



Reactions of ethanol over CeO₂ and Ru/CeO₂ catalysts



K. Mudiyansele^a, I. Al-Shankiti^a, A. Foulis^c, J. Llorca^b, H. Idriss^{a,*}

^a Fundamental Catalysis, Centre for Research and Development (CRD), SABIC-KAUST, Thuwal, Saudi Arabia

^b Institute of Energy Technologies and Centre for Research in Nanoengineering, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain

^c Department of Chemistry, University of Aberdeen, Aberdeen, UK

ARTICLE INFO

Article history:

Received 18 December 2015

Received in revised form 27 March 2016

Accepted 29 March 2016

Available online 29 March 2016

Keywords:

Cerium oxide

Ruthenium/cerium oxide

Ethanol reforming reaction

Ethanol TPD

Water gas shift

Temperature programmed desorption

ABSTRACT

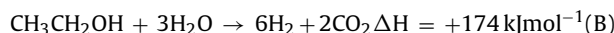
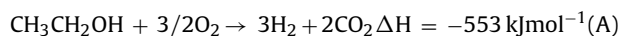
The reaction of ethanol has been investigated on Ru/CeO₂ in steady state conditions as well as with temperature programmed desorption (TPD). High resolution transmission electron microscopy (HRTEM) images indicated that the used catalyst contained Ru particles with a mean size of ca. 1.5 nm well dispersed on CeO₂ (of about 12–15 nm in size). Surface uptake of ethanol was measured by changing exposure to ethanol followed by TPD. Saturation coverage is found to be between 0.25 and 0.33 of a monolayer for CeO₂ that has been prior heated with O₂ at 773 K. The main reactions of ethanol on CeO₂ during TPD are: re-combinative desorption of ethanol; dehydrogenation to acetaldehyde; and dehydration to ethylene. The dehydration to ethylene occurs mainly in a small temperature window at about 700 K and it is attributed to ethoxides adsorbed on surface-oxygen defects. The presence of Ru considerably modified the reaction of ceria towards ethanol. It has switched the desorption products to CO, CO₂, CH₄ and H₂. These latter products are typical reforming products. Ethanol steam reforming (ESR) conducted on Ru/CeO₂ indicated that optimal reaction activity is at about 673 K above which CO₂ production declines (together with that of H₂) due to reverse water gas shift. This trend was well captured during ethanol TPD where CO₂ desorbed about 50 K below than CO on both oxidized and reduced Ru/CeO₂ catalysts.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen generation from renewables and its use as a clean fuel is attractive since upon oxidation only water is formed while the released energy is the highest known per unit weight of a chemical compound (120.7 kJ/g). Because low molecular weight oxygenates can be stored and distributed readily they are used as hydrogen carriers for on-board generation. Methanol and ethanol, in particular, are promising liquid feeds for onboard hydrogen production due to their high hydrogen to carbon (H/C) atomic ratio. Steam reforming of oxygenated hydrocarbons for the production of hydrogen is thermodynamically more favored at relatively low temperatures compared with that of hydrocarbons [1]. A major advantage of ethanol production from biomass and its use for the energy generation is the absence of carbon emissions because carbohydrates are initially formed by photosynthesis. Producing hydrogen from the catalytic decomposition of ethanol has been investigated for almost

two decades now. The two main reactions are partial oxidation (Reaction A), and steam reforming (Reaction B).



Reaction B, despite being energetically more demanding than Reaction A, yields more hydrogen and can be achieved with high selectivity. The reaction requires a catalyst with three main properties. First, it should be capable of breaking the C–C bond of the adsorbed ethoxide (formed upon dissociative adsorption on the catalysts surface). Second, it needs to be active for water gas shift (WGS) and reforming reactions. Third, it needs to have fast hydrogen–hydrogen bond generation kinetics [2]. Therefore, a combination of a reducible metal oxide and metals capable of both C–C bond dissociation and water gas shift reaction is needed.

