Steam reforming, partial oxidation, and oxidative steam reforming of ethanol over Pt/CeZrO$_2$ catalyst

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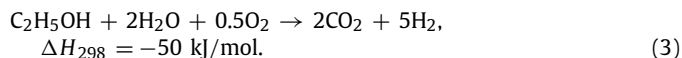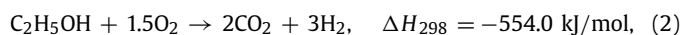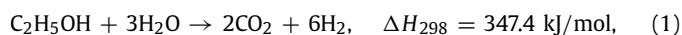
ABSTRACT

The catalytic performance of a Pt/CeZrO$_2$ catalyst was tested for ethanol decomposition, steam reforming, partial oxidation, and oxidative steam reforming. At low temperature, the catalyst underwent significant deactivation during ethanol decomposition and steam reforming reactions. Co-feeding oxygen decreased the deactivation rate of the catalyst but adversely affected the selectivity to hydrogen. Increasing the reaction temperature greatly improved the stability of the catalyst. A reaction mechanism was proposed based on results obtained from in situ diffuse reflectance infrared spectroscopy analyses carried out under reaction conditions. Ethanol adsorbs as ethoxy species, which may follow one of two distinct pathways: (i) decomposition and production of CO, CH$_4$, and H$_2$ or (ii) dehydrogenation to acetaldehyde and acetyl species. The dehydrogenated species may undergo oxidation to acetate species. The addition of water to the feed promoted the formation of acetate species. Water also facilitated the decomposition of acetaldehyde and acetate reactions, resulting in the formation of methane, CO, and carbonate.

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1. Introduction

The electrochemical conversion of hydrogen to power via polymer electrolyte membrane (PEM) fuel cell technology may alleviate global dependence on fossil fuels, as well as decrease emissions of greenhouse gases and other atmospheric pollutants [1]. Recently, ethanol has been claimed to be an alternative source of hydrogen production for fuel cells, because it can be manufactured from biomass and does not contribute to net CO$_2$ emissions. The United States, Brazil, and other countries have established an ethanol production and distribution infrastructure.

Hydrogen may be generated from ethanol by different technologies, including steam reforming (SR) (reaction (1)), partial oxidation (POX) (reaction (2)), and oxidative steam reforming (OSR) (reaction (3)) [2]:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2, \quad \Delta H_{298} = 347.4 \text{ kJ/mol}, \quad (1)$$

$$C_2H_5OH + 1.5O_2 \rightarrow 2CO_2 + 3H_2, \quad \Delta H_{298} = -554.0 \text{ kJ/mol}, \quad (2)$$

$$C_2H_5OH + 2H_2O + 0.5O_2 \rightarrow 2CO_2 + 5H_2,$$
$$\Delta H_{298} = -50 \text{ kJ/mol}. \quad (3)$$

All of these reactions have one major drawback, however. Various reaction pathways may operate depending on the conditions selected and the choice of the catalyst. The reaction network may include (i) ethanol decomposition to methane, CO and hydrogen;

(ii) ethanol dehydrogenation to acetaldehyde; (iii) ethanol dehydration to ethylene; (iv) methane steam reforming; (v) the water–gas shift reaction; (vi) methane decomposition to carbon and hydrogen; and (vii) the Boudouard carbon deposition reaction [3–5]. A wide range of undesirable byproducts, such as oxygenated compounds (acetaldehyde, acetone) and hydrocarbons like methane and ethane, are formed at low reaction temperatures. Some of these reactions lead to the formation of coke, which can in turn induce catalyst deactivation. At high reaction temperatures, CO production is thermodynamically favored, which, if left unconverted, will poison the electrodes of the PEM fuel cell. Therefore, further purification steps are required, which increases not only the final cost of the hydrogen produced, but also the size and the weight of the fuel processor.

The nature of the metal and support strongly affects the stability and product distribution [3,4]. CeZrO$_2$ has been proposed as a support for the ethanol conversion reactions due to its high oxygen storage capacity (OSC), which improves catalyst stability. In addition, the strong metal–support interaction prevents metal particle sintering, which also contributes to catalyst deactivation [6,7]. Romero-Sarria et al. [7] reported that the use of a catalytic system based on Ce–Zr mixed oxides doped with Co, Ni, Rh, Rh–Co, or Rh–Ni reduced the formation of carbonaceous deposits during SR. In addition, other authors [8,9] have observed that ceria/zirconia-supported metal catalysts exhibit higher H$_2$ yield than other supports during SR. Recently, we investigated the performance of supported Pt catalysts for POX [10] and SR [11]. The Pt/CeZrO$_2$ catalyst exhibited good activity and stability for POX, which was attributed

to the material's high OSC [10]. It also exhibited good selectivity to H_2 during SR [11]. Furthermore, a comparison between the results obtained for the $Pt/CeZrO_2$ and Pt/CeO_2 catalysts in SR showed that adding Zr to ceria improved the stability and decreased the CO selectivity of the Pt/CeO_2 catalyst.

Designing an optimum catalyst for hydrogen production from ethanol requires additional insight into the reaction mechanism. The literature contains some studies of the reaction mechanism of ethanol over different catalysts. Most of the ethanol reaction mechanisms proposed in the literature relied on infrared spectroscopy (IR) results that were not measured under steady state conditions. Alternatively, temperature-programmed desorption (TPD) of adsorbed ethanol or ethanol + water mixture was employed. At each temperature of interest, the system was evacuated to determine the adsorbed species present on the catalyst surface [5,12–19].

