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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_2O_3 and $MgAl_2O_4$, 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 $Ce_{0.8}Zr_{0.2}O_2$. A 2%Rh/$Ce_{0.8}Zr_{0.2}O_2$ 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 $Ce_{0.8}Zr_{0.2}O_2$ 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+} 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_xO_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_2O_3 (99%, SASOL), $MgAl_2O_4$ (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 CuKα 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 ($H/Rh_s = 1$).

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 sieve 5A and PoraPlot Q columns. The H_2 yield is defined as:

$$H_2 \text{ yield} = \text{moles of } H_2 \text{ produced/moles of EtOH fed.} \quad (1)$$

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/$MgAl_2O_4$ > Rh/Al_2O_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 $Ce_{1-x}Zr_xO_2$ 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

Table 1
Characteristics of the supports used in this study

Support	Surf. area (m^2/g)	Pore vol. (cm^3/g)	Pore size (nm)	Dispersion[a] (%)	Phase[b]
Al_2O_3	170	0.51	12	32	Gamma
$MgAl_2O_4$	146	0.63	17	48	Spinel
ZrO_2	23	0.15	26	18	Monoclinic
$Ce_{0.13}ZrO_{0.87}$	43	0.31	28	–	Tetragonal
$Ce_{0.8}Zr_{0.2}$ O_2[c]	61	0.21	14	–	Cubic

[a] Dispersion was estimated from H_2 chemisorption over 1%Rh catalysts.
[b] Phase of support was analyzed by XRD.
[c] Calcined at 500 °C.

showed a tetragonal phase [22]. The presence of only the tetragonal phase also indicates that Ce and Zr are highly homogeneously distributed. In the case of ZrO_2, only the monoclinic phase is present [22].

3.2. Reaction results

Figure 1 shows the effect of reaction temperature on H_2 yield over the 1%Rh/Al_2O_3 and 1%Rh/$Ce_{0.13}Zr_{0.87}O_2$ catalysts. The H_2 yield is close to the equilibrium value for both catalysts above 500 °C. However, the effect of support on H_2 yield is significant at temperatures below 500 °C, with the 1%Rh/$Ce_{0.13}Zr_{0.87}O_2$ exhibiting higher than equilibrium hydrogen yield. As a result, we focused on ethanol steam reforming at low temperatures with the aim to increase H_2 selectivity by controlling the reaction kinetics.

In the initial stages of our work, the role of the catalyst support was examined for ethanol steam reforming using Rh as the active metal. The Rh was chosen since it is known to exhibit the highest activity among all the precious metals for ethanol steam reforming [5, 6].

Table 2 summarizes the results with 1%Rh over the different supports at 450 °C and 85,320 cm^3/g cat-h space velocity. The H_2 yield was highest with the Rh/$Ce_{0.13}Zr_{0.87}O_2$ catalyst. The support identity appears to be more significant than metal dispersion. It is apparent that the acidic Al_2O_3 support strongly favors ethylene formation, as the ethylene selectivity over Rh/Al_2O_3 catalyst is 68%. The basic support, $MgAl_2O_4$ also produced some ethylene (10%). The $Ce_{0.13}Zr_{0.87}O_2$ is unique in that no ethylene was observed in the product. Cavallaro [32] has proposed that the ethanol is first converted either into ethylene by dehydration or into acetaldehyde by dehydrogenation. Acetaldehyde can readily undergo decarbonylation to form CH_4 and CO. Thus, kinetic control of acetaldehyde conversion must be applied to reduce the CH_4/H_2 ratio that would result from the pathway proposed by Cavallaro.

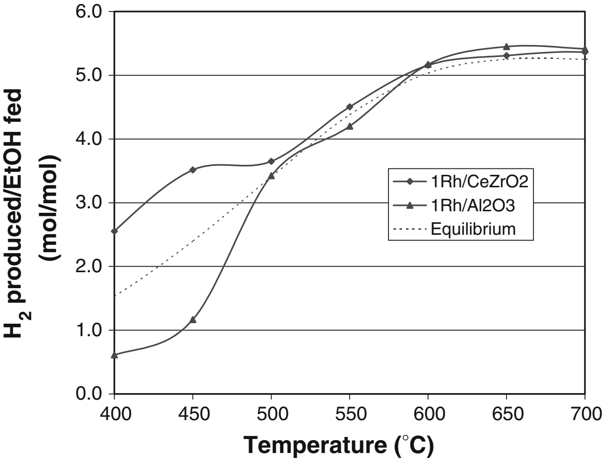

Figure 1. H_2 yield depending on reaction temperature over 1%Rh/Al_2O_3 and 1%Rh/$Ce_{0.13}Zr_{0.87}O_2$ catalysts.

