from ethanol as carbon source. The target was to obtain maximum yields, this is the reason why a quite high amount of the carbonaceous reactant (ethanol: 50 vol%) was introduced in the reactor without adding hydrogen known to avoid the formation of not well organized carbon materials. The results were compared with those obtained with the $LaNiO_3$ perovskite.

2. Experimental

2.1. Catalyst preparation

The perovskites $LaNiO_3$ and $LaFeO_3$ were prepared by the self combustion method. Glycine ($H_2NCH_2CO_2H$) used as ignition promoter was added to an aqueous solution of metal nitrates with the appropriate stoichiometry in order to get a $NO_3{}^-/NH_2 = 1$ ratio. The resulting solution was slowly evaporated until a glassy green gel was obtained. The gel was heated up to around 250 °C, temperature at which the ignition reaction occurs producing a powdered precursor which still contains carbon residues. Calcination at 700 °C for 8 hours eliminates all of the remaining carbon and leads to the formation of the perovskite structure.

2.2. Catalyst characterization

High resolution transmission electron microscopy (HRTEM) was carried out using a JEOL 2100 UHR instrument with a LaB_6 filament, at 200 kV accelerating voltage. HRTEM images of deposited carbon were taken after acid treatment of the sample. The sample was crushed and dispersed in isopropanol. A drop of this solution was deposited on a Cu grid for TEM observations.

The catalysts were characterized by X-ray diffraction (XRD) using a Siemens D-5005 diffractometer with Cu $K\alpha = 1.5417$ Å, operated at 40 kV and 30 mA. The diffraction patterns were recorded in the 2θ range of 10–90° with a step interval of 0.02° and period of 1 s.

Temperature programmed reduction (TPR) analysis was carried out with a Micromeritics Autochem 2910 analyzer using approximately 100 mg of catalyst. The experiments were performed using a $5\%H_2/Ar$ flow and the temperature was raised at 5 °C min^{-1} from room temperature to 900 °C.

Raman spectra of carbon nanotubes were obtained using a HORIVA Jabin Yvon Raman U-1000 equipment with a microscopy BX 40. Patterns were recorded at a wavelength of 514.5 nm from 10 cm^{-1} to 4000 cm^{-1} with a step size of 1.5 cm^{-1} and 20 s per step. In order to acquire statistically meaningful data, between 10 and 15 spectra were recorded for each sample.

2.3. Catalytic activity

The reaction was carried out in a horizontal reactor (22 mm internal diameter) in order to avoid sub-pressure during the formation of CNT. About 50 mg of the catalyst was placed directly into the reactor and pre-reduced with pure hydrogen (99.999%) at a flow rate of 30 mL min^{-1}, at 700 or 900 °C for 1 h. The reduced catalyst was then purged during 30 min under helium flow (99.999%) at a flow rate of 30 mL min^{-1}. The temperature of the reactor was then adjusted at the desired value (700 or 900 °C). About 0.04 mL min^{-1} of absolute ethanol (99.5%) was fed to an evaporator with the help of an HPLC pump. Ethanol was heated at 100 °C in order to evaporate it before becoming in contact with the catalyst. The ethanol vapor was transported into the reactor using nitrogen (99.999%) as carrier gas (50%, v/v). The decomposition reactions were performed at 700, 800 and 900 °C during 4 h.

Table 1
Specific surface areas (m^2/g), elemental composition (%) in parenthesis: theoretical value.

Catalyst	S_{BET} (m^2/g)	La%	Fe%	Ni%
$LaNiO_3$	7.5	53.6 (56.5)	–	22.6 (23.9)
$LaFeO_3$	12.7	55.6 (57.2)	22.8 (23.0)	–

The amount of carbon produced was determined by weighting the solid compounds present after 4 h of reaction, the amount of carbon produced corresponding to the difference between the total mass of solid after reaction and the mass of catalyst used.

All the experiments were performed twice with a good accuracy of the results within an error of 5%.

3. Results and discussion

3.1. Characterization of the catalysts before reaction

The composition of the perovskites determined by ICP-OES are reported in Table 1. The amount of lanthanum and nickel or iron in the materials is close to the theoretical values. The BET surface areas are low: 7.5 and 12.7 m^2 g^{-1} respectively for $LaNiO_3$ and $LaFeO_3$.

The TPR profiles for $LaNiO_3$ and $LaFeO_3$ are reported in Fig. 1. $LaNiO_3$ presents three reduction peaks attributed to the formation of intermediate phases: $La_4Ni_3O_{10}$ and La_2NiO_4 before a complete reduction into metallic nickel and lanthanum oxide at 700 °C [18]. The perovskite $LaFeO_3$ is much more difficult to reduce as shown by Provendier et al. [19]. A very small and large reduction peak appears between 400 and 500 °C attributed to the reduction of iron from Fe^{4+} to Fe^{3+} as reported by P. Ciambelli et al. [20]. The peak at 900 °C corresponds to the reduction of part of Fe^{3+} to Fe^0.

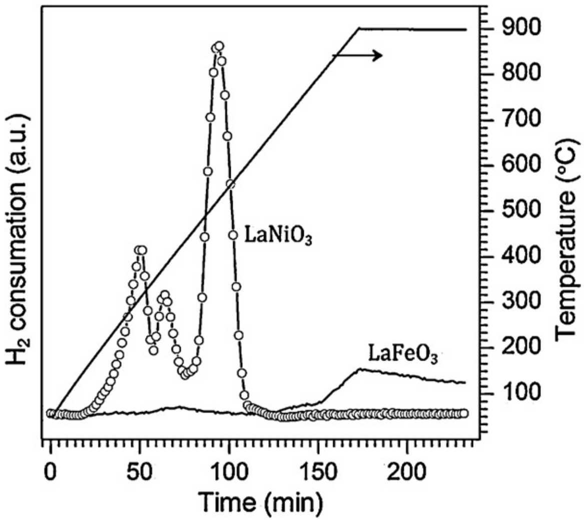

Fig. 1. Temperature-programmed reduction obtained over $LaNiO_3$ and $LaFeO_3$.