

## Glass-Ceramics Foam for Hydrogen Production

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Glass-ceramic foams belonging to the LZSA ( $\text{Li}_2\text{O}-\text{ZrO}_2-\text{SiO}_2-\text{Al}_2\text{O}_3$ ) system were processed as catalytic supports for the ethanol decomposition. The active phases of the support (Ni, Co) were prepared by wet impregnation. The impregnated supports were dried, calcined and reduced under a  $\text{H}_2$  flow at 700 °C for 120 min. The catalytic activity tests were performed at 550 °C for 120 min in a tubular fixed bed reactor at atmospheric pressure, with flow rate of liquid ethanol and gaseous nitrogen of 0.08 mL/min and 33.5 mL/min, respectively. The materials were characterized in terms of their physical, morphological and microstructural, thermal and mechanical properties. The results showed that the supported nickel catalysts presented a higher conversion of ethanol to form hydrogen.

### 1. Introduction

Ethanol is becoming attractive for hydrogen production due to increasing search for new sources of low-polluting energy obtained from renewable resources, reducing the share of oil in the energetic matrix and increasing the use of this gas as a “clean” fuel. Such motivation is related mainly to concerns about environmental issues and the reduction of deposits of fossil energy sources (Palma et al., 2012). The improvement of production techniques, storage and transportation of hydrogen, in recent years, has aroused interest in the automotive industry for this application in fuel cells. The electricity generated by an electrochemical cell can be applied in both mobile sources and in stationary sources, due to its high efficiency and energetic flexibility (Fierro et al., 2005). Among the processes for generating hydrogen from ethanol stand out the ethanol steam reforming, partial oxidation, oxidative steam reforming and ethanol decomposition (Palma et al., 2012). The use of catalytic metals (Ni and Co) supported on various oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ ,  $\text{ZrO}_2$  and  $\text{MgO}$ ) has been tested in the reactions of decomposition of ethanol to produce hydrogen and carbon nanotubes (Mezalira et al., 2011). In this work, a composition of the LZSA ( $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{ZrO}_2$ ) system was chosen to produce glass-ceramic foams by gelcasting (Pozzobom et al., 2014). The addition of foaming agent and polymerization in situ of monomers added previously to the ceramic suspension allowed the production of highly porous structures (> 90 %), which were used as catalytic supports in the decomposition of ethanol using Ni and Co as active phases.

### 2. Materials and methods

Glass-ceramic foams of the LZSA system (9.53 %  $\text{Li}_2\text{O}$ ,  $\text{ZrO}_2$  13.37 %, 62.96 %  $\text{SiO}_2$ , 14.14 %  $\text{Al}_2\text{O}_3$ ,  $d_{50} = 3.8$   $\mu\text{m}$  and density of 2.63  $\text{g}/\text{cm}^3$ ) with different concentrations (0.2 to 1.0 %) of a foaming agent (30 EG Alkolan CP), were fired at 750 °C for 30 min. Details on the processing of the produced foams can be obtained in POZZOBOM et al. (2014). The geometric density ( $\rho_{\text{geo}}$ ) was calculated from the dimensions and mass of the samples. The true density of the vitreous powder ( $\rho_t$ ) was determined by gas (He) pycnometry (Multi-Pycnometer, MVP-4DC). The void fraction (porosity ( $\epsilon$ )) was determined by considering the relation between

