

Partial oxidation, steam reforming and autothermal reforming of ethanol over Pt/Ce_{0.75}Zr_{0.25}O₂ catalyst

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Introduction

The use of H₂ to generate electric power through fuel cell is one of the most promising technologies that can contribute to the reduction of global dependence on fossil fuels, of greenhouse gas emissions and of atmospheric pollution. Recently, ethanol has been claimed as the best source of H₂ production for fuel cells since it can be manufactured from biomass and does not contribute to CO₂ emissions. Moreover, in countries like Brazil and USA, the ethanol production and distribution infrastructure was already established. Hydrogen can be produced from ethanol by steam reforming, partial oxidation and autothermal reforming. However, the routes for production of hydrogen from ethanol involve a complex reaction system [1]. Several reaction pathways take place depending on the catalysts and reaction conditions. Some of these reactions lead to the formation of by-products, which can affect the efficiency of fuel cells, and to the catalyst deactivation. Recently, we have investigated the performance of supported Pt catalysts on partial oxidation of ethanol [2,3]. Pt/CeO₂ and Pt/CeZrO₂ catalysts revealed to be the best catalyst for fuel processors to PEM fuel cell based on the partial oxidation of ethanol since they exhibited good stability and activity on this reaction. The good performance of these materials was attributed to its high oxygen storage capacity. The aim of this work is to compare the performance of Pt/CeZrO₂ catalyst on the steam reforming (SR), partial oxidation (POX) and autothermal reforming of ethanol (ATR).

Materials and Methods

Ce_{0.75}Zr_{0.25}O₂ support was synthesized following the co-precipitation method reported by Mattos et al [3]. The support was calcined at 1073 K for 1 h. Pt (1.5 wt.%) was added to the support by incipient wetness impregnation with an aqueous solution containing H₂PtCl₆·6H₂O. The catalysts were characterized by BET surface area, X-ray diffraction and oxygen storage capacity (OSC). The Pt dispersion was measured by the cyclohexane dehydrogenation reaction. The reactions were performed in a fixed bed reactor at atmospheric pressure. Prior to reaction, the catalysts were reduced at 773 K for 1 h. The reactions were carried out at 773 K and W/Q = 0.02 g.s/cm³. It was used H₂O/ethanol molar ratio = 2.0 (for SR and ATR) and O₂/ethanol molar ratio = 0.5 (for POX and ATR). The exit gases were analyzed on line using a chromatograph equipped with thermal conductivity detector.

Results and Discussion

The BET surface area of Pt/Ce_{0.75}Zr_{0.25}O₂ catalyst was 34 m²/g. The X-ray diffraction patterns of Ce_{0.75}Zr_{0.25}O₂ support showed that the zirconia was incorporated into the CeO₂ lattice and a solid solution with cubic symmetry was formed. The OSC value of Pt/Ce_{0.75}Zr_{0.25}O₂ catalyst was very high (626 μmol/g_{cat}). This is attributed to the high oxygen mobility of the solid solution formed, which was identified by the XRD data. The Pt dispersion

was 22 %. For POX and ATR reactions, the initial ethanol conversions were similar and they were higher than that observed for SR reaction (Figure 1a). The activity strongly decreased at the beginning of the SR reaction, but the catalyst became practically stable after 2 h time on stream (TOS). In the case of POX reaction, the catalyst was stable after an initial period of deactivation. However, for ATR reaction, the catalyst exhibited a continuous deactivation during 6 h TOS. These results showed that the increase of O₂ amounts in the feed favored the stability of the catalyst. The H₂ production on SR followed the same trend as ethanol conversion. For POX reaction, the H₂ formation was very low and it was no longer detected after 1 h TOS. The catalyst produced large amounts of H₂ during 3 h TOS on ATR reaction. After that, the H₂ selectivity strongly decreased. Furthermore, it was also observed the production of CO₂, acetaldehyde, water and traces amount of ethene on all reactions. The CO formation was only detected on SR and POX reaction. The products distribution at the same conversion (Figure 1b) showed that the H₂ was only observed on SR reaction. Moreover, the production of acetaldehyde and CO₂ was higher on ATR and POX reactions, while the CO formation was higher on POX reaction. These results indicate that the addition of O₂ did not have a positive effect on H₂ formation probably due to its oxidation to water. On the other hand, the presence of O₂ favored the production of CO₂ and acetaldehyde. A reaction mechanism was proposed in order to explain the product distribution observed in each reaction based on our previous knowledge of ethanol partial oxidation [2].

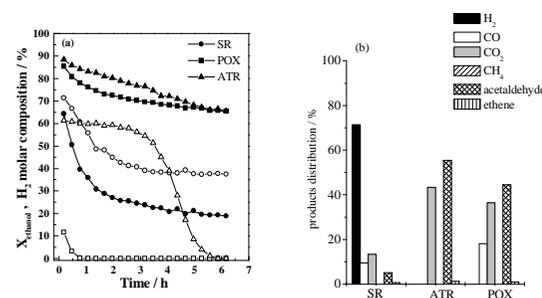


Figure 1. (a) Ethanol conversion (full symbols) and H₂ molar composition (open symbols) vs. reaction time; (b) products distribution obtained at the same conversion in dry basis.

Significance

The aim of this work is to develop a catalyst to H₂ production from ethanol for fuel processors to PEM fuel cell

References

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