Rh Supported on Y$_2$O$_3$ Nanotube: A Novel Catalyst for Steam Reforming of Ethanol to Hydrogen

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Introduction

Over the last decade, production of H$_2$ from renewable sources has been extensively investigated as alternative energy sources [1]. Ethanol, one of renewable sources, has been considered to be a suitable candidate for production of H$_2$ because it is less toxic, biodegradable, and easily transportable [2]. Steam reforming of ethanol (SRE) has attracted intense research interests recently due to its high yield of hydrogen and relatively milder reaction temperature than those required for steam reforming of methane.

Since Rh is known to be a very active catalyst for SRE [3], in the present study we have supported Rh on Y$_2$O$_3$ nanotubes newly-synthesized in our lab and used it, for the first time, as a novel catalyst for SRE reaction. Among the catalysts investigated, Rh/Y$_2$O$_3$ nanotube catalyst is found to be very active in SRE reaction to produce high yield of hydrogen.

Materials and Methods

Y$_2$O$_3$ nanotubes were fabricated by hydrothermal synthesis method. Rh/Y$_2$O$_3$ nanotube catalysts were prepared by impregnation method with aqueous solution of RhCl$_3$ salt to yield 1 wt.% metal content. 1% Rh/Y$_2$O$_3$, 1% Rh/CeO$_2$, and 1% Ni/Y$_2$O$_3$ catalysts were prepared by impregnating Ce(NO$_3$)$_3$·6H$_2$O or Y(NO$_3$)$_3$·6H$_2$O with the aqueous solution of Rh(NO$_3$)$_3$, or Ni(NO$_3$)$_2$·6H$_2$O, respectively. XRD, FESEM, TEM, BET and TPD were used to characterize the catalysts.

Catalytic reactions were performed in a fixed bed stainless steel tube reactor fitted in one tube furnace at reaction temperatures ranging from 550°C to 800°C. The gas product was analyzed by online gas chromatography to obtain the molar percentage of each component. Typically, 100 mg of catalysts were used and reduced under stream of 25% hydrogen/nitrogen mixed gas at 450°C prior to catalytic measurement.

Results and Discussion

Figure 1 shows the TEM image of Rh/Y$_2$O$_3$ nanotube, clearly displaying that most of Y$_2$O$_3$ nanotubes appear intact after high temperature calcination. Due to the unique structural properties of Y$_2$O$_3$ nanotubes, the percentage of Rh over Y$_2$O$_3$ nanotube surface is higher than that over CeO$_2$ and Y$_2$O$_3$ surface, as confirmed by total H$_2$ uptake of four Rh-based catalysts (not shown). The H$_2$ uptake of Rh/Y$_2$O$_3$ nanotube catalyst is higher than that of Rh/Y$_2$O$_3$, Rh/CeO$_2$, and Ni/Y$_2$O$_3$ because most of Rh species could still still be highly dispersed on the Y$_2$O$_3$ nanotube surface, while a higher percentage of Rh species diffused into CeO$_2$ and Y$_2$O$_3$ phase. Hence, the high activity of Rh/Y$_2$O$_3$ nanotube catalyst is attributed to the improved dispersion of Rh species on the unique nanotube surface.

Figure 2 shows the hydrogen production rate over four Rh-based catalysts. At reaction temperatures ranging from 550 to 650°C, the hydrogen production rate of Rh/Y$_2$O$_3$ nanotube catalyst is around 40% higher than that of Rh/Y$_2$O$_3$ and Rh/CeO$_2$. This is because Rh/Y$_2$O$_3$ nanotube catalyst, which is found using NH$_3$-TPD (not shown) to contain much smaller quantity of acid sites than other catalysts, converted higher percentage of ethanol in the main steam reforming of ethanol to directly produce higher hydrogen yield. Therefore, Rh/Y$_2$O$_3$ nanotube catalyst is an active and selective SRE catalyst to produce higher yield of hydrogen at relatively milder reaction temperature.

Figure 3 shows the product selectivity of Rh/Y$_2$O$_3$ nanotube catalyst, whereby the dehydration of ethanol to produce ethylene - which is favored over acid sites - has been highly suppressed and the main steam reforming of ethanol to produce higher yield of hydrogen has been highly promoted over this Rh/Y$_2$O$_3$ nanotube catalyst. Furthermore, the TPD-NH$_3$ results (not shown) in fact shows that Rh/Y$_2$O$_3$ nanotube catalyst has the smallest amount of acid sites among the four catalysts investigated in this study.

Significance

1. Order of the activity of catalysts is: Rh/Y$_2$O$_3$ nanotubes > Rh/Y$_2$O$_3$ > Rh/CeO$_2$ > Ni/Y$_2$O$_3$.
2. Rh/Y$_2$O$_3$ nanotube catalyst has the smallest amount of acid sites, hence suppressing dehydration of ethanol to ethylene and improving steam reforming of ethanol to hydrogen.
3. Rh/Y$_2$O$_3$ nanotube catalyst has the highest Rh dispersion due to the unique structural property of Y$_2$O$_3$ nanotube.

References