the densities, that is,  $[1 (\rho_{\text{geo}}/\rho_t)]$ . The specific surface area of the glass-ceramic foams was determined by the BET method (NOVA 1200e, Quantachrome Instruments). The mechanical strength of the foams was determined by averaging five cylindrical samples, with nominal diameters of 12 mm, using a universal testing machine (EMIC DL 2000), with loading speed of 0.5 mm/min. In the evaluation of the glass-ceramic foams as catalytic supports, Ni and Co were used as active phases. A known amount of the salts of nickel nitrate and cobalt nitrate hexahydrated were dissolved in water to obtain the desired percentage of metal masses (10 %). The solution was added to the catalytic support and then stirred and heated (around 90 °C) until all water was removed. The impregnated support was dried at 100 °C for 24 h and calcined in air at 700 °C for 5 h. The catalytic decomposition tests for ethanol were carried out in gas phase under atmospheric pressure in a quartz tubular reactor with fixed bed and continuous flow and inserted into a vertical furnace. The calcined supports (0.5 g) were placed in the reactor and activated (reduced) in the own catalytic bed under a flow of 25 mL/min of hydrogen at 700 °C for 120 min, with a heating rate of 10 °C/min. The reactions were carried at 550 °C for 120 min with a flow rate of 0.08 mL/min liquid ethanol (absolute ethyl alcohol 99.5 %) introduced into the reactor via a peristaltic pump (Gilson - Minipuls 3) and 33.5 mL/min of nitrogen gas used as carrier gas. The ethanol conversion was calculated using Eq(1).

$$\text{Ethanol conversion(\%)} = \frac{v \text{ ethanol in} - v \text{ ethanol out}}{v \text{ ethanol in}} \times 100 \quad (1)$$

The amount of carbonaceous material deposited for 2 h reaction on the catalyst surface was calculated in accordance with Eq(2).

$$C_{\text{produced}} \left( \frac{\text{g}}{\text{gcat}} \right) = \frac{(m_{\text{Total}} - m_{\text{calcined support}})}{m_{\text{calcined support}}} \quad (2)$$

Where  $m_{\text{Total}}$  is the total mass of calcined support and carbon produced after 2 h of reaction.

To determine the crystalline phases formed in the calcined supports containing NiO and CoO and in the supported catalysts (Ni and Co), powdered samples were analysed using computer assisted X-ray diffractometry, XRD (Philips PW 3710) with CuK $\alpha$  radiation. To identify the crystalline phases in the analysed materials the JCPDS and ICSD data bases were used. The morphology of the catalytic support (glass-ceramic foam) and supported catalysts was analysed by scanning electron microscope, SEM (Philips XL 30). The frequency and average pore diameter were determined using image analysis software (Image J). Metal particles (Co and Ni) were identified by transmission electron microscope, TEM (JEOL, JEM-1011) after the reduction step. The carbonaceous materials produced after the catalytic tests were analysed by TEM and by thermal analysis (TA Instruments, SDT Q600 - Simultaneous TGA-DSC) at a heating rate of 10 °C/min with a flow of synthetic air of 10 cm<sup>3</sup>/min.

### 3. Results and discussion

Table 1 shows the specific surface areas of the glass-ceramic foams produced with different concentrations of foaming agent. It is observed in Table 1 that the surface area of the produced foams for concentrations from 0.2 to 1.0 % of foaming agent, varied in a narrow range (5.4 to 11.7 m<sup>2</sup>/g).

*Table 1: Specific surface area of the produced LZSA glass-ceramic foams with different concentrations of foaming agent (30 EG Alkolan CP)*

Foaming agent (%)	0.2	0.4	0.6	0.8	1.0
Specific surface area (m <sup>2</sup> /g)	5.4	9.5	6.7	7.9	11.7

Figure 1 shows the relationship between porosity and mechanical strength of produced foams in function of the percentage of foaming agent. It is observed in Figure 1, that the mechanical strength decreases as the percentage of foaming agent increases. The porosity is lower for smaller percentages of foaming agent (0.2 %) increasing, however, for higher concentrations of foaming agent and remaining almost constant up to 1 %. Glass-ceramic foams with percentages between the extremes of the used foaming agent (0.2 and 1.0 %) were impregnated (using nickel nitrate and cobalt nitrate hexahydrated), calcined and reduced to be evaluated as catalytic supports in the decomposition reaction of ethanol at 550 °C.

