

Rh/CeO₂-ZrO₂ catalyst deactivation patterns during ethanol-steam reforming at low temperatures

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Introduction

Bio-ethanol constitutes a promising and increasingly important renewable liquid fuel candidate for hydrogen generation via reforming, for fuel cell applications [1]. Prior research by our group has identified 2%Rh/Ce_{0.8}Zr_{0.2}O₂ as the most active and hydrogen selective catalyst for ethanol steam reforming among several Rh/ceria-zirconia formulations evaluated [2]. Catalyst deactivation was explained by a gradual build-up of a carbonaceous species that could easily be removed at 200 °C in dilute oxygen to restore activity [3]. Recently, acetate-like surface species [4, 5] or oligomers derived from acetic acid and acetone [6] were found to interfere with the desirable reaction pathways, resulting in catalyst deactivation. Promotion with a low amount of potassium slowed catalyst deactivation [3], possibly by decreasing the stability of the undesired acetate surface species [5]. In this work the possible cause of deactivation was investigated by researching the effects of the observed intermediate reaction products upon catalyst deactivation.

Materials and Methods

Catalysts containing 2 wt% and 5 wt% Rh on Ce_{0.8}Zr_{0.2}O₂ (2RhCZ82 and 5RhCZ82, respectively) were prepared and characterized by BET surface area, ethanol steam reforming (ESR) activity and post-reaction TPO, according to refs. [2,3]. Textural changes were assessed by HRTEM imaging. The catalyst weight gain during ESR was monitored by TGA. Deactivation tests were performed in a quartz tubular microreactor. Baseline experiments were performed at 450 °C on 2RhCZ82 with a feed composed of C₂H₅OH: H₂O:N₂=1:8:9, at a space velocity of 2,000,000 scc/g_{cat}·h. Several feed additives were evaluated individually by substituting a certain molar percentage of ethanol: acetaldehyde, acetic acid, and acetone (5%); and ethylene (9%), all previously identified as ESR reaction intermediates. In other co-feed experiments, H₂ (23%) and O₂ (1%) were added to the N₂ stream. Analytically, the oxygenates in the feed were treated as reactants, while CO_x and CH₄ as measured by GC in the gaseous reaction effluent, were accounted for as products. Deactivation parameters were calculated by data fitting first-order kinetics, considering a random-order deactivation function assumed independent of concentrations [7]. Values for initial rate constants (*k*₀), deactivation constants (*k*_d) and deactivation orders (*d*) were compared with the baseline test.

Results and Discussion

HRTEM imaging evidenced no textural changes in the spent catalyst, with Rh particle sizes between ca. 2-5 nm. In situ TGA weight gain rates at 350 and 500 °C were different (Fig 1.A) confirming that the deactivating ESR intermediates are less stable at higher temperatures [5]. The residual ethanol conversion correlated inversely with the build-up of carbonaceous deposits as detected by TPO in the spent catalyst, which amount up to almost one monolayer (~9 carbon atoms/nm²; Fig 1.B). Co-fed ethylene and acetone appear to be the most deleterious additives (and reaction intermediates,) producing more than twice the deactivation

rates seen in the baseline deactivation tests (Table 1). Deactivation orders changed when co-feeding ethylene, acetone, H₂ and O₂, suggesting a modified deactivation mechanism. Acetic acid did not significantly alter the catalyst deactivation patterns. Acetaldehyde dramatically affected the initial rate constant while the deactivation order remained practically unchanged. The significantly slower deactivation rate indicates that competitive adsorption in the presence of acetaldehyde leaves fewer active sites available for both reforming and buildup of deactivating species. Oxygen was the most beneficial additive, significantly lowering the deactivation rate while still preserving favorable CO₂ and hydrogen selectivities.

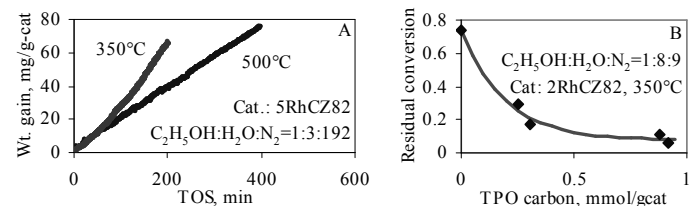


Figure 1. (A) TGA weight gain curves during ESR; (B) Correlation between the residual ESR conversion and the amount of carbonaceous deposits.

Table 1. Effect of ESR feed additives on conversion and product distribution at 60 min on stream, and on the deactivation parameters

| Additive | Conv. | CO Sel. | CO ₂ Sel. | CH ₄ Sel. | H ₂ Yield | <i>k</i> ₀ , 1/min | <i>k</i> _d , 1/min | <i>d</i> |
|----------------------|-------|---------|----------------------|----------------------|----------------------|-------------------------------|-------------------------------|----------|
| - | 0.40 | 0.34 | 0.43 | 0.23 | 4.08 | 5461 | 0.13 | 2.8 |
| O ₂ | 0.48 | 0.33 | 0.43 | 0.24 | 3.57 | 5124 | 0.09 | 3.1 |
| H ₂ | 0.48 | 0.39 | 0.29 | 0.32 | 3.09 | 4881 | 0.15 | 3.4 |
| Ethylene | 0.37 | 0.31 | 0.33 | 0.19 | 4.37 | 5259 | 0.31 | 3.4 |
| Acetaldehyde | 0.37 | 0.28 | 0.48 | 0.24 | 4.00 | 2928 | 0.05 | 3.0 |
| Acetone (40 min TOS) | 0.34 | 0.24 | 0.49 | 0.26 | 4.68 | 4681 | 0.28 | 3.2 |
| Acetic acid | 0.37 | 0.24 | 0.48 | 0.28 | 3.66 | 5625 | 0.12 | 2.5 |

Significance

The results presented identify undesirable reaction conditions and intermediates for the Rh/ceria-zirconia ESR catalysts.

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