CeO₂ is one of the most active redox binary metal oxides [3] known. Part of the reasons is the low activation energy for O anions diffusion [4] and the relatively low oxygen vacancy formation energy [5]. In addition to its use in automobile catalytic converters [6], and as a WGS support [7] it was also, for the same reasons, found to be an excellent support for reforming of ethanol. Our groups have previously studied the reactions of ethanol oxidation

* Corresponding author.

E-mail address: idirish@sabic.com (H. Idriss).

and steam reforming by infrared (IR) spectroscopy, and temperature programmed desorption (TPD), over CeO_2 [8], Pd/CeO_2 [8], Pt/CeO_2 [9], Rh/CeO_2 [10], Pt-Rh/CeO_2 [11], Pd-Rh/CeO_2 [12], Au/CeO_2 [13], Au-Rh/CeO_2 [14] and $\text{Rh/CeO}_2\text{-ZrO}_2$ [15]. The most active of these catalysts was the Rh-Pd/CeO_2 [16]. Many other researchers have also worked on this reaction and a large number of catalysts based on other metals and oxides have been synthesized and tested [17–20]. While the use of non-noble metals is possible, noble metals, in particular Pt and Pd are unique, as they do not form coke and therefore are not easily poised to deactivation. In brief, a metal such as Rh is needed for efficient C–C bond dissociation. It is to be noted that Rh has a unique role within the 4d transition metals for C–H bond dissociation reaction [21], a requirement prior to the C–C bond dissociation reaction, and Pt (or Pd) is needed for fast hydrogen–hydrogen recombination reactions, while CeO_2 provides the active support for the redox process. Ru is akin to Rh in many properties (such as for C–C and C–H bond breaking reactions). Its introduction onto CeO_2 and $(\text{CeZr})\text{O}_2$ has shown benefits for hydrogen production from glycerol [22]. Ru based catalysts have been studied previously for steam reforming of ethanol [23], oxidative steam reforming [24], CO_2 activation [25], and ammonia synthesis [26]. Previously we have synthesized and conducted preliminary studies on Ru-Pt/CeO_2 on the water gas shift reaction [27] and found it to be of high activity.

In this work, we limit our attention on CeO_2 and Ru/CeO_2 in order to determine the reaction mechanisms of ethanol where investigation of elementary steps can be extracted. Among the many reactions that ethanol can have on the surface of CeO_2 are dehydrogenation to acetaldehyde [28], dehydration to ethylene, oxidation to acetates, condensation to higher aldehydes, and other C–C bond making reactions [29,30]. The addition of Ru (initially in the form of RuO_2) is poised to change these reactions and accelerate the C–C bond dissociation reaction resulting in WGS and reforming reactions. We also attempt to link TPD results to catalytic performances in order to probe into the reforming reaction.

2. Experimental

2.1. Catalyst preparation

Cerium oxide (CeO_2) was prepared via precipitation from a solution of white crystalline cerous nitrate, $(\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$ (100 g), in deionised water (0.40 L) with mild stirring. The temperature was kept constant at 373 K (pH 8–8.5) and ammonia (0.91 mol L^{-1}) was added drop wise (ca. 30 mL). The resulting white precipitate was collected by filtration, washed with deionised water and left to dry in an oven for 12 h (373 K) before being calcined (773 K) for 4 h under air-flow. Ruthenium (III) chloride (0.5008 g) was dissolved in approximately 150 mL of double distilled water and stirred using a magnetic stirrer. Once the salt had dissolved in the water, a dark solution was formed (without the formation of a precipitate). The solution was then transferred to a standard volumetric flask (1 L) and made up to the 1000 mL with double distilled water. The resulting solution was stirred to ensure a homogenous mixture was produced. Ru/CeO_2 was prepared using the impregnation method. 0.5 wt.% of Ru metal was calculated relative to 5 g of the total amount of catalyst and the correct amount of metal stock solution was obtained. The accurate amount of cerium oxide was added into a beaker before adding the metal chloride solutions. The resulting solution was then stirred and heated slowly in a beaker wrapped in aluminium foil in order to maintain homogenous heating. Care was taken to ensure the temperature remained constant at 373 K until the majority of liquid had vaporised. The resulting dark paste-like material was then dried overnight in the oven at 373 K. Upon drying, the catalyst underwent calcinations in the open-ended fur-

nace at 673 K for 3 h under air-flow. The final product was grounded into a fine powder and is used as the catalyst.