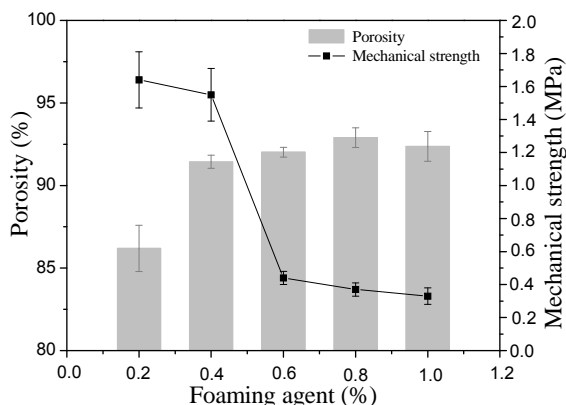


Figure 1: Porosity and mechanical strength of foams fired at 750 °C for 30 min in function of the concentration of foaming agent

Figure 2 shows XRD patterns related to: (a) the LZSA catalytic support fired at 750 °C for 30 min; (b) the LZSA catalytic support produced with 0.2 % foaming agent and impregnated with cobalt salt and calcined at 700°C for 5 h; (c) the supported catalyst containing 10 % Co, after reduction in hydrogen at 700 °C for 2 h; (d) the LZSA catalytic support produced with 0.2 % foaming agent and impregnated with nickel salt and calcined at 700 °C for 5 h; and (e) the supported catalyst containing 10 % Ni, after reduction in hydrogen at 700 °C for 2 h. Figure 2 (a) shows peaks related to the principal crystalline phases formed in the LZSA glass-ceramic, i.e.,  $\beta$ -spodumene (JCPDS 35-0794), zirconium silicate (JCPDS 72-0402) and zirconium oxide (JCPDS 78-0047). In Figure 2 (b), the peak at  $2\theta = 36.5^\circ$  is characteristic of CoO (ICSD 01-074-2392) after the calcination step.

Figure 2 (c) shows a peak at  $2\theta = 44^\circ$  (ICSD 01-089-4308), characteristic of metallic cobalt after the reduction process. In Figure 2 (d), the peaks at  $2\theta = 37^\circ, 43^\circ, 63^\circ$  and  $75^\circ$  are characteristic of NiO (ICSD-01-071-1179) after the calcination step. Figure 2 (e) shows peaks at  $2\theta = 44^\circ, 52^\circ$  and  $76^\circ$ , which are characteristic of metallic nickel after reduction process.

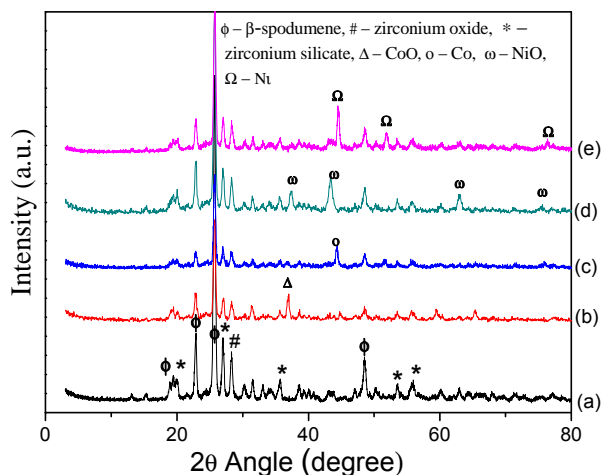


Figure 2: X-ray diffraction patterns related to: (a) the LZSA catalytic support fired at 750 °C/30 min; (b) the LZSA catalytic support produced with 0.2 % foaming agent and impregnated with cobalt salt and calcined at 700 °C/5 h; (c) the supported catalyst containing 10 % Co, after reduction in hydrogen at 700 °C/2 h; (d) the LZSA catalytic support produced with 0.2 % foaming agent and impregnated with nickel salt and calcined at 700 °C/5 h; and (e) the supported catalyst containing 10 % Ni, after reduction in hydrogen at 700 °C/2 h

