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Ethanol steam reforming over Rh/$Ce_xZr_{1-x}O_2$ catalysts: Impact of the CO–CO_2–CH_4 interconversion reactions on the H_2 production

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Abstract

$Ce_xZr_{1-x}O_2$ mixed oxide-supported 1 wt.%Rh catalysts were prepared by wet impregnation using Rh nitrate as a precursor and calcined at 900 °C. They were characterized by BET surface area, XRD, CO_2 chemisorption and H_2 chemisorption at −85 °C and tested in the ethanol steam reforming at 600 °C under atmospheric pressure, with water to ethanol molar ratio equal to 4, without carrier gas. The best performances, i.e. the highest hydrogen yield and the lowest coke deposition, were obtained over Rh/$Ce_{0.5}Zr_{0.5}O_2$, i.e. 3.63 mol H_2/$mol_{ethanol}$. This catalyst was subsequently evaluated under various reaction conditions. Whatever the temperature and the water to ethanol ratio, the ethanol steam reforming yielded a large amount of methane, which tends to reduce the H_2 production. To elucidate the origin of the methane production, CO/CO_2/CH_4 interconversion reactions were studied. It was shown that such catalyst favours the formation of methane via CO hydrogenation. The direct hydrogenation of CO_2 was not observed. In parallel, the catalyst was active in the reverse water gas shift (RWGS) reaction between CO_2 and H_2, leading CO and H_2O.

Keywords: Ethanol steam reforming; Rh/ceria–zirconia catalysts; CO and CO_2 hydrogenation; Water gas shift; Reverse water gas shift

1. Introduction

A rapid decrease of the fossil fuel resources has led most industrial countries to look for alternative energy sources or vectors such as hydrogen. For environmental reasons as well, the demand for hydrogen to run fuel cell-powered vehicles and small auxiliary power units (APU) should increase in the next 10 years. Today, hydrogen is produced on an industrial scale (5×10^{11} m^3 in 2000) by steam reforming (SR) of fossil fuels, mainly natural gas or naphtha [1]. SR reactors are connected to water gas shift units to increase the hydrogen yield. Virtually all carbon atoms are transformed into CO_2, which is the main SR by-product. Since greenhouse gas emissions must be reduced, hydrogen should at least be partly produced from renewable resources such as ethanol, which can be obtained from biomass. The catalytic steam reforming of ethanol constitutes a promising route to the sustainable hydrogen production [2–6].

Steam reforming catalysts mainly consist of metals deposited on stable oxides. Rh is very active but Ni is preferred for practical applications. The specific role of the support was early recognized by Rostrup-Nielsen in the methane steam reforming reaction [7]. Grenoble [8] and Duprez [9,10] proposed a bifunctional mechanism for the steam reforming of hydrocarbons, especially aromatics. According to this mechanism, the water molecules are adsorbed on the support in the form of mobile hydroxyl groups and the hydrocarbon molecules are mainly activated on the metallic sites. A similar mechanism was proposed for the ethanol steam reforming. As a consequence, hydrophilic supports, with a high oxygen mobility, are expected to act as promoters in steam reforming reactions [8,11–13]. Furthermore, mobile oxygen species supplied by the support may participate in SR reactions and prevent the formation of coke on the metal particles [14]. However, several steps (dehydration to ethylene, dehydrogenation to acetaldehyde, condensation to acetone, cracking to C1 compounds) should be added to the hydrocarbon SR reaction mechanism since ethanol may react at both metallic and support sites [15–18].

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Ceria–zirconia mixed oxides have attracted a great attention as supports for Rh [19–22], Ni [23], Co and various metals [3,24] since they possess high oxygen mobility and tuneable surface properties (acid–base, redox). In the present work, the ethanol steam reforming reaction was studied over Rh catalysts supported on ceria–zirconia mixed oxides. Both the reaction temperature and the water to ethanol ratio R were varied in order to optimize the catalyst performances and selectivity.

Furthermore, significant amounts of methane were shown to form as a primary product upon the ethanol steam reforming reaction and, as far as the interconversion reactions between CO, CO_2 and H_2 might well be responsible for the formation of methane, these latter reactions were studied. Indeed, these reactions have been essentially studied up to now at temperatures lower than 350 °C [25–28]. Therefore, the last part of this paper will be devoted to the study of the interconversion reactions ($CO + H_2$ and $CO_2 + H_2$) at the ethanol steam reforming reaction temperature.