2.2. Catalyst characterisation and reaction conditions

The surface area of CeO_2 and Ru/CeO_2 determined using the Brunauer, Emmett and Teller (BET) was found to be $\sim 55 \text{ m}^2/\text{g}$ and changed very little with metal deposition (0.5 wt.%).

High-Resolution Transmission Electron Microscopy (HRTEM) was carried out at 200 kV with a JEOL JEM 2100 instrument equipped with a LaB_6 source. The point-to-point resolution of the microscope was 0.19 nm. Samples were deposited on holey-carbon-coated Cu grids from alcohol suspensions. For each sample, more than one hundred particles were used for particle size distribution calculation. Local structural information from individual metal particles was obtained by Fourier filtering.

Temperature-programmed reduction (TPR) analyses were performed in a sample quartz tube coupled to a thermal conductivity detector (AutoChem 2920, Micrometrics). A mixture of 10% H_2 in Ar was flowed through the sample, and the temperature was raised at a heating rate of $10^\circ \text{C min}^{-1}$ and consumption of the H_2 was monitored by Thermal Conductivity Detector (TCD). H_2 consumption was pre-calibrated so that extraction of moles required per unit weight of the materials reduction was made possible.

Ethanol Temperature programmed desorption (TPD) of CeO_2 and Ru/CeO_2 was performed in U-shaped quartz fixed bed micro reactor at atmospheric pressure. Samples (100 mg) were loaded onto the sinter of the reactor where, prior to any reactions, the sample catalysts were either reduced or oxidized at 450°C overnight under hydrogen or oxygen flow, respectively. The reaction chamber was then allowed to cool to room temperature with continuous gas flow. The reactor was then pumped down to base pressure ($\sim 10^{-2}$ Torr) by a roughing pump to remove any loosely adsorbed gas on the surface of the catalyst and to clean the reaction line. This would typically take 15–20 min. The system was then pumped further by the diffusion pump to pressures of ca. 10^{-7} Torr. Typically this took around 30–60 min. Ethanol was injected using a microsyringe onto the surface of the catalyst and was left for around 15 mins. The system was then pumped for a further hour using both the roughing and diffusion pumps to remove any loosely adsorbed ethanol molecules on the catalyst surface and in the reaction line. A constant pressure of $\sim 10^{-5}$ Torr was again achieved in the high vacuum chamber (HVC). Following this, the reactor was placed into a high temperature-heating furnace, which was connected to a programmed temperature controller. A thermocouple was placed into the furnace in which the tip was in-line with the reactor bed. To measure the desorption profiles a quadrupole mass spectrometer was used. The quadrupole mass spectrometer was connected to a computer running mass spectrometer software (RGA for Windows). The quadrupole mass spectrometer was then started and the signal at $m/z=31$ (principal fragment of ethanol) was monitored before any data was collected. Once the signal at $m/z=31$ stabilized, the other fragments were monitored in the same way. The experiment began when all 12 fragments (maximum number to be recorded per run) had stabilized at which the temperature controller was also started simultaneously. The reaction was initiated at room temperature and the furnace was heated at a linear rate of 20 K/min^{-1} . The scan rate for the 12 masses was approximately 5 s per scan. Quantitatively, the peak area under each peak was calculated using the trapezoidal method which is an approximation for computing the total area under a series of data points. The correction factor for each individual fragment was then calculated. Normalization of each desorption profile was obtained by multiplying the product desorption spectrum by the correction factor. Contributions of different masses were subtracted. For example in the case of ethanol the m/e 29 signal resulting from ethanol

Download English Version:

<https://daneshyari.com/en/article/45510>

Download Persian Version:

<https://daneshyari.com/article/45510>

[Daneshyari.com](https://daneshyari.com)