Applied Catalysis A: General 352 (2009) 95–113

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Ethanol decomposition and steam reforming of ethanol over $CeZrO_2$ and $Pt/CeZrO_2$ catalyst: Reaction mechanism and deactivation

Sania M. de Lima [a,1], Adriana M. Silva [a], Uschi M. Graham [b], Gary Jacobs [b], Burtron H. Davis [b], Lisiane V. Mattos [a], Fábio B. Noronha [a,*]

[a] Instituto Nacional de Tecnologia – INT, Av. Venezuela 82, CEP 20081-312, Rio de Janeiro, Brazil
[b] Center for Applied Energy Research, The University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA

ARTICLE INFO

Article history:
Received 10 June 2008
Received in revised form 26 September 2008
Accepted 30 September 2008
Available online 21 October 2008

Keywords:
Fuel cell
Fuel processor
Hydrogen production
Steam reforming of ethanol
Ethanol decomposition
$CeZrO_2$
$Pt/CeZrO_2$
Deactivation

ABSTRACT

The catalyst performance and the deactivation profiles of $CeZrO_2$ and $Pt/CeZrO_2$ were evaluated for the ethanol decomposition and steam reforming of ethanol reactions at 773 K. Unpromoted $CeZrO_2$ was quite stable whereas $Pt/CeZrO_2$ catalyst deactivated for all feed compositions studied. A reaction mechanism was proposed based on diffuse reflectance infrared spectroscopy analyses carried out under reaction conditions. The decomposition of the dehydrogenated and the acetate species is facilitated by the presence of the metal and resulted in high selectivity to hydrogen, methane, CO and CO_2 over $Pt/CeZrO_2$. Diffuse reflectance infrared spectroscopy, transmission electron microscopy and temperature programmed oxidation and desorption analyses indicate that the loss of the Pt-support synergy leads to a buildup of carbonaceous residue, which is the likely reason of the deactivation of $Pt/CeZrO_2$. In addition, once the interfacial boundary is lost, the demethanation of acetate becomes hindered, resulting in an increase in acetaldehyde selectivity with time onstream.

1. Introduction

Alcohols such as methanol and ethanol are being strongly considered as potential chemical carriers for hydrogen for use in mobile polymer electrolyte membrane (PEM) fuel cell applications [1]. Methanol is a highly flexible intermediary fuel source, since it can be produced from any source of syngas (e.g., coal, natural gas, biomass, etc.) or from the hydrogenation of CO_2, while ethanol is less hazardous, and can be produced by fermentation of any of the number of sources of carbohydrates (e.g., sugar cane, corn, etc.), and may lead to decreases in CO_2 emissions.

Most of the studies reported to date have used supported base metals or noble metals as catalysts for the steam reforming of ethanol. Activity and selectivity are strongly dependent on the nature of metal and support used. Actually, the support itself exhibits activity for this reaction and may influence the product distribution. However, only few studies were dedicated to the steam reforming of ethanol over metal oxides [2–4]. In spite of their lower activity than supported metal catalysts, metal oxides are able to produce hydrogen free of CO as well as carbon deposits, depending on the reaction conditions used. On the other hand, a greater selectivity to by-products (e.g., ethene, acetaldehyde and acetone) is observed over metal oxides than with supported metal catalysts.

New bifunctional catalysts, based on a partially reducible oxide component and a metal promoter, show promise for effectively activating and turning over simple alcohol molecules. Ceria and ceria-containing mixed oxides have been proposed as a catalytically active component for ethanol conversion reactions due to their high oxygen storage capacity, which improves catalyst stability [5–7], and their ability to promote the dissociation of molecules of the type ROH (e.g., H_2O and ethanol) [8]. In addition, the strong metal–support interaction (SMSI) prevents metal particle sintering, which also contributes to catalyst deactivation [9]. Different base metals (Ni, Co, Cu) and noble metals (Pd, Pt, Rh, Ru) have been tested for the steam reforming of ethanol. However,

---

[*] Corresponding author. Fax: +55 21 2123 1051.
E-mail address: fabiobel@int.gov.br (F.B. Noronha).

[1] Present address: Universidade Estadual do Oeste do Paraná – Unioeste, Campus de Toledo, Rua da Faculdade, 645, Jd. La Salle, CEP 85903-000, Toledo, Brazil.

0926-860X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2008.09.040

only few investigators have reported the effect of the nature of the metal during steam reforming of ethanol [10–12]. Breen et al. [10] studied the performance of Rh, Pd, Pt and Ni catalysts supported on $CeZrO_2$. According to them, the order of activity observed was: Pt > Rh > Pd. However, the role of the support and the mechanism of the ethanol steam reforming reaction were not defined.

In fact, the detailed catalytic surface mechanism for alcohol steam reforming over these bifunctional catalysts is still not entirely understood and represents a formidable challenge to improve catalyst design. Though the previous studies have been helpful in improving understanding about the mechanism, one problem is that most of the ethanol reaction mechanisms proposed in the literature relied on infrared spectroscopy (IR) results not measured under steady state reaction conditions [13–20]. For example, in studies by some of us [8], the activation and turnover of ROH probe molecules, including ethanol, was carried out in the context of investigating the low temperature water–gas shift mechanism under H_2 co-feeding. In that work, ethanol was first adsorbed and then, we switched to a stream containing inert gas. The transient turnover of the ethoxy species to acetate, and in turn, acetate to carbonate was observed, suggesting a viable mechanism; however, studies under steady state reaction conditions were not carried out at that time.

