

## Low temperature steam reforming of ethanol for hydrogen production over Rh/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts.

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### Introduction

Ethanol steam reforming (ESR) has recently attracted attention from many research groups as an option to generate hydrogen for fuel cell use. When produced from biomass, bioethanol can be considered as a renewable source for H<sub>2</sub> production. ESR has been shown to be thermodynamically feasible [1,2] at temperatures as low as 300°C; however H<sub>2</sub> production is not favored at these temperatures since CH<sub>4</sub>, being one of the main products, is not reformed unless higher temperatures are used (~550°C). Thus, catalysts capable to avoid the formation of CH<sub>4</sub> during the reaction are required. Rh catalysts have been shown to be very active in this kind of reactions since they readily dissociate the ethanol carbon-carbon bond [3-6]. Nevertheless it is also a requirement for catalysts to be able to oxidize CO and CH<sub>x</sub> adsorbed species in order to yield higher H<sub>2</sub> selectivities appropriate for its use in fuel cells. CeO<sub>2</sub> and CeO<sub>2</sub>-ZrO<sub>2</sub> based catalysts have been studied recently [7], showing better performances in comparison with other oxides (i.e. Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>). However the effect of the composition and structure of these catalysts in the activity and selectivity of the ESR has not been reported to our knowledge. Taking that into account, we studied the influence of the support composition of different Rh/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts in the activity and selectivity of the ESR reaction at low reforming temperatures (300 – 400°C).

### Materials and Methods

Supports were synthesized following the coprecipitation method using Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (ex-N series) and (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> (ex-A series) as Ce precursors, and ZrO(NO<sub>3</sub>)<sub>2</sub> as Zr precursor. Ammonium hydroxide was used as precipitating agent; the precipitated hydroxides were washed with deionized water and were let dry at room temperature overnight. Finally, they were calcined at 500°C. Catalysts were prepared by wet impregnation using rhodium nitrate as Rh precursor. Catalysts were first dried at 120°C and then calcined at 450°C. Materials were characterized by N<sub>2</sub> physisorption, XRD, UV-Vis diffuse reflectance electronic spectroscopy, TPR and HRTEM. Catalytic activity experiments were carried out in a glass packed reactor at atmospheric pressure (150 mg of catalyst, 0.03 ml/min liquid flow rate, 100 ml/min N<sub>2</sub> as carrier). Reactor outlet was analyzed by GC, the only products observed were H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and CH<sub>3</sub>CHO.

### Results and Discussion

Structural and textural changes on the carriers were observed depending on the cerium precursor. Ex-A mixed oxides presented a 2-fold increase in their specific surface areas (>100 m<sup>2</sup>/g) in comparison with pure oxides and ex-N materials (~50m<sup>2</sup>/g) in agreement with results published elsewhere [8]. Besides, XRD patterns revealed the formation of solid

solutions for the ex-A supports (confirmed by the decrease in the cell parameter) while ex-N mixed oxides presented crystalline phase segregation. TPR results revealed an increase in the reducibility of the CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides, regardless of the precursor used during the synthesis of the materials. Besides a change in the dispersion of Rh supported particles was also observed. The catalytic behavior of catalysts varied with both the cerium precursor and the support composition, as shown in Table 1.

**Table 1. Ethanol conversion and products composition at 300°C**

Catalyst	Conv.,%	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO	CH <sub>3</sub> CHO
Rh/CeO <sub>2</sub> ex-A	6.9	0.50	0.00	0.00	0.00	0.50
Rh/Ce <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub> ex-A	75.6	0.32	0.02	0.36	0.30	0.00
Rh/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub> ex-A	83.8	0.71	0.23	0.04	0.02	0.00
Rh/ZrO <sub>2</sub>	45.8	0.61	0.10	0.11	0.15	0.03
Rh/CeO <sub>2</sub> ex-N	67.5	0.61	0.16	0.12	0.12	0.00
Rh/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub> ex-N	21.4	0.69	0.15	0.06	0.05	0.05
Rh/Ce <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub> ex-N	61.7	0.61	0.15	0.11	0.12	0.01

For ex-A catalysts an increase in activity was observed when increasing the Zr content in the supports. When comparing the selectivities of the ex-A mixed oxides supported catalysts an improvement in the redox properties can be observed due to an increase in both the H<sub>2</sub> and CO<sub>2</sub> selectivities and a decrease in the CH<sub>4</sub> and CO selectivities. Acetaldehyde and H<sub>2</sub> were the only products observed with the Rh/CeO<sub>2</sub> ex-A catalyst, indicating that ethanol dehydrogenation is the first reaction to take place in this system. On the other hand, the ex-N catalysts showed no apparent relationship between catalytic activity and support composition. These results are discussed further in terms of the structural differences observed from the characterization results by XRD, UV-vis DRS, TPR and HRTEM. From this work, it is clear that the preparation of the support for the Rh/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> system is a key issue in order to synthesize highly active and selective catalysts for the ESR.

### Significance

This work points towards the design of catalysts suitable for the ESR at low temperature to produce H<sub>2</sub>, particularly the Rh/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> ex-A seems to be an option to consider for further work.

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