

## Ceria supported metal catalysts for partial oxidation of ethanol

Lídia Oazem de Oliveira da Costa<sup>1,2</sup>, Adriana Maria da Silva<sup>1</sup>, Lisiane Veiga Mattos<sup>1</sup>, André Luiz Pinto<sup>2</sup>, Luiz Eduardo Pizarro Borges<sup>2</sup>, Fabio Bellot Noronha<sup>1\*</sup>

<sup>1</sup>Instituto Nacional de Tecnologia (INT) Laboratório de Catálise, sala 518. Av. Venezuela 82, CEP 20081-310, Rio de Janeiro (Brazil)

<sup>2</sup>Instituto Militar de Engenharia Praça General Tibúrcio, CEP 22290-270, Rio de Janeiro. (Brazil).

\*fabibel@int.gov.br

### Introduction

Ethanol has been considered a promising renewable fuel for H<sub>2</sub> production since it can be manufactured from biomass and does not contribute to CO<sub>2</sub> emissions. Hydrogen may be generated from ethanol by different technologies: steam reforming (SR); partial oxidation (POX) and oxidative steam reforming (OSR) [1]. All of these reactions face two major drawbacks: by-product formation and catalyst deactivation. Various reaction pathways may operate depending on the conditions selected and the choice of the catalyst. Catalyst deactivation has been attributed to the deposition of carbonaceous species or sintering of the metal particles.

Recently, we reported that the support plays an important role on the product distribution obtained on POX over Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub> and CeZrO<sub>2</sub> supported Pt catalysts [2]. Pt/CeO<sub>2</sub> and Pt/CeZrO<sub>2</sub> catalyst exhibited good activity and stability on POX, which was attributed to the material's high oxygen storage capacity (OSC).

The aim of this work was to study the effect of the metal nature on the performance of ceria supported metal catalysts for the ethanol partial oxidation for hydrogen production. In addition, the nature of carbon formed was also evaluated. The reaction mechanism was investigated using diffuse reflectance infrared spectroscopy (DRIFTS) carried out under steady state reaction conditions.

### Materials and Methods

CeO<sub>2</sub> support was calcinated at 1073 K, for 1 h. The metals (1 wt. %: Pt, Pd, Rh, Ru; 10 wt. %: Co and Ni) were added to the support by incipient wetness impregnation with aqueous solutions. The catalysts were characterized by BET, XRF, TPR, DRS, DRX and TGA. The metallic dispersion and the carbon formation were determined by TEM/SEM/EDS.

The partial oxidation of ethanol was investigated within the temperature range of 473-1073 K in a fixed bed reactor at atmospheric pressure and O<sub>2</sub>/ethanol molar ratio of 0.5. The reaction mechanism was studied through DRIFTS and TPSR techniques.

### Results and Discussion

The complete ethanol conversion was achieved at around 873K, except for Pd/CeO<sub>2</sub> catalyst (973K). The following order was observed for the ethanol conversion at 673K: Ni ≈ Co > Ru > Rh ≈ Pt > Pd. Below 773 K, the product distributions basically comprises acetaldehyde and water. Above 773K, hydrogen and CO were the main products along with methane and CO<sub>2</sub>. The highest hydrogen selectivity occurred at 1073K and varied between 48 % (Rh and Pd) to 35% (Ru). The product distributions obtained on a dry basis at the same level of conversion (~ 65 %) for different catalysts are presented in Table 1. Nickel based catalyst exhibited the highest hydrogen selectivity and the lowest acetaldehyde formation. In addition, the percentage of hydrogen, methane and CO was the same, indicating that ethanol

decomposition is the main reaction taking place on this catalyst. On the other hand, acetaldehyde was one of the main products observed for Rh, Ru, Co and Pt catalysts. A reaction mechanism was proposed based on DRIFTS experiments. Adsorption of ethanol gives rise to ethoxy species, which can be decomposed, producing CH<sub>4</sub>, H<sub>2</sub> and CO, and dehydrogenated, forming acetaldehyde. Acetaldehyde desorbs or can be further oxidized to acetate species. Furthermore, the acetate species previously formed can be decomposed to CH<sub>4</sub>, CO and/or oxidized to CO<sub>2</sub> via carbonate species. A correlation between the product distributions and the metal nature was established based on the reaction mechanism determined by DRIFTS experiments.

Long term run was carried out over Ni/CeO<sub>2</sub> catalyst, since the highest H<sub>2</sub> production and the lowest by-product formation were obtained for this catalyst. In order to study in greater detail the effect of a high formation of acetaldehyde on catalyst stability, Rh/CeO<sub>2</sub> catalyst was also tested. Ni/CeO<sub>2</sub> catalyst was quite stable during 50h TOS (773 K) in spite of the detection of some carbon filaments (Figure 1a). Rh/CeO<sub>2</sub> catalyst also kept the activity during 96h TOS, which agrees well with the absence of carbonaceous deposits (Figure 1b). The high stability of both catalysts is likely due to the redox properties of ceria.

Table 1. Product distributions obtained at the same level of conversion for different ceria supported catalysts for partial oxidation ethanol

Catalysts	%H <sub>2</sub>	%CH <sub>4</sub>	%CO	%CO <sub>2</sub>	%Acetaldehyde	%Acetate
Pt	17.21	8.59	16.79	30.93	26.23	0.23
Pd	11.55	25.37	28.13	21.92	12.69	0.32
Ru	4.02	6.80	33.65	19.96	34.55	0.30
Rh	4.99	11.50	15.27	30.81	35.40	0.81
Co	9.48	2.26	17.09	35.41	32.19	2.99
Ni	26.77	25.00	27.61	19.56	2.00	0

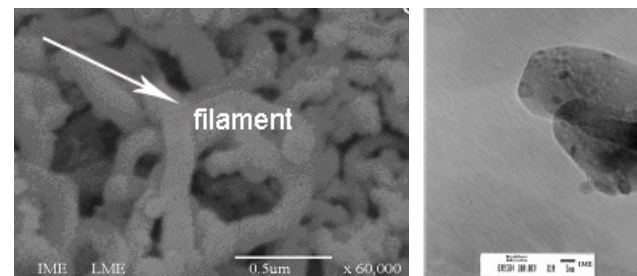


Figure 1: SEM image of Ni/CeO<sub>2</sub> and TEM image of Rh/CeO<sub>2</sub> spent catalysts.

### Significance

Development of a highly active, selective and stable catalyst for H<sub>2</sub> production

### References

1. R.M. Navarro, M.C. Alvarez-Galvan, M.C. Sanchez-Sanchez, F., Rosa, J.L.G. Fierro, *Applied Catal. B: Environmental* 55, 223 (2004).
2. L. V. Mattos, F. B. Noronha, *J. Power Sources* 145, 10 (2005).