As the nature of intermediate species formed on the surface may be strongly affected by the reaction conditions, part of the aim of this work is to carry out infrared studies under reaction conditions by flowing the reaction mixture at different temperatures. By carrying out diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of the steam reforming of ethanol over the mixed oxide component alone and in combination with Pt, we would like to determine separately the role of the oxide component and the metal function in the reaction mechanism.

The second and main goal of the work is to gain insight into why most catalysts to date relying on the synergy between metal and partially reducible oxide display rapid deactivation profiles. Catalyst stability is probably the most important issue in catalyst design that hinders the goal of achieving hydrogen production from ethanol. Catalyst deactivation is generally attributed to the deposition of carbonaceous species or sintering of the metal particles. The carbon deposits following ethanol steam reforming have been studied by Raman spectroscopy, temperature programmed oxidation (TPO) and electron microscopy analysis [21–23], and include both carbon filaments and amorphous carbon covering the metallic particle and the support. Roh et al. [24] attributed catalyst deactivation to carbon deposition. Platon et al. [25] went into further detail, suggesting that a significant build-up of reaction intermediates occurs during the reaction, which can contribute to catalyst deactivation. For example, they suggested that ethylene and acetone produced the most intense deactivation. Erdohelyi et al. [19] reported that hydrogen selectivity decreased while acetaldehyde selectivity increased with time on stream. They reported that acetate-like species accumulate over the support during steam reforming of ethanol, and that these in turn hinder the formation of ethoxy species and consequently the dehydrogenation of these species via the metal–support interaction. In agreement with this perspective, Guil et al. [22] also proposed that deactivation was likely due to the blockage of the active sites by acetaldehyde. Instead of acetaldehyde conversion to acetate surface species, which produces the desired H_2 and CO_2 products, acetaldehyde was suggested to polymerize and decompose to methane and CO. Therefore, the mechanism of catalyst deactivation is still unclear. The focus of this work is two-fold: (1) to shed light on the mechanistic pathways of ethanol steam reforming and ethanol decomposition reactions using a combination of reaction testing, temperature programmed oxidation and temperature programmed desorption (TPD), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements taken under suitable reaction conditions, and (2) to gain insight into the deactivation mechanism(s) by analyzing particle size changes, if any, by transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM), assessing by DRIFTS the holdup of adsorbed species, which may inhibit the catalytic cycle, and explore the deposition of carbonaceous deposits by TPO, TPD and HR-TEM imaging. Finally, to provide further insight on the nature of the deactivation, the regeneration of the catalyst was attempted by carrying out an oxidation–reduction cycle.

2. Experimental

2.1. Catalyst preparation

$CeZrO_2$ support (Ce/Zr ratio = 3.0) was obtained by the precipitation method as described by Hori et al. [26]. The choice of Ce/Zr ratio was based on previous work [27], which showed that $Pt/CeZrO_2$ catalyst containing the Ce/Zr ratio of 3.0 exhibited a good performance during SR. An aqueous solution of cerium (IV) ammonium nitrate and zirconium nitrate (Aldrich) was prepared with the desired Ce/Zr ratio. Then, the ceria and zirconium hydroxides were co-precipitated by the addition of an excess amount of ammonium hydroxide. Finally, the precipitate was washed with distilled water and calcined at 1073 K for 1 h in a muffle furnace. A silica support from Davison Grace was also used (Davison Grace 955). Platinum was added to the support by the incipient wetness impregnation technique using an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$. After impregnation of 1.5 wt% of platinum, the samples were dried at 393 K and calcined under air flow (50 mL/min) at 673 K for 2 h.

2.2. BET surface area

The BET surface areas of the samples were measured using a Micromeritics ASAP 2000 analyzer by nitrogen adsorption at the boiling temperature of liquid nitrogen.

2.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) measurements were carried out using a RIGAKU diffractometer with CuKα radiation (λ = 1.5406 Å). After calcination of the samples, the XRD data were collected between $2\theta = 25^\circ$ and 75° (0.04°/step; 1 s/step). Crystallite sizes were estimated from the integral width of the highest intensity line using the Scherrer equation.

2.4. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) measurements were carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Omnistar, Balzers). The samples (300 mg) were dehydrated at 423 K for 30 min in a He flow prior to reduction. After cooling to room temperature under He, a mixture of 2% H_2 in Ar was flowed through the sample at 30 mL/min, while the temperature was raised to 1273 K at a heating rate of 10 K/min. The hydrogen consumption rate was monitored using a quadrupole mass spectrometer.

2.5. Temperature programmed desorption (TPD) of ethanol

Temperature programmed desorption (TPD) experiments of adsorbed ethanol were carried out in the same equipment previously described for TPR measurements. Prior to TPD analyses,