

# Catalysts evaluation CuO/n-type semiconductor oxide/ $\text{Al}_2\text{O}_3$ in ethanol steam reforming reaction for obtaining hydrogen to fuel cell

G. L. B. Zortea<sup>1</sup>

J. Friedrich<sup>1</sup>

T. P. de Almeida<sup>1</sup>

M. P. Cantão<sup>1</sup>

R. C. P. Rizzo-Domingues<sup>2</sup>

## Abstract

The electric power generation, and hydrogen as a vector, in fuel cells, is a process of high energy efficiency and low environmental impact. However, hydrogen production has its still high cost, because the  $\text{H}_2$  gas is not available in nature. Therefore, we study the steam reforming reaction of ethanol for the production of  $\text{H}_2$ , featuring an environmentally friendly process, with low  $\text{CO}_2$  emissions in nature as well as being economically viable in Brazil, a major world producer of ethanol. Assuming the reform of ethanol follows similar mechanism to the methanol reforming, whose catalyst for industrial use is composed of  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ , it can be considered that copper catalysts on n-type semiconductor oxide should be effective in reforming reaction ethanol. Thus, replacement of zinc oxide of niobium pentoxide, both characteristics semicondução n-type catalysts may generate similarly. In this work study the performance of the catalysts  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  (commercial catalyst HiFUEL Alfa Aesar) and  $\text{Cu}/\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$  in the ethanol steam reforming reaction. The catalysts were characterized by adsorption/desorption of  $\text{N}_2$  and  $\text{NH}_3$ -TPD analysis. The catalytic tests were carried out using a mixture of water:ethanol in a molar ratio equal to 10:1, reactant liquid flow rate of 1 ml/min to 573K. The gaseous product was analyzed on-line by gas chromatography. Results of the textural analysis show that the synthesized catalyst has a specific surface area about three times greater than the commercial catalyst, which has micropores on its surface. For  $\text{NH}_3$ -TPD analysis it showed that the strongest acid sites are the commercial catalyst than in the synthesized catalysts. This may occur due to the provision of

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1 Federal University of Paraná, Curitiba, Paraná, Brazil.

2 Federal Technological University of Paraná, Curitiba, Paraná, Brazil.

materials on the catalyst surface, a consequence of the preparation method of the catalyst and the use of different materials. The catalysts showed similar behavior as the selectivity for hydrogen, but the synthesized catalyst showed higher conversion than the commercial catalyst. In analyzing the gaseous products, there was significant production of  $H_2$  and  $CH_4$  in the reaction with both, and small amounts of  $CO_2$ ,  $C_2H_4$  and  $C_2H_6$  but only the synthesized catalyst was carbon monoxide. The catalytic tests show that the conversion and the production of hydrogen by the reaction between water and ethanol is more satisfactory the weaker the acidity of the catalyst, disfavoring the ethanol dehydration reaction.

**Keywords:** ethanol reforming, hydrogen production, Cu/n-type semiconductor oxide /  $Al_2O_3$  catalyst.

## 1. Introduction

The new age of renewable energy is stronger every day, and the hydrogen energy guarantees environmentally and climatically clean transportation. Fuel cells will, undoubtedly, find widespread use in the conversion of chemical to electrical energy, as they offer very high efficiencies and have unique scalability in electricity-generation applications. The production of  $H_2$  through the steam reforming of ethanol in spite of attractive using of fuel no fossil in compensation to the natural gas, has an impediment that is the great variety of reactions that usually happen. Many researchers have suggested that catalysts containing copper promote dehydrogenation of ethanol to acetaldehyde, while the presence of nickel favors the breaking of carbon-to-carbon bond formation of methane, carbon monoxide and hydrogen. Shinoki et. al. (2011) study of performance of the two catalysts,  $Cu/ZnO/Al_2O_3$  and  $Ru/Al_2O_3$ . As a result, the  $Cu/ZnO/Al_2O_3$  catalyst shows rather high performance at low-reaction-temperature, which suggests that the  $Cu/ZnO/Al_2O_3$  catalyst promotes the ethanol-steam-reforming and the water-gas shift reactions, but does not promote the methanation reaction. In this way that work has begun with a selection of catalysts to be used in the hydrogen production through the ethanol steam reforming in unit of bench to study the interaction of metal and support.

## 2. Experimental

### 2.1 Preparation and treatment of the support

$Nb_2O_5$  addition to the procedure mentioned, also a wash with deionized water at room temperature and then was calcined be performed. The treatment

was performed by a prior calcination of the material at a temperature of 773 K for 5 hours.

## 2.2 Synthesis of catalyst

Preparation of catalysts  $\text{Cu}/\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$  was by the method of wet impregnation with Cu concentration equal to 42%,  $\text{Nb}_2\text{O}_5$  equal to 15% and  $\text{Al}_2\text{O}_3$  equal to 43%, the same percentage of commercial catalyst. The catalysts characterization was studied by adsorption/desorption of  $\text{N}_2$  and  $\text{NH}_3$ -TPD analysis.

## 2.3 Catalytic tests

Before starting the reaction, it was necessary to perform the procedure of activating the catalyst, letting a stream of  $\text{N}_2/\text{H}_2$  with gradual increase of the temperature to the level of 773 K. The reaction occurred with all catalysts employing 3,5 g sample in unit bench with catalyst bed (Figure 1) operating at 573K. The gaseous products were analyzed online by gas chromatography Thermo TRACE GC Finnigam, equipped with column Porapak N and Molecular Sieve 13X, the liquid products were stored and later analyzed in the same gas chromatograph, but with a PONA column.



