Low temperature and H$_2$ selective catalysts for ethanol steam reforming

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Supported Rh catalysts have been developed for selective H$_2$ production at low temperatures. Ethanol dehydration is favorable over either acidic or basic supports such as γ-Al$_2$O$_3$ and MgAl$_2$O$_4$, while ethanol dehydrogenation is more favorable over neutral supports. CeO$_2$–ZrO$_2$-supported Rh catalysts were found to be especially effective for hydrogen production. We focused on a support prepared by a co-precipitation method having composition Ce$_{0.9}$Zr$_{0.5}$O$_2$. A 2%Rh/Ce$_{0.9}$Zr$_{0.5}$O$_2$ catalyst, prepared via impregnation without pre-calcination of support, exhibited the highest H$_2$ yield at 450 °C among various supported Rh catalysts evaluated in this study. This may be due to both the strong interaction between Rh and CeO$_2$–ZrO$_2$ and the high oxygen transfer rate favoring reforming of acetaldehyde instead of methane production.

**KEY WORDS:** H$_2$; ethanol steam reforming; acetaldehyde; Rh; CeO$_2$–ZrO$_2$.

1. Introduction

Hydrogen attracts significant research interest because it is a clean fuel emitting only water without co-production of greenhouse gases. Commercially, hydrogen has been produced from catalytic steam reforming of fossil fuels, for example, methane [1]. To reduce greenhouse gas emissions, hydrogen should be derived from renewable energy sources such as bio-ethanol [2–4]. As a consequence, ethanol steam reforming has been studied, as it provides an alternative fuel source for hydrogen production [4–6].

For the purpose of H$_2$ production for use in molten carbonate fuel cells (MCFC), ethanol steam reforming has been studied over the temperature range of 600–700 °C, the operating temperature of anode in MCFC [7–9]. At such high temperatures, high H$_2$ selectivity was demonstrated consistent with thermodynamic predictions [10–13].

In the case of ethanol reforming to produce H$_2$ for PEM fuel cells, high-reforming temperatures also favor CO formation, which poisons the anode. As a result, downstream CO reduction processes such as water gas shift are required. The high-reforming temperature coupled with a lower temperature water gas shift step suffers from thermal inefficiencies.

Thermodynamically, ethanol steam reforming is possible at low temperatures. Low-temperature reforming can increase overall system efficiency and reduce the material costs of hardware construction. However, low-temperature ethanol steam reforming faces challenges of formation of undesirable reaction byproducts such as CH$_4$ and carbon. These are thermodynamically favored at low temperatures [10–13], leading to reduced H$_2$ selectivity and poor catalyst life. Thus, kinetic rather than thermodynamic control of the reaction is required. Raney Cu–Ni catalyst has recently been reported to exhibit stable activity for low-temperature ethanol reforming (250–300 °C) [14]. However, hydrogen yield is low due to low-steam reforming activity with this catalyst. Oxidative steam reforming has also recently been studied to improve the low-temperature ethanol steam reforming activity and hydrogen yield [15]. Introduction of oxygen has the disadvantage of either requiring an expensive oxygen separation or resulting in dilution of hydrogen with N$_2$, which lowers fuel cell efficiency.

The objective of the present study is to develop an active and selective catalyst for ethanol steam reforming at temperatures at or below 450 °C. Since it is well known that Rh is the most effective catalytic metal for ethanol steam reforming, as a result of high C–C bond breaking capability [5, 6], our catalyst development was based on use of Rh as the active metal component.

CeO$_2$ is one of the most important rare earth elements in catalysis. It plays an important role in three-way catalysis (TWC) and fluid catalytic cracking (FCC) [16, 17]. It is known that the high-oxygen storage capacity (OSC) of CeO$_2$ improves catalytic performance by storing oxygen under oxidative atmosphere and releasing it under reductive atmosphere [16, 17]. It has also been reported that the addition of ZrO$_2$ to CeO$_2$ leads to improvements in the OSC of CeO$_2$, its redox properties, and its thermal resistance. ZrO$_2$ addition to CeO$_2$ also helps to increase metal dispersion [17–19]. It has been shown that Ce$_4^{4+}$ can be partially substituted by Zr$^{4+}$ in the lattice of CeO$_2$, resulting in formation of a solid solution [18, 20]. Because of its thermal stability

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as well as possessing enhanced oxygen mobility, the Ce\(_{1-x}\)Zr\(_x\)O\(_2\) system has shown promise as a support for catalytic methane reforming, including methane steam reforming (MSR), partial oxidation of methane (POM), and CO\(_2\) reforming of methane [21–25]. Diagne et al. has evaluated such catalysts for ethanol steam reforming. He has reported that all the Rh/CeO\(_2\)–ZrO\(_2\) catalysts, prepared with a range of CeO\(_2\)/ZrO\(_2\) ratios, showed high activity and selectivity to H\(_2\) at 400–500 °C without significant difference in the product distributions. The product compositions in all cases were very close to thermodynamic equilibrium [26, 27]. Based on the above results, we have designed Rh/CeO\(_2\)–ZrO\(_2\) catalysts for ethanol steam reforming at low temperatures, in an attempt to kinetically control selectivity toward H\(_2\) against CH\(_4\) by increasing the interaction between Rh and CeO\(_2\)–ZrO\(_2\) and increasing the rate of oxygen transfer between support and metal.