Figure 3 shows SEM micrographs and graphics showing the average pore size distribution of the catalytic support prepared with 0.2 % foaming agent (Figure 3 (a, b)), the supported catalyst with 10 % Co (Figure 3 (c, d)) and supported catalyst with 10 % Ni (Figure 3 (e, f)). In the micrographs (Figure 3 (a, c, e)), it can be seen structures with pores tending to a spherical geometry, interconnected by windows in the cell walls. With respect to the average pore size distribution of the catalytic support (Figure 3 (b)) and supported catalysts (Ni and Co) as shown in Figure 3 (d, f), it is observed that the variation was from 20 to 400  $\mu\text{m}$  for the catalyst

support, from 20 to 380  $\mu\text{m}$  with the presence of Co and from 20 to 340  $\mu\text{m}$  with the presence of Ni, indicating that there was a slight variation of pore sizes with the presence of catalysts. This variation is a little more evident when the catalyst (Ni and Co) are impregnated which results in increased dimensions of the smaller pores (40 to 60  $\mu\text{m}$ ).

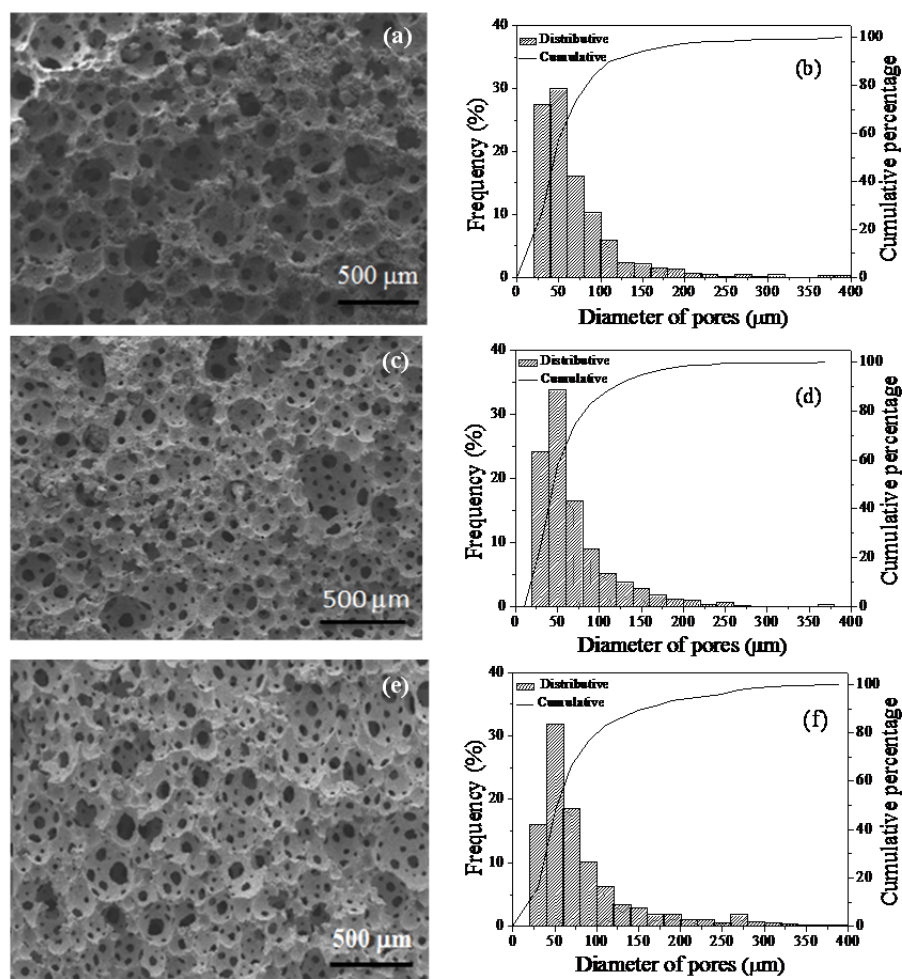


Figure 3: SEM micrographs and average pore size distribution. (a, b): catalytic support prepared with 0.2 % foaming agent, fired at 750 °C for 30 min; (c, d): supported catalysts with 10 % Co; (e, f): supported catalyst with 10 % Ni