**Figure 1** Unit for reaction steam reforming of ethanol.

### 3. Results and discussion

#### 3.1 Characterizations of catalysts

The results of analysis of  $N_2$  adsorption/desorption noted that the synthesized catalyst has a specific surface area of about three times greater than the commercial catalyst having micropores in its surface. (Table 1).

**Table 1** Analysis of the catalysts textural – Technique for adsorption/desorption of  $N_2$ .

Catalysts	$S_g$ ( $m^2/g$ )	$S_{Externa}$ ( $m^2/g$ )	$S_{Microporos}$ ( $m^2/g$ )	$V_{Microporos}$ ( $cm^3/g$ )	$V_{Total}$ ( $cm^3/g$ )	$D_{medio}$ ( $\text{\AA}$ )
<b>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub></b>	69,32	68,44	0,889	0,00007754	0,1731	99,89
<b>Cu/Nb<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub></b>	240,9	240,9	–	–	0,2975	49,39

For  $NH_3$ -TPD analysis (Table 2) it showed that the strongest acid sites are the commercial catalyst than in the synthesized catalysts.

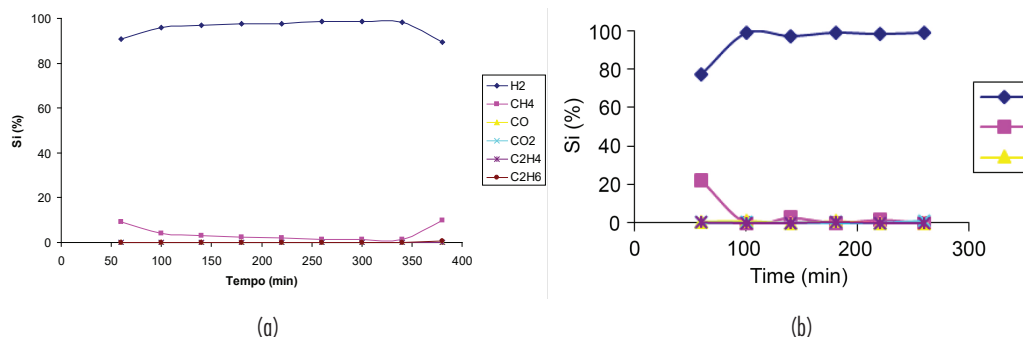
**Table 2** Acidity and desorption temperature maximum to:  $Nb_2O_5$ ,  $Cu/Nb_2O_5/Al_2O_3$  and  $Cu/ZnO/Al_2O_3$ .

Catalyst	Acidity (mmol of $NH_3/g$ of catalyst)	Maximum Tem- perature ( $^{\circ}C$ )
<b>Nb<sub>2</sub>O<sub>5</sub></b>	0,0620	264
<b>Cu/Nb<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub></b>	0,0356	296
<b>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub></b>	0,1126	257 and 577

#### 3.2 Ethanol steam reforming tests

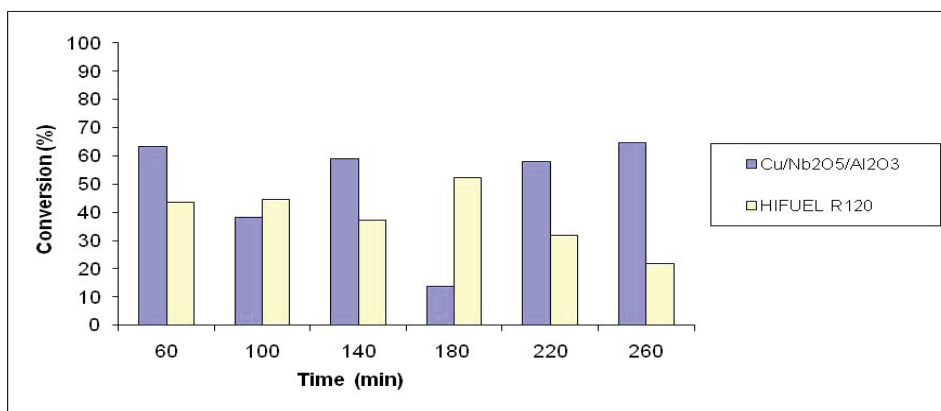
The results of the catalytic tests are shown in Figure 2 e 3, which presents the selectivity for each catalyst. It can be observed that the catalysts showed great se-

lectivity for H<sub>2</sub>, but by different mechanisms, Cu/Nb<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> had high selectivity for CH<sub>4</sub> and CO, the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst showed high selectivity for CH<sub>4</sub> and CO<sub>2</sub>, the same result in Sinoki et. al. (2011) research. All catalysts showed high selectivity for H<sub>2</sub>



**Figure 2** Selectivity of gaseous products: a) Cu/Nb<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>; b) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (Reaction temperature: 300°C; Molar ratio of reagent water: ethanol = 10: 1)

The catalytic tests show that the conversion and the production of hydrogen by the reaction between water and ethanol is more satisfactory the weaker the acidity of the catalyst, disfavoring the ethanol dehydration reaction.



**Figure 3** Conversion of the ethanol reforming

## 4. Conclusion

The characterization showed that the synthesized catalyst had a high surface area and less acid sites than the commercial catalyst. The performance of both catalysts was satisfactory in the production of hydrogen, but Nb<sub>2</sub>O<sub>5</sub> catalyst achieved a higher conversion than with ZnO catalyst.

Both catalysts showed a good performance for the production of hydrogen from ethanol. It is considered promising catalysts for this reaction

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