Rh Supported on Y_2O_3 Nanotube: A Novel Catalyst for Steam Reforming of Ethanol to Hydrogen

X. S. Wu and S. Kawi *

*Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, *chekawis@nus.edu.sg*

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_2O_3 nanotube 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_2O_3 nanotube catalyst is found to be very active in SRE reaction to produce high yield of hydrogen.

Materials and Methods

Y_2O_3 nanotubes were fabricated by hydrothermal synthesis method. Rh/Y_2O_3 nanotube catalysts were prepared by impregnation method with aqueous solution of $RhCl_3$ salt to yield 1 wt.% metal content. 1% Rh/Y_2O_3, 1% Rh/CeO_2, and 1% Ni/Y_2O_3 catalysts were prepared by impregnating $Ce(NO_3)_3{\cdot}6H_2O$ or $Y(NO_3)_3{\cdot}6H_2O$ with the aqueous solution of $Rh(NO_3)_3$ or $Ni(NO_3)_2{\cdot}6H_2O$, 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 an 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_2O_3 nanotube, clearly displaying that most of Y_2O_3 nanotubes appear intact after high temperature calcination. Due to the unique structural properties of Y_2O_3 nanotube, the percentage of Rh over Y_2O_3 nanotube surface is higher than that over CeO_2 and Y_2O_3 surface, as confirmed by total H_2 uptake of four Rh-based catalysts (not shown). The H_2 uptake of Rh/Y_2O_3 nanotube catalyst is higher than that of Rh/Y_2O_3, Rh/CeO_2, and Ni/Y_2O_3 because most of Rh species could still still be highly dispersed on the Y_2O_3 nanotube surface, while a higher percentage of Rh species diffused into CeO_2 and Y_2O_3 phase. Hence, the high activity of Rh/Y_2O_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_2O_3 nanotube catalyst is around 40% higher than that of Rh/Y_2O_3 and Rh/CeO_2. This is because Rh/Y_2O_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_2O_3 nanotube catalyst is an active and selective SRE catalyst to produce higher yield of hydrogen at relatively milder reaction temperature.

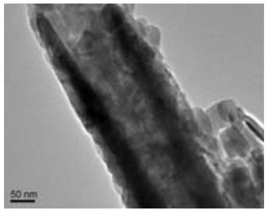
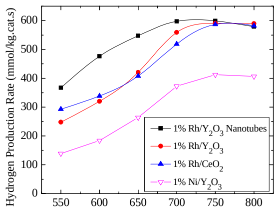


Figure 1. TEM of Rh/Y_2O_3 nanotube



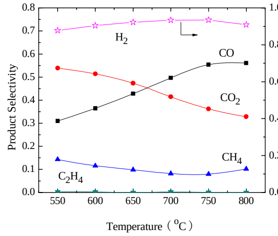


Figure 2. H_2 production rate of Rh catalysts **Figure 3.** Product selectivity of Rh/Y_2O_3 nanotube

Figure 3 shows the product selectivity of Rh/Y_2O_3 nanotube catalyst, whereby the dehydration of ethanol to produce ethylene - which is favored over acid sites - has been fully suppressed and the main steam reforming of ethanol to produce higher yield of hydrogen has been highly promoted over this Rh/Y_2O_3 nanotube catalyst. Furthermore, the TPD-NH_3 results (not shown) in fact shows that Rh/Y_2O_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_2O_3 nanotubes > Rh/Y_2O_3 > Rh/CeO_2 > Ni/Y_2O_3.
2. Rh/Y_2O_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_2O_3 nanotube catalyst has the highest Rh dispersion due to the unique structural property of Y_2O_3 nanotube.

References

1. A. N. Fatsikostas, X. E. Verykios. *J. Catal.* 225, 439 (2004).
2. M. Benito, J.L. Sanz, R. Isabel, R. Arjona, L. Daza. *J. Power Sources* 151, 11 (2005).
3. F. Aupretre, C. Descorme, D. Duprez, D. Casanave, Denis Uzio. *J. Catal.* 233, 464 (2005).