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# Decomposition of ethanol over $Ni/Al_2O_3$ catalysts to produce hydrogen and carbon nanostructured materials

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ABSTRACT

γ-Alumina-supported 10, 20 and 33 wt.% nickel catalysts were prepared and used to investigate the decomposition of ethanol to hydrogen and carbon materials at 500 and 700 °C. It was verified that the ethanol conversion was complete for all nickel loadings at 500 and 700 °C. A low nickel loading (10 and 20%) favored the formation of the very stable spinel phase $NiAl_2O_4$, which has low activity in the production of solid carbon. The maximum hydrogen and carbon production was obtained using a nickel loading of 33%: more than 6 g of solid carbon per gram of catalyst ($gC/g_{cat}$) was produced at 700 °C and 22.2 $gC/g_{cat}$ when the reaction was performed at 500 °C. At 500 °C, nanofibers were mainly formed, while at 700 °C the production of multiwalled nanotubes was favored. The selectivity in terms of the gaseous products was dependent on the nickel loading and temperature used. At high temperature the partial thermal decomposition of ethanol was favored leading, mainly, to the production of hydrogen, methane, and carbon monoxide. At 500 °C, there was the production of ethylene on the $Al_2O_3$ surface with low nickel loading. With high nickel loading (33%) ethanol decomposition to hydrogen and nanostructured carbon was favored

## 1. Introduction

Hydrogen production is of great industrial interest since hydrogen is considered to be an ideal fuel for fuel cells. Hydrogen is mainly produced by steam reforming of natural gas and more recently also by decomposition of methane. The latter has the advantage of generating carbon nanostructured materials (carbon nanofibers and nanotubes) [1–3].

Carbon nanotubes (CNTs) and carbon nanofibres (CNFs) offer many extraordinary physical and chemical properties, for instance, they can be used as supports for metal catalysts [4] and to strengthen composite materials [5]. CNTs can be produced by three technologies: carbon-arc discharge, laser-ablation and catalytic decomposition processes. The latter method has been reported to be the most selective toward carbon nanotube formation; arc discharge and laser-ablation leading to mixtures of carbon materials. Transition metals, such as nickel, iron and cobalt, are the most commonly used catalysts for the growth of filamentous carbon [6–8]. The source of carbon is hydrocarbons, mainly methane, from natural gas.

In order to make the processes more environmental friendly the use of ethanol, easily produced from biomass, has been developed to produce hydrogen by steam reforming [9,10]. The use of ethanol as a carbon source for the synthesis of CNTs was first reported by Maruyama et al. [11].

More recently, Li et al. [12,13] have reported an interest in using ethanol to produce hydrogen and CNTs simultaneously. The authors showed that $Fe/Al_2O_3$ and Co/C catalysts were quite active in the production of CNTs and hydrogen.

Wang et al. [14] studied the catalytic performance of $Ni/Al_2O_3$ catalyst prepared by a hydrothermal method for the decomposition of ethanol to produce hydrogen and CNTs. The authors focused on the effect of Ni loadings and reaction temperature on the production of $H_2$ and CNTs. They showed that the hydrogen production increased with increasing temperature (from 500 to 800 °C) while the quantity and quality of nanotubes decreased due to the sintering of Ni particles.

In this study we propose an extensive investigation of the catalytic decomposition of ethanol using $Ni/Al_2O_3$ catalyst prepared by a wet impregnation method. We focus on the composition of the gas phase in order to determine what are the main reactions involved in the process at two different temperatures: 500 and 700 °C. The effect of nickel loading and calcinations temperature were investigated. The influence of the catalyst composition on the simultaneous production of hydrogen and MWCNTs is discussed.

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## 2. Experimental part

### 2.1. Catalyst preparation

Ni catalysts were prepared by the wet impregnation method, using nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] (Sigma–Aldrich) as the metal precursor. Known amounts of the nickel salt (to obtain a metal content of 10, 20, and 30%) were dissolved in water and commercial aluminum oxide [$\gamma$-$Al_2O_3$] (AL-3996R, Engelhard Exceptional Technologies) was added under continuous stirring. The slurries thus obtained were heated slowly to 90 °C and maintained at that temperature until nearly all the water had evaporated. The solid residues were dried at 100 °C for 24 h and then calcined in air at 700 °C for 5 h. The catalyst with 30 wt.% of nickel was calcined at 300, 500 and 700 °C, for 5 h.

### 2.2. Characterization of catalyst and reaction products

Catalyst samples were characterized using $N_2$ physisorption isotherms (Micromeritics TriStar - Surface and Porosity Analyzer). Specific surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method. Prior to the measurements, the samples were outgassed at 350 °C for 8 h.

Nickel loading was measured using a Perkin Elmer (Optima 2000 DV) inductively coupled plasma-optical emission spectrometer (ICP-OES) after the catalyst calcinations.

The catalysts were characterized by X-Ray Diffraction (XRD) using a Siemens D-5005 diffractometer with CuK$\alpha$ = 1.5417 Å, operated at 40 kV and 30 mA. The diffraction patterns were recorded in the $2\theta$ 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. These 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 and maintained at this temperature for 30 min.

Transmission Electron Microscopy (TEM) images were obtained on a Philips CM120 instrument equipped with a $LaB_6$ filament. The sample was deposited on a Cu grid for observation by TEM. The diameters of carbon nanotubes were evaluated from about 20 images and 100 measurements.