2. Experimental

2.1. Catalyst preparation

The $Ce_xZr_{1-x}O_2$ oxide supports ($x = 0$, 0.50, 0.63, 0.68 and 1) were directly supplied by Rhodia Electronics & Catalysis (La Rochelle, France) as ultra-thin powders. They were calcined beforehand for 6 h at 900 °C. Rh catalysts were prepared by wet impregnation of the supports with aqueous solutions of Rh nitrate to obtain 1 wt.% metal. Catalysts were dried at 120 °C for 24 h and subsequently calcined under flowing air (30 cm^3/min) at 700 °C for 4 h.

2.2. Catalyst characterization

The structure of the $Ce_xZr_{1-x}O_2$ supports was determined by XRD using a Siemens D5005 diffractometer (Cu Kα radiation, $\lambda = 1.5406$ Å). Crystalline phases were identified by comparison with ICDD files and the average crystallite size was derived using the Debye–Scherrer relation.

The BET surface area was measured by N_2 adsorption at −196 °C. Measurements were carried out in a Micromeritics flowsorb II apparatus.

CO_2 chemisorption measurements were carried out in a pulse chromatographic system [29]. The oxide sample (0.1 g) was first heated from room temperature to 450 °C (10 °C min^{-1}) under He and oxidized by O_2 pulses (0.25 cm^3 pulse every other minute) until the saturation was reached. Then, the sample was cooled down to room temperature under He. Pulses of CO_2 (0.25 cm^3 pulse every other minute) were injected until saturation.

The metallic phase dispersion was calculated from H_2 chemisorption experiments at low temperature (−85 °C) to limit ‘‘spillover’’ phenomenon [30]. A pulse chromatographic apparatus was used for such measurements. After reduction under hydrogen at 400 °C for 1 h and outgassing under flowing argon at the same temperature, the sample (0.15 g) was cooled down to RT under flowing argon. Then, the reactor was placed in liquid nitrogen–acetone mixture to obtain the temperature of −85 °C. Afterwards, pulses of hydrogen were injected until saturation as indicated by the constant peak area of the last few pulses. As a result, the total hydrogen uptake (H_{C1}) was determined. Subsequently, the catalyst was flushed for 10 min under argon to remove the physically adsorbed hydrogen molecules. Finally, hydrogen was pulsed again until saturation (H_{C2}). The amount of chemisorbed hydrogen was derived as $H_C = H_{C1} - H_{C2}$.

2.3. Ethanol steam reforming

The ethanol steam reforming reaction was carried out in a fixed bed reactor ($L = 550$ mm, $\Phi_{int} = 12.5$ mm) made of refractory steel (TP310Z15CNS25). The catalyst (0.2 g), mixed together with carborundum (4.6 g), was placed in the middle of the reactor and pretreated under flowing H_2 (100 cm^3 min^{-1}) for 1 h at 500 °C and atmospheric pressure.

After such a pretreatment, the temperature was increased to the reaction temperature under flowing H_2. Ethanol and water were introduced in the reactor via a HPLC pump. The ethanol flow rate was set at 0.098 mol h^{-1} and the water flow rate was adjusted in order to obtain a water to ethanol molar ratio R equal to 4, 6 or 8. The weight hourly space velocity (WHSV) in gram of ethanol per gram of catalyst and per hour was equal to 22.54 h^{-1} throughout this study. The mixture was preheated before entering the reactor. No carrier gas was fed to the system during the reaction.

The reaction temperature was checked using a thermocouple placed in the catalytic bed. Condensable vapours (ethanol, acetaldehyde, water, acetone, etc.) were trapped at +0.5 °C at the reactor outlet and further analyzed by HPLC equipped with an Aminex HPX-87H column, a refractometer and a UV diode array detector. Gas analysis was performed on line using a combination of three gas chromatographs, equipped with either TCD or FID detectors. The product distribution is given after 7 h of reaction.

The thermal decomposition of ethanol was studied under the same reaction conditions but in the absence of catalyst.

2.4. Hydrogenation of CO and CO_2

The CO and CO_2 hydrogenation reactions were performed in a fixed bed reactor. The catalyst (0.3 g) was pretreated under flowing H_2 (100 cm^3/min) for 1 h at 500 °C and atmospheric pressure. The H_2:CO and H_2:CO_2 ratio were fixed at 4 in both cases. The reaction products were analyzed on line by TCD for H_2, CO, CO_2 and CH_4 and FID for the hydrocarbons.

2.5. Thermodynamic calculations

Gas compositions at equilibrium were obtained using a home-made program (THERMO). To run the calculations, the following inputs were required: (i) molar composition of the starting mixture, (ii) list of reactants and products. These calculations were based on (i) the minimization of the gas mixture Gibbs free energy and (ii) the mass conservation of the