Steam Reforming of Ethanol to Hydrogen over Rh/Y_2O_3 Catalyst

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Introduction

Production of H_2 has attracted intense research interests recently due to the ever-increasing demand of alternative energy sources, especially in the implementation of fuel cell system [1]. Steam reforming of ethanol (SRE) has been widely investigated because ethanol is renewable, biodegradable, easy to transport and easily decomposed in the presence of water to produce hydrogen-rich product [2]. Metals such as Ni, Rh, Pt, Co, and Pd have been used as the active component of catalysts in SRE [3, 4]. Among these active metals, Rh is the most active metal in SRE and the order of the activity of metals in SRE is as follows: Rh > Pd > Ni = Pt [5].

In this study, a new Rh/Y_2O_3 catalyst, which has not been reported in the literature before, has been found to have much higher hydrogen production rate as compared with Rh/CeO_2, Rh/Al_2O_3, and Rh/La_2O_3 at 650-800°C. Moreover, a new evaluation factor H_2/C has been established in this study to evaluate the performance of catalysts in SRE as it relates to the efficiency of the catalysts in converting ethanol stoichiometrically.

Materials and Methods

Rh/Y_2O_3, Rh/CeO_2, Rh/La_2O_3 and Rh/Al_2O_3 catalysts were prepared by wet impregnation method. The starting solution was prepared by mixing $Ce(NO_3)_3{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}6H_2O$ with the solution of $Rh(NO_3)_3$, respectively. The catalysts were characterized using XRD, TPR, FESEM, XPS and TGA/DTA.

Steam reforming of ethanol reaction was conducted in a stainless steel tube reactor fitted in one tube furnace and linked to an online gas chromatography to analyze the molar percentage of each component in reaction gas product. Typically, 100 mg of catalysts were used for each reaction and the catalyst was reduced under stream of 25% H_2/N_2 at 450°C for 30 min prior to steam reforming reactions.

Results and Discussion

Figure 1(a) shows the conversion of ethanol as a function of temperature over four Rh-based catalysts. Rh/Y_2O_3 catalyst is found to have the highest ethanol conversion at temperature higher than 600°C.

Figure 1(b) shows that Rh/CeO_2 has higher hydrogen production rate than Rh/Y_2O_3 at temperature below 630°C due to the higher water gas shift activity of Rh/CeO_2 at 400-600°C. However, at temperature above 630°C, the hydrogen production rate of Rh/Y_2O_3 becomes higher than that of Rh/CeO_2. Our TPR result (not shown) shows that the excellent performance of Rh/Y_2O_3 around 650-750°C is attributed to the easier reducibility of Y_2O_3 at this temperature range.

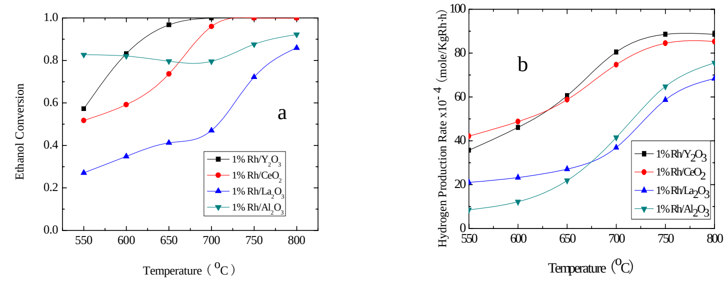

Figure 1. Effect of reaction temperature on (a) Ethanol conversion and (b) Hydrogen production rate over various Rh-based catalysts.

Rh/Y_2O_3 is found to be the most active catalysts among the four catalysts investigated in this study, with Rh/La_2O_3 displaying the poorest activity. At 650-800°C, the order of the activity of catalysts is as follows: Rh/Y_2O_3 > Rh/CeO_2 > Rh/Al_2O_3 > Rh/La_2O_3. Several catalytic properties have been observed on these four Rh-based catalysts: (1) doubling the feed flow rate results in doubling the hydrogen production rate (an optimal GHSV of 105,000 h^{-1} over Rh/Y_2O_3 at 700°C has been found to maximize H_2/CO molar ratio value); (2) increasing reaction temperature from 550°C to 700°C causes a substantial increase of hydrogen production rate; (3) Rh/Y_2O_3 shows the highest hydrogen production rate at 650-800°C, even better than Rh/CeO_2 catalyst which has been investigated extensively by many researchers. Furthermore, not only Y_2O_3 produces higher hydrogen production rate, but also the price of Y_2O_3 is generally half the price of CeO_2. Therefore, Y_2O_3 is a potential commercial SRE catalyst support and Rh/Y_2O_3 is a good choice of catalyst for SRE.

Significance

1. Order of the activity of catalysts is: Rh/Y_2O_3 > Rh/CeO_2 > Rh/Al_2O_3 > Rh/La_2O_3.
2. Y_2O_3 can be reduced at lower temperature than CeO_2, hence Rh/Y_2O_3 produces higher hydrogen yield at the optimal SRE reaction temperature of around 700°C.
3. Y_2O_3 is much cheaper than CeO_2, hence Y_2O_3 is a potential commercial SRE catalyst support.

References

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