Selective Production of H_2 from Bio-Ethanol at Low Temperatures over Rh/CeO_2-ZrO_2 Catalysts

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Introduction

Ethanol steam reforming has been the subject of several studies targeting hydrogen production from renewable resources [1-4]. Undesirable reaction byproducts are CH_4 and carbon. Thermodynamically, coke and CH_4 formation become disfavored whereas H_2 becomes increasingly favored with increasing temperature. However, high temperature reforming provides a thermal mismatch with proton-exchange membrane fuel cells (PEMFC), and ethanol steam reforming is thermodynamically possible at low temperatures. In addition, low temperature reforming can increase overall system efficiency and reduce the material costs of hardware construction. In this paper, we have evaluated a series of supported metal catalysts in an effort to identify the most promising for low temperature hydrogen production.

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%) catalyst support was prepared by co-precipitation at 80 °C and pH of 10 using a 15% ammonia solution. The precipitate was digested at 80 °C for 3 days. Supported Rh catalysts were prepared by the incipient wetness method using the metal nitrate. 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. We also employed as-synthesized (AS) support material without calcination. For example, 500/AS means the catalyst was calcined at 500°C and the support was the as-synthesized material.

Catalytic activity measurements were conducted in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm at 1 atm [4]. Catalyst charge was 50 mg, and SiC was employed as a catalyst diluent. A steam to carbon ratio of 4 and a space velocity of 133,333 cm^3/g cat-h were used, unless otherwise indicated.

Results and Discussion

Table 1. Comparison of reaction results at 450 °C and 85,320 cm^3/g cat-h space velocity

Support	X_{EtOH} (%)	H_2/EtOH (m/m)	S_{CH4} (%)	S_{CO} (%)	S_{CO2} (%)	$S_{C=C}$ (%)	Rh dispersion (%)
$Ce_{0.13}Zr_{0.87}O_2$	100	3.5	31	16	52	0	-
ZrO_2	42	1.4	27	55	12	10	18
Al_2O_3	98	1.2	3	25	2	68	32
$MgAl_2O_4$	74	1.8	29	50	10	10	48
Equilibrium	100	2.4	44	2	53	0	-

In the initial stages of the work, the role of the catalyst support was examined for ethanol steam reforming using Rh as the active metal. Rh was chosen since it is known to exhibit the highest activity of all the precious metals [1-4]. Table 1 summarizes the results with 1%Rh catalysts at 450 °C and 85,320 cm^3/g cat-h space velocity. Apparently, support identity rather than metal dispersion has significant effects on the activity with Rh/CeO_2-ZrO_2 exhibiting the best H_2 yield among the catalysts studied. In a subsequent series of experiments, the CeO_2-ZrO_2 support pre-calcination and catalyst calcination temperatures were systematically varied to evaluate the metal-support interaction and the related effects on H_2 yield. Table 2 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. 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 behavior, indicating that the support pre-calcination temperature is not a significant factor between 500 and 800 °C despite the potential for sintering the CeO_2 phase. 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.

It has been established that acetaldehyde is a reaction intermediate and easily undergoes decarbonylation to form CH_4 and CO [3]. Once CH_4 forms, high temperatures are required to reform it into CO and H_2. Therefore, in order to maximize H_2 formation, the CH_3 group (which is the precursor to CH_4) needs to be oxidized with steam before CH_4 is allowed to form (Figure 1). It is possible that Ce sites in CeO_2-ZrO_2 are partially oxidized under reforming conditions [5] and these partially oxidized sites provide active oxygen species, which may suppress CH_4 formation. We speculate that the 500/AS catalyst has better interaction between Rh and support as a result of the single calcination, resulting in more effective oxygen transfer. Further physicochemical characterization of this catalyst system will be presented.

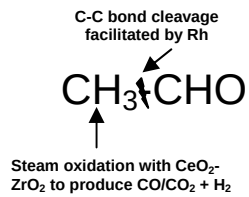

Figure 1. Approach to increase H_2 selectivity from acetaldehyde

Table 2. Comparison of EtOH conversion and selectivities to CH_4, CO, and CO_2 at 450 °C

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

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