Figure 4 shows TEM images of the supported catalysts after the reduction step, in which was possible to identify the presence of Co (Figure 4 (a)) and Ni (Figure 4 (b)) in the supports (darker shades). It can also see in Figure 4 that the metal particles tend to have a spherical geometry.

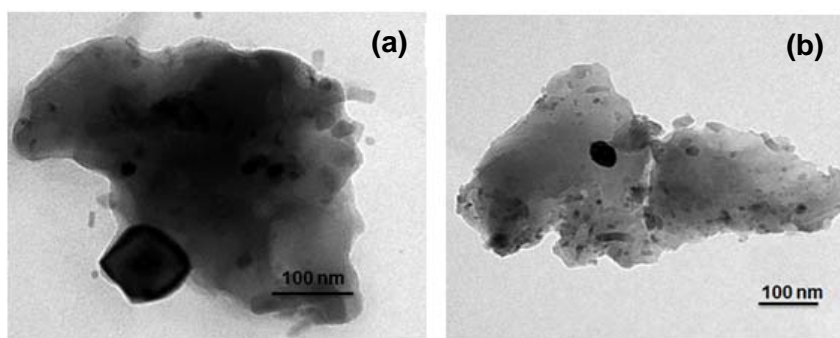


Figure 4: TEM micrographs of the supported catalysts after the step of reduction with hydrogen at 700 °C for 120 min: (a) 10 % Co, (b) 10 % Ni

The production of nanostructured carbon after 120 min of reaction by using a 10 % Co supported catalyst was 0.49 g/g<sub>cat</sub>, with a conversion of 48 % ethanol. For the reactions with 10 % Ni, the conversion was 88 %, with formation of 0.58 g/g<sub>cat</sub>. In this case, the quantity was higher for the reaction with 10 % Ni, probably due to decomposition of ethanol.

The thermogravimetric analyses were carried out in an oxidizing atmosphere up to 800 °C, allowing to study the stability of the formed carbon after 120 min of reaction. Figure 5 shows DTA/DSC curves of the carbonaceous material produced in the reactions at 550 °C using 10 % Co and 10 % Ni. It is observed which for the reaction with 10 % Co, there was a weight loss of about 50 % and with 10 % Ni, the loss was about 73 %.

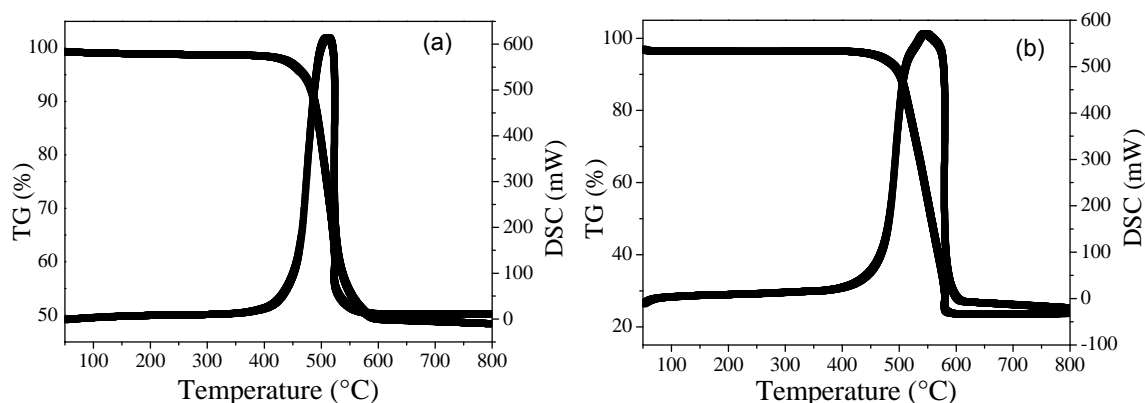


Figure 5: TG/DSC curves of the produced carbonaceous materials in the decomposition reactions of ethanol at 550 °C for 120 min by using: (a) 10 % Co and (b) 10 % Ni