2. Experimental

Support materials employed in this study were γ-Al\(_2\)O\(_3\) (99%, SASOL), MgAl\(_2\)O\(_4\) (99%, SASOL), ZrO\(_2\) (99%, MEL Chemicals), and CeO\(_2\)/ZrO\(_2\) (CeO\(_2\): 13 mol%, MEL Chemicals). The supports were pre-calcined at 800 °C for 6 h in air, unless otherwise stated. The CeO\(_2\)/ZrO\(_2\) (CeO\(_2\): 80 mol%) support was prepared by a co-precipitation method [23]. Stoichiometric quantities of zirconyl nitrate solution (20 wt.% in ZrO\(_2\) base, MEL Chemicals) and cerium nitrate (99.9%, Aldrich) were dissolved in distilled water. To this solution 15% ammonia solution was added drop-wise at 80 °C to attain a pH of 10. The precipitate was digested at 80 °C for 3 days. Supported Rh catalysts were prepared by the incipient wetness method using the metal nitrate. Here, we use an A/B nomenclature to specify the catalyst preparation conditions, where A is the final catalyst calcination temperature and B is the support pre-calcination temperature. For example, 500/AS means the catalyst was calcined at 500 °C and the support was the as-synthesized material.

The BET surface area was measured by nitrogen adsorption at −196 °C using a Micromeritics (ASAP-2400) surface area measurement apparatus. The XRD patterns were recorded using a Rigaku 2155D6 diffractometer (Ni filtered CuK\(_\alpha\) radiation, 40 kV, 50 mA).

H\(_2\) pulse chemisorption measurements were performed with an ASDI RXM-100 apparatus using the pulse equilibrium adsorption method. About 0.2 g of catalyst was placed in a quartz reactor. Before pulse chemisorption, the sample was reduced in 5% H\(_2\)/Ar at 350 °C for 1 h and evacuated at this temperature for 15 min before being cooled to 20 °C while evacuating. The total adsorption isotherm was measured volumetrically by consecutively expanding hydrogen trapped in a calibrated sample loop into the reactor containing the catalyst sample. The physisorption isotherm was measured similarly after a 10 min evacuation. Hydrogen chemisorption at 20 °C was determined as the difference between the total adsorption and physisorption isotherms. About 5% H\(_2\)/Ar and H\(_2\) (ultra high purity, 99.999%) were used without further purification. The calculation method of metal dispersion is the same as that described in ref. [28], which assumes the adsorption stoichiometry of one hydrogen atom per Rh surface atom (H/Rh\(_\text{cat}\) = 1).

Catalytic activity measurements were conducted at atmospheric pressure in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm. The catalyst charge was 50 mg, and SiC was used as a diluent. Special care was taken to minimize mass and heat transport limitations. Thermocouples were placed at various locations within the reactor system. Prior to each catalytic measurement, the catalyst was reduced in H\(_2\)/N\(_2\) (10% H\(_2\) in vol.) at 350 °C for 1 h. A steam to carbon ratio (S/C) of 4 and a space velocity of 133,333 cm\(^3\) gas fed/g cat-h were used, unless otherwise indicated. The mixture of ethanol and water was fed using a syringe pump and was vaporized at 250 °C in a vaporizer [29]. The reformate was chilled, passed through an ice-trap to condense residual water and ethanol, and then analyzed on-line using an Agilent micro-GC with mole sieves 5A and Poraplot Q columns. The H\(_2\) yield is defined as:

\[
\text{H}_2 \text{ yield} = \text{moles of } \text{H}_2 \text{ produced/moles of EtOH fed.}
\]

3. Results and discussion

3.1. Catalyst characterization

Table 1 summarizes the characteristics of the catalyst supports used in this study. The surface area of Ce\(_{0.13}\)Zr\(_{0.87}\)O\(_2\) is 43 m\(^2\)/g and that of Ce\(_{0.8}\)Zr\(_{0.2}\)O\(_2\) is 61 m\(^2\)/g. The Ce\(_{0.8}\)Zr\(_{0.2}\)O\(_2\) support was prepared by the co-precipitation method and it showed higher surface area than the commercially supplied Ce\(_{0.13}\)Zr\(_{0.87}\)O\(_2\). It is known that the co-precipitation method is more effective than other methods to achieve high-surface area [23]. The Rh dispersion decreased in the order: Rh/MgAl\(_2\)O\(_4\) > Rh/Al\(_2\)O\(_3\) > Rh/ZrO\(_2\). In the case of CeO\(_2\)–ZrO\(_2\) supported catalysts, it is not possible to obtain accurate dispersion values via hydrogen chemisorption due to the presence of hydrogen spillover to the support [30, 31]. The XRD patterns confirmed that Ce\(_{0.8}\)Zr\(_{0.2}\)O\(_2\) has cubic phase [23]. It is generally accepted that Ce\(_1\)\(_x\)Zr\(_{1-x}\)O\(_2\) preferably crystallizes into a cubic structure if \(x\) is lower than 0.5 [20]. The presence of the cubic phase indicates that Ce and Zr are highly homogeneously distributed. The Ce\(_{0.13}\)Zr\(_{0.87}\)O\(_2\) commercial sample

\[
\text{Ce}^{4+} + \text{H}_2 \rightarrow \text{Ce}^{3+} + \text{H}_2\text{O}
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