Rh catalyst supported on core-shell structured Ce-Zr-Al oxide for steam reforming of toluene

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Abstract: Steam reforming of toluene as a biomass tar model compound was investigated over Rh/CeO_2-ZrO_2-Al_2O_3 catalysts with different support structures. The catalyst with a core-shell structure, consisting of centered CeO_2-ZrO_2 solid solution and surrounding Al_2O_3 particles, exhibited higher activity than that without the core-shell structure. The results of isotopic labeling, H_2-TPR and operando XAFS experiments indicated that a three-phase interface of Rh, CeO_2-ZrO_2 and Al_2O_3 particles were formed on the core-shell structure and promoted reduction of RhO_x species and activation of H_2O at lower temperatures.

Keywords: steam reforming, ceria-zirconia-alumina, core-shell.

1. Introduction

Utilization of biomass has attracted attentions as a renewable energy source. One of the critical problems in H_2 rich gas production is tar condensation at low temperatures. In order to remove the biomass tar, several catalysts for steam reforming have been reported, in which toluene is often used as a biomass tar model compound [1]. In this paper, we used Rh catalyst supported on a core-shell structured Ce-Zr-Al oxide for steam reforming of toluene and the effect of core-shell structure was investigated.

2. Experimental

A powdery CeO_2-ZrO_2-Al_2O_3 support with a core-shell structure (CS) was synthesized by coprecipitation method, followed by hydrothermal treatment at 393K for 2h and by calcination at 873K for 5h. Another powdery CeO_2-ZrO_2-Al_2O_3 support without the core-shell (NCS) was synthesized by the same method, but without hydrothermal treatment. These two supports have the same composition (Ce/Zr/Al = 61/10/29 at%). Powdery CeO_2 (JRC-CEO-3), CeO_2-ZrO_2 and Al_2O_3 were used as reference supports. Supported Rh catalysts were prepared by wet impregnation of the above supports with a $Rh(NO_3)_3$ solution. Portions of the catalysts were aged in 5% H_2/N_2 at 1023K for 5h and in 10% O_2/N_2 at 1073K for 5h.

The characterization of the catalysts was conducted by using XPS, TEM and BET techniques. Toluene steam reforming test was performed in a fixed-bed flow reactor. The conversion was calculated by detected gas concentration with GC-TCD as follows; toluene conversion = (1-(produced CO + produced CO_2 + produced CH_4)/(fed C