

## Hydrogen production from partial oxidation of ethanol over Rh catalysts

Lídia O. O. Costa<sup>1,2</sup>, Adriana M. Silva<sup>1</sup>, Lisiane V. Mattos<sup>1</sup>, Sônia M. R. Vasconcelos<sup>3</sup>, André L. Pinto<sup>2</sup>, Luiz E. P. Borges<sup>2</sup> and Fábio B. Noronha<sup>1</sup>\*,

<sup>1</sup>Instituto Nacional de Tecnologia, Av. Venezuela, 82, 518, Rio de Janeiro, CEP 20081-310 (Brazil); <sup>2</sup>Instituto Militar de Engenharia, Praça General Tibúrcio, 80, Praia Vermelha, Rio de Janeiro CEP, 22290-270 (Brazil); <sup>3</sup>NUCAT/PEQ/COPPE – Universidade Federal do Rio de Janeiro, Bloco G, sala 128, CEP 21945-970 – Rio de Janeiro (Brazil)

\*fabiobel@int.gov.br

### Introduction

The development of alternatives to fossil fuels has become crucial in order to meet the world demand energy and the new environmental standards. Hydrogen production to fuel cell represents a promising alternative. In Particular, H<sub>2</sub> production from ethanol does not contribute to the increase of CO<sub>2</sub> emissions. Furthermore, the infrastructure needed for ethanol production and distribution is already established in countries like Brazil and USA. However, the production of H<sub>2</sub> from ethanol would require the development of suitable catalysts to avoid formation of by-products such as acetaldehyde [1] and carbon deposits [2].

The aim of this work is to study the performance of Rh/CeO<sub>2</sub> and Rh/Y<sub>2</sub>O<sub>3</sub> catalysts on the partial oxidation of ethanol.

### Materials and Methods

CeO<sub>2</sub> support was prepared by calcination of (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> at 1073 K for 1h. The catalyst was prepared by incipient wetness impregnation with an aqueous solution of RhCl<sub>3</sub>·H<sub>2</sub>O salt. The partial oxidation of ethanol was performed in a fixed bed reactor at atmospheric pressure and the catalysts were diluted in SiC (SiC/Catalyst = 3). The reaction was carried out at different temperatures (473-1073K), using a W/Q = 0.16 g s/cm<sup>3</sup> and an ethanol/O<sub>2</sub> molar ratio of 2. Prior to reaction the samples were reduced under H<sub>2</sub> at 773 K, for 1 hour. exit gases were analyzed on line with a gas chromatograph (VARIAN, CP 3800).

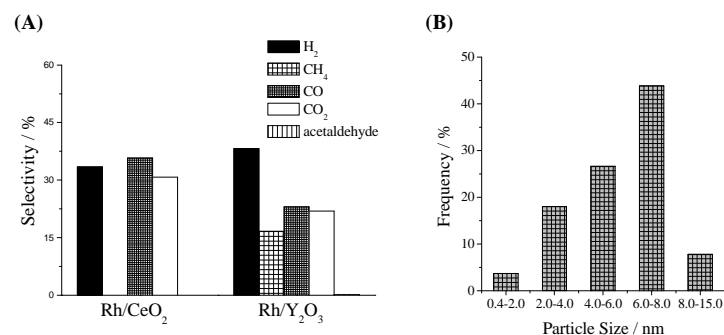
### Results and Discussion

In terms of catalytic activity, Rh/CeO<sub>2</sub> exhibited the higher activity in all temperatures studied. The products identified over both catalysts were H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, acetaldehyde and water. Nevertheless, the products distribution was affected by the nature of support and reaction temperature. At low temperature the main products were acetaldehyde, CH<sub>4</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O (not shown). However, on Rh/Y<sub>2</sub>O<sub>3</sub>, the selectivity to acetaldehyde reached 50 % at 473 K while on Rh/CeO<sub>2</sub> only traces were detected. As the temperature increased acetaldehyde formation was suppressed and H<sub>2</sub> formation increased. The maximum H<sub>2</sub> selectivity was achieved at 1073 K over Rh/Y<sub>2</sub>O<sub>3</sub> (48 %) and at 873 K (36%) on Rh/CeO<sub>2</sub> catalyst. The CO selectivity increased with the temperature on Rh/Y<sub>2</sub>O<sub>3</sub> catalyst and reached a maximum (33 %) at 1073 K. However, CO selectivity on Rh/CeO<sub>2</sub> was around 20% on all the temperature range investigated. Moreover, Rh/Y<sub>2</sub>O<sub>3</sub> was more selective than Rh/CeO<sub>2</sub> toward CH<sub>4</sub> formation.

The selectivity results at isoconversion in dry basis (Figure 1A) show that both catalysts presented similar H<sub>2</sub> selectivity. On the other hand, Rh/CeO<sub>2</sub> exhibited higher CO

formation (33%) than Rh/Y<sub>2</sub>O<sub>3</sub> (20%). The CH<sub>4</sub> production (~13%) was only detected on Rh/Y<sub>2</sub>O<sub>3</sub> catalyst.

These results can be attributed to the Rh particle size on each catalyst. As a matter of fact, the metal dispersion on Rh/Y<sub>2</sub>O<sub>3</sub> was 50 % (with particle diameter of 2nm) while on Rh/CeO<sub>2</sub> it was around 18 % (with particle diameter of 5.4nm) (Figure1B). Moreover, TEM micrograph of Rh/CeO<sub>2</sub> fresh catalyst shows regions containing metallic particle with different sizes. These results are in agreement with some studies of Rh/SiO<sub>2</sub> that suggested the Rh cluster formation with different sizes [3]. In our work, the presence of large Rh particles on Rh/CeO<sub>2</sub> could promote the ethanol molecule adsorption via cyclic intermediate [4] which can explain the high CO selectivity exhibited by this catalyst. On the other hand, the high metal dispersion verified on Rh/Y<sub>2</sub>O<sub>3</sub> could favor the hydrogen formation preferentially via decomposition of ethoxy species. DRIFTS analyses are in agreement with this mechanism.



**Figure 1** – (A) Products distribution at isoconversion and dry basis over Rh catalysts, at 773 K; (B) Particle size distribution histogram of Rh/CeO<sub>2</sub>.

### Significance

This paper points promising catalysts for hydrogen production from ethanol, which is highly relevant to attempt the environmental and energetic requirement.

### References

1. Mattos, L. V. and Noronha, F. B., *J. of Catal.* 233, 453 (2005).
2. Cavallaro, S., Chiodo, V., Vita, A. and Freni, S., *J. Phys. Chem. B.* 109, 10813 (2005).
3. Graydon, W.F. and Langan, M.D., *J. of Catal.* 69,180 (1981).
4. M. Mavrikakis and M. A. Barteau, *J. Mol. Catal.* 131, 135 (1998).