In a previous investigation by some of us [20], a transient diffuse reflectance infrared spectroscopy (DRIFTS) technique was used to study the activation/turnover of probe molecules of ROH type to gain insight into the low-temperature water–gas shift mechanism under H_2 cofeeding conditions. In that context, CO (from the low-temperature shift) was replaced by ethanol, which was used as a probe molecule to demonstrate two important points: (i) Under conditions of H_2 cofeeding, the activation of ROH molecules is dissociative and common in the water–gas shift, methanol SR, and ethanol SR reactions, and (ii) at least under conditions of H_2 cofeeding and a high H_2O/reactant ratio (reactant = CO, CH_3OH, or C_2H_5OH), formate or acetate plays an important role as an intermediate in these three reactions. Formate, produced from the reaction of CO with –OH during a low-temperature shift or from the conversion of methoxy during methanol SR, is dehydrogenated, and, in an analogous manner, acetate produced from conversion of ethoxy species is demethanated during ethanol SR. In fact, methanol and ethanol were used as probe molecules to shed light on the water–gas shift mechanism, which requires a H_2 cofeed.

These studies were not carried out under reaction conditions by flowing the reaction mixture at different temperatures, however. The nature of intermediate species formed on the surface may be strongly affected by the reaction conditions.

The present study was conducted to investigate the reaction mechanisms for SR, POX, and OSR under realistic stoichiometric feed ratios over the $Pt/CeZrO_2$ catalyst system. The reaction mechanisms were investigated using DRIFTS carried out under steady-state reaction conditions using appropriate feed conditions to mimic ED, SR, and POX. In particular, the effect of oxygen and water on the nature and populations of surface species were assessed.

2. Experimental

2.1. Catalyst preparation

The $CeZrO_2$ support (Ce/Zr ratio = 3) was obtained by the precipitation method as described by Hori et al. [19]. The choice of Ce/Zr ratio was based on findings of our previous study [11] showing that the $Pt/CeZrO_2$ catalyst containing the Ce/Zr ratio of 3.0 exhibited good performance during SR. An aqueous solution of cerium(IV) ammonium nitrate and zirconyl nitrate (Aldrich). Then the ceria and zirconium hydroxides were coprecipitated by the addition of an excess of ammonium hydroxide. Finally, the precipitate was washed with distilled water and calcined at 1073 K for 1 h in a muffle furnace. Platinum was added to $CeZrO_2$ 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 (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. OSC

OSC measurements were carried out in a microreactor coupled to a Balzers Omnistar quadrupole mass spectrometer. Before OSC analysis, the samples were reduced under flowing H_2 at 773 K for 1 h, then cooled to 723 K, and kept at this temperature during the analysis. The mass spectrometer was used to measure the composition of the reactor effluent as a function of time while a 5% O_2/He mixture was passed through the catalyst. Oxygen consumption was calculated from the curve corresponding to $m/e = 32$.

2.4. Cyclohexane (CH) dehydrogenation

Platinum dispersion was estimated by running a reaction to probe the metallic function. CH dehydrogenation was selected, because it is considered a rather structurally insensitive reaction [21]. Because H_2 and CO spillover occurs from the metal to the CeO_2, metal dispersion could not be determined from chemisorption of either gas [22]. Therefore, to provide an estimate of the dispersion of the $Pt/CeZrO_2$ catalyst, a correlation between the rate of CH dehydrogenation and the metal dispersion measured by hydrogen chemisorption was established. The reference catalysts for this procedure were Pt/Al_2O_3 catalysts of varying metal particle size.

CH dehydrogenation was performed in a fixed-bed reactor at atmospheric pressure. The catalyst was reduced at 773 K for 1 h, and the reaction was carried out at 543 K and WHSV = 170 h^{-1}. The reactants were fed to the reactor by bubbling H_2 through a saturator containing cyclohexane to obtain the desired H_2/CH ratio (13:1). The exit gases were analyzed using a Varian 300 gas chromatograph equipped with a HP-INNOWAX column.

2.5. TPD of ethanol

TPD experiments of adsorbed ethanol were carried out in the same equipment described previously for OSC measurements. Before TPD analyses, the samples were reduced under flowing H_2 (30 mL/min) by ramping to 773 K (10 K/min), and holding at this temperature for 1 h. After reduction, the system was purged with helium at 773 K for 30 min and cooled to room temperature. The adsorption of ethanol was carried out at room temperature using an ethanol/He mixture, which was obtained by flowing He through a saturator containing ethanol at 298 K. After adsorption, the catalyst was heated at 20 K/min to 773 K under flowing helium (60 mL/min). The products were monitored using a quadrupole mass spectrometer.

2.6. DRIFTS

DRIFTS spectra were recorded using a Nicolet Nexus 870 spectrometer equipped with a DTGS-TEC detector. A Thermo Spectra-Tech cell capable of high-pressure/high-temperature operation and fitted with ZnSe windows served as the reaction chamber for in-situ adsorption and reaction measurements. Scans were obtained at a resolution of 4 to give a data spacing of 1.928 cm^{-1}. Depending on the signal-to-noise ratio, the number of scans ranged from 256 to 1024. The amount of catalyst was ~40 mg.

Samples were first reduced by ramping in 200 mL/min H_2:He (1:1) at ~10 K/min and holding at 773 K for 1 h. The catalyst was purged in flowing He at 773 K before being cooled in flowing He to 313 K.