The thermograms show that no amorphous carbon was produced, due to the absence of that characteristic peak around 320 °C (Li et al., 2008). Thus, it can be assumed that the formed material is constituted only by nanotubes and/or carbon nanofibers. The mass loss peak for the reactions carried out with 10 % Co (Figure 5 (a)) and 10 % Ni (Figure 5 (b)) showed, respectively, mass loss peaks around 510 °C and 545 °C indicating the formation of a more readily oxidisable material (Mezalira et al., 2013).

Figure 6 shows TEM images of produced carbonaceous materials in the decomposition reactions of ethanol at 550 °C for 120 min. It is observed in Figures 6 (a, b), that there was formation of nanostructured carbon being present, mainly as carbon nanofibers. The low decomposition temperature of the material analysed by TGA/DSC confirms this result. Carbon nanofibers were also evidenced by MEZALIRA et al. (2011) in the decomposition reactions of ethanol at 500 °C.

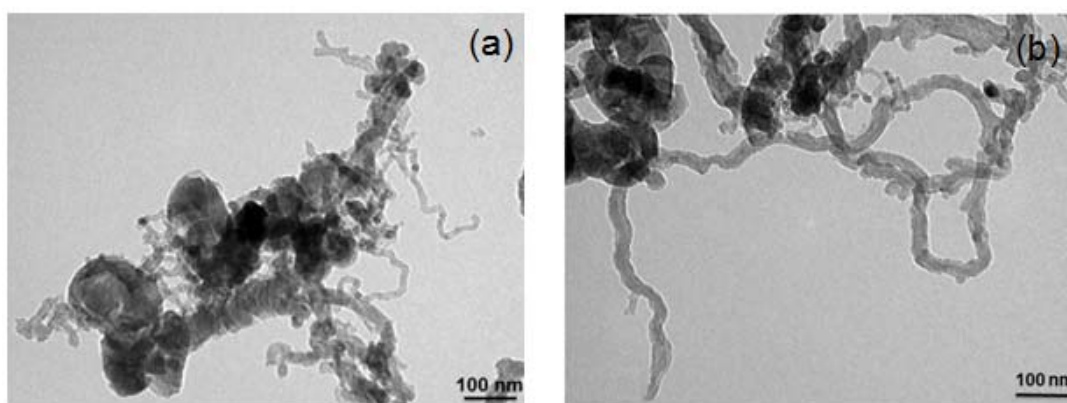


Figure 6: TEM Images of the produced carbonaceous materials after 120 min of reaction at 550 °C using: (a) 10 % Co and (b) 10 % Ni

Catalytic supports were also tested with 1.0 % foaming agent and 10 % Ni in the reaction at 550 °C, but because they have incomplete decomposition of ethanol (30 %), they were not evaluated.

#### 4. Conclusions

The catalytic tests performed in the decomposition reaction of ethanol at 550 °C, using LZSA glass-ceramic foams with 0.2 % foaming agent as catalytic supports and Co and Ni as active phases (10 %), showed that Ni was the main responsible by favouring the reaction.

The use of 10 % Co in the reactions resulted in conversion of 48 % ethanol, whereas for the reaction with 10 % Ni, the conversion was 88 %.

Both reactions lead to deposition of nanostructured carbon, especially carbon nanofibers, according to TGA/DSC analysis which indicated low decomposition temperatures for this material.

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