Thermogravimetric analysis (TGA) was carried out with a SDT 2960 thermobalance TA Instruments analyzer in Pt crucibles to determine the stability of the carbon formed. The measurement of several samples was performed under an airflow of 100 cm$^3$ h$^{-1}$ on heating from room temperature to approximately 700 °C with a heating rate of 5 °C min$^{-1}$.

Raman spectra (Stokes spectra) were obtained at room temperature, using an HR UV 800 confocal scanning spectrometer (Horiba Jobin Yvon) equipped with a Peltier-cooled charge-coupled device (1152 × 298 pixels) for detection. The Raman scattering was excited using a 632.81 nm excitation wavelength supplied by an internal He–Ne laser through an Olympus high-stability BXFM confocal microscope. Patterns were recorded in the 50–1000 cm$^{-1}$ Raman shift range with a spectral resolution of 0.5 cm$^{-1}$. LabSPEC v. 5 software was used for data acquisition and processing.

### 2.3. Catalytic reaction

Catalytic decomposition of ethanol was carried out at atmospheric pressure, in a horizontal fixed-bed reactor at a temperature of either 500 or 700 °C. Prior to this step, the catalyst was reduced *in situ* using a 15% $H_2/N_2$ flow at 700 °C for 30 min. Ethanol was pumped into a tubular furnace (0.04 mL min$^{-1}$) and vaporized. The gaseous ethanol was then mixed with nitrogen (volumetric mixture ratio of ethanol/nitrogen = 1/1). A total flow rate of 40 mL min$^{-1}$ was then fed to the reactor containing 100 mg of the catalyst. Effluents released by the reactor were analyzed using a gas chromatograph (Perkin-Elmer) equipped with a Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD). Separations were performed using a carboxen 1000 column for CO and $CO_2$, a Poraplot Q column for $CH_4$, $C_2H_6$ and $C_2H_4$, and a molecular sieve 5A column for $H_2$. Reaction data were recorded for 4 h. Catalyst activity was evaluated in terms of ethanol conversion. We defined ethanol conversion as:

**Table 1**
Catalyst active phase loading and specific surface area before and after calcination at 700 °C.

| Catalysts | Ni (wt.%) ICP-OES | $S_{BET}$ (m$^2$ g$^{-1}$) | |
|---|---|---|---|
| | | Before reduction | After reduction |
| 10 wt.% $Ni/Al_2O_3$ | 9.8 | 162 | 156 |
| 20 wt.% $Ni/Al_2O_3$ | 20.4 | 104 | 102 |
| 30 wt.% $Ni/Al_2O_3$ | 33.3 | 116 | 100 |

$$\text{Ethanol conversion}(\%) = \frac{\text{mol ethanol in} - \text{mol ethanol out}}{\text{mol ethanol out}} \times 100$$

The molar concentration of products was calculated using a standard mixture. The calculation is expressed as follows:

$$\text{Molar concentration of products}(\%) = \frac{ni}{n\ \text{total}} \times 100$$

where $ni$ is the moles of $i$ gas product ($H_2$, $CH_4$, CO, $CO_2$, $C_2H_4$, $C_2H_6$), $n$ total is the total moles of gas ($N_2$, $H_2$, $CH_4$, CO, $CO_2$, $C_2H_4$, $C_2H_6$).

## 3. Results and discussion

### 3.1. Characterization of the catalyst before reaction: nickel loading and influence of the calcination temperature

The nickel loadings of the catalysts as determined by ICP-OES are reported in Table 1. It can be observed that the amount of nickel for the catalysts with 10 and 20 wt.% is close to the target value, while the third catalyst is composed of 33% nickel. To simplify the notation the samples were designated as 10NiAL, 20NiAl and 33NiAl.

The specific surface areas of the catalysts calcined at 700 °C are also indicated in Table 1, and the values exceeded 100 m$^2$ g$^{-1}$ for all nickel loadings.

With the aim of identifying the phases present in the catalytic samples, X-ray diffraction and TPR analysis were carried out. After the drying step, samples of the catalyst 33NiAl were calcined at 300, 500 and 700 °C under air for 5 h. Fig. 1 shows the XRD profiles. Broad peaks indicate that the $Al_2O_3$ phase is weakly crystallized. In the presence of nickel, as the calcination temperature increases the formation of the spinel $NiAl_2O_4$ occurs. It is difficult to identify precisely the diffraction lines of $NiAl_2O_4$ due to overlap with those of the $\gamma$-$Al_2O_3$ phase and some diffraction lines of NiO. Nevertheless, the presence of $NiAl_2O_4$ when the calcination temperature exceeds 500 °C is well documented in the literature [15]. The presence of NiO can be evidenced by the diffraction peak at $2\theta = 63°$ corresponding to the NiO (2 2 0) plane. When the calcination temperature increases the peaks become more intense and narrower, indicating an increase in the average NiO crystallite size [16].

Fig. 2 shows the XRD patterns obtained for the 10NiAl, 20NiAl and 33NiAl samples after calcination at 700 °C. Broad peaks were obtained with lower nickel loadings (10 and 20%) and the peaks were narrower for the highest nickel loading indicating the presence of larger NiO crystallites.