

Low temperature ethanol steam reforming for hydrogen production over Rh, Pt and Rh-Pt catalysts.

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Introduction

Ethanol steam reforming (ESR) has recently attracted attention from many researchers as an option to generate hydrogen for fuel cells use. Bio-ethanol can be considered as a renewable source for H₂ production. ESR has shown to be thermodynamically feasible [1] at temperatures as low as 250°C. However, at this temperature methane (CH₄) formation reactions are carried out, a disadvantage for H₂ production. Thus, catalysts capable to avoid CH₄ formation during the reaction, via the oxidation of adsorbed species are required. In addition, catalysts must be high C-C and C-H bond breaking capable and active in water-gas shift reaction (WGSR). Rh has proved to be a very active in ethanol C-C bond breaking [2], which has been linked directly to oxametallacycles formation [3]. At low temperatures, Pt also exhibited an activity close to that for Rh [4]. Furthermore, Pt is active in the WGSR and dehydrogenation [5]. The solid solution Ce_{0.5}Zr_{0.5}O₂ (CZ) has demonstrated outstanding redox properties when used in ESR [6]. Recent works [7] suggested that oxametallacycles are also formed in RhPt/CeO₂, and showed improvement in yields of H₂ compared with the monometallic catalyst. However, the effect of this mixed CZ in bimetallic Rh-Pt systems on the activity and yields of the ESR have not been reported to our knowledge. Based on the facts above, we studied the influence of contact-time and composition of metal Rh-Pt catalyst on the activity and yields in the ESR at low temperatures (250-300°C).

Materials and Methods

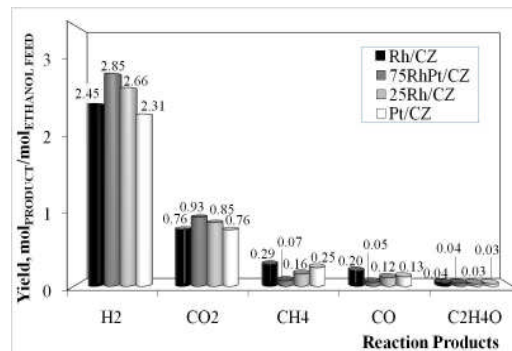
Supports were synthesized following the co-precipitation method using (NH₄)₂Ce(NO₃)₆ as Ce precursor, and ZrO(NO₃)₂ as Zr precursor. NH₄OH was used as precipitating agent. The precipitated hydroxides were washed and dried at room temperature overnight. Finally, they were calcined at 500°C. Catalyst were prepared by wet impregnation using Rh(NO₃)₃·xH₂O as Rh precursor and H₂PtCl₆·xH₂O as Pt precursor. Catalysts were first dried at 120°C and then calcined at 450°C. Materials were characterized by N₂ physisorption, XRD, TPR and HRTEM. Catalytic activity experiments were carried out in a glass-packed reactor at atmospheric pressure (100 mg of catalyst, 100 ml/min He carrier and 0.01-0.08 ml/min liquid-flow rate of water:ethanol=3:1 mix). Reactor outlet was analyzed by GC; products observed were H₂, CO, CO₂, CH₄ and CH₃CHO.

Results and Discussion

The mixed oxide presented an increase in their specific surface area (>100 m²/g) in comparison with pure oxides (~50 m²/g). XRD patterns revealed the formation of solid solution CZ, confirmed by a decrease in the cell parameter in comparison with CeO₂. TPR results

revealed an increase in surface reducibility of the mixed oxide and a drop in temperature reduction, both surface and bulk. This effect has been linked with Zr incorporation inside the crystalline structure of CeO₂. The catalyst promoted with metal showed a considerable decrease in the consumption for H₂ (60% on monometallic and 75% on bimetallic). This effect is related to a partial reduction of the material, due to the formation of oxygen vacancies product of the incorporation of the metallic phase on the surface. The catalytic behavior varied with metal composition, contact-time and temperature. In all cases, a raise in contact-time mainly increased the yield of H₂ and CO₂. We also observed minimum increases in CO and CH₄.

The bimetallic Rh-Pt catalyst showed slightly higher activity than monometallic Rh or Pt catalyst. However the bimetallic catalysts showed significant advantages in terms of yields of H₂ and CO₂, reducing yields of CO and CH₄ (Figure 1). These results suggest a promoting effect on the properties of surface oxidation due to addition of small amounts of Pt in Rh catalyst. These results are discussed further in terms of the structural differences observed from



the characterization results by TPR, XRD and HRTEM. From this work, it is clear that the combination of both metals phases for the system RhPt/Ce_{0.5}Zr_{0.5}O₂ is key issue in order to devise highly and selective catalysts for ESR.

Figure 1. Comparison of yield products for catalysts Rh, Pt and Rh-Pt supported on Ce_{0.5}Zr_{0.5}O₂ (CZ). Conditions: T=250°C, 60% conv.

Significance

This work points towards the design of catalysts suitable for the ESR at low temperatures to produce H₂. Particularly, a catalyst containing Rh and Pt, 75RhPt/Ce_{0.5}Zr_{0.5}O₂, seems to be a good option to consider for further work.

References

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