To study the effect of support composition, a $Ce_{0.8}Zr_{0.2}O_2$ support was prepared for comparison with the commercial $Ce_{0.13}Zr_{0.87}O_2$ support. The Rh loading was varied as well. Table 3 summarizes the ethanol steam reforming test results on these catalysts. It is clear that the Rh/$Ce_{0.8}Zr_{0.2}O_2$ catalysts are more H_2-selective than the Rh/$Ce_{0.13}Zr_{0.87}O_2$ catalysts. This is probably due to the higher cerium content of the cubic $Ce_{0.8}Zr_{0.2}O_2$, resulting in more mobile oxygen species than with the tetragonal $Ce_{0.13}Zr_{0.87}O_2$ [24]. Among the Rh/$Ce_{0.8}Zr_{0.2}O_2$ catalysts, the 2%Rh loading exhibited the highest H_2 yield and a low-CH_4 selectivity. In the case of 5%Rh catalyst, the product compositions are close to equilibrium values, suggesting that too high a metal loading can adversely affect H_2 yield.

In a subsequent series of experiments, the CeO_2–ZrO_2 support pre-calcination and catalyst calcination temperatures were systematically varied to determine their possible role in affecting H_2 yield. Table 4 summarizes EtOH conversion and C_1 selectivity for this series of experiments. The 500/AS catalyst exhibited the highest H_2 yield (about 4.3 mol H_2/mol EtOH fed) and stable time-on-stream performance (figure 2) over the duration of the test. With the 800/800 catalyst, H_2 yield decreased with time on stream due to catalyst deactivation. Both the 500/500 and 500/800 catalysts showed similar stable behavior and product selectivity, indicating that the support pre-calcination temperature is not a significant factor between 500 and 800 °C despite the potential sintering of the CeO_2 phase. However, absence of

Table 2
The effect of support on EtOH steam reforming at 450°C and 85,320 cm^3/g cat-h space velocity (Rh = 1 wt.%)

Support	X_{EtOH} (%)	H_2/EtOH (m/m)	S_{CH4} (%)	S_{CO} (%)	S_{CO2} (%)	$S_{C=C}$ (%)
$Ce_{0.13}Zr_{0.87}O_2$	100	3.5	31	16	52	0
ZrO_2	42	1.4	27	55	12	10
Al_2O_3	98	1.2	3	25	2	68
$MgAl_2O_4$	74	1.8	29	50	10	10
Equilibrium	100	2.4	44	2	53	0

Table 3
The effects of Rh loading and CeO_2/ZrO_2 ratio on EtOH steam reforming at 450 °C and 85,320 cm^3/g cat-h space velocity (Rh = 1 wt.%)

Catalyst	X_{EtOH} (%)	H_2/EtOH (m/m)	S_{CH4} (%)	S_{CO} (%)	S_{CO2} (%)
1%Rh/$Ce_{0.13}Zr_{0.87}O_2$	100	3.5	31	16	52
3%Rh/$Ce_{0.13}Zr_{0.87}O_2$	100	2.7	43	3	54
1%Rh/$Ce_{0.80}Zr_{0.20}O_2$	80	3.6	20	37	42
2%Rh/$Ce_{0.80}Zr_{0.20}O_2$	100	4.3	25	11	64
5%Rh/$Ce_{0.80}Zr_{0.20}O_2$	100	2.8	43	2	55

Table 4
The effect of preparation method on EtOH conversion and selectivities to CH_4, CO, and CO_2 at 450°C. All catalyst supports had composition CeO_2 80%–ZrO_2 20%

Catalyst	X_{EtOH} (%)	H_2/EtOH (m/m)	S_{CH4} (%)	S_{CO} (%)	S_{CO2} (%)
500/AS	100	4.3	25	11	64
500/500	100	3.5	37	4	59
500/800	100	3.5	37	4	59
800/800	84	3.5	22	32	46

pre-calcination of the support (500/AS) provided better performance than either 500/500 or 500/800. We believe this is due to a strong interaction between Rh metal and the support in the AS/500 case. We note that the thermodynamic yield of H_2 from EtOH at 450 °C is 2.4 (mol/mol), so that in all cases the reaction is occurring under kinetic rather than thermodynamic control.

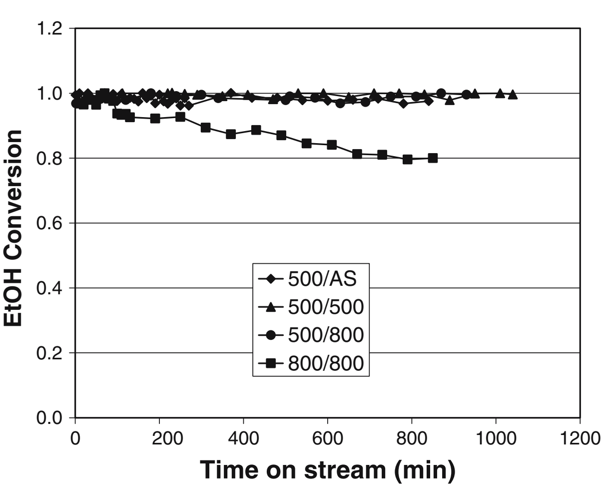

Figure 2. The effect of preparation method on activity maintenance at 450 °C over 2%Rh/$Ce_{0.8}Zr_{0.2}O_2$ catalysts.

It has been established that acetaldehyde is a reaction intermediate that can readily undergo decarbonylation to form CH_4 and CO [32]. We have also seen acetaldehyde as a product [33]. Once CH_4 forms, high temperatures are required to reform it into CO and H_2. Therefore, in order to maximize H_2 selectivity, the adsorbed CH_3 group (which is the precursor to CH_4) needs to be converted to H_2 and CO by reaction with steam or mobile oxygen provided by the support, as shown in figure 3. It is possible that Ce sites in CeO_2–ZrO_2 are partially oxidized under reforming conditions [24] and these partially oxidized sites provide active oxygen species, which may suppress CH_4 formation. We speculate that the 500/AS catalyst has a better interaction between Rh and support as a result of the single calcination, resulting in more effective oxygen transfer and lower CH_4 selectivity.

4. Conclusions

At low temperatures, support plays an important role in ethanol steam reforming. Ethylene formation is significant over either acidic or basic supports such as

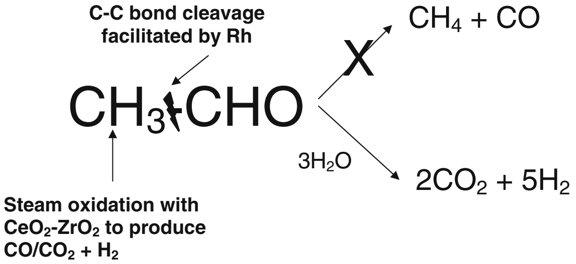

Figure 3. Possible reaction pathway for steam reforming of CH_3CHO over Rh/CeO_2–ZrO_2 to increase H_2 selectivity.

Rh/Al_2O_3 or $MgAl_2O_4$. On zirconia-promoted ceria supports, the reaction pathway favors an acetaldehyde intermediate. A 2%$Rh/Ce_{0.8}Zr_{0}.2O_2$ catalyst, with the support prepared by co-precipitation, exhibits the highest H_2 yield at low temperatures. Hydrogen yield exceeding thermodynamic equilibrium can be achieved over this catalyst. In addition, stable catalyst performance was demonstrated for 15 h at 450 °C. High-Ce content increases H_2 yield, possibly due to high-oxygen storage capacity. A strong interaction between Rh and support also appears to play an important role in enhancing oxygen transfer efficiency during ethanol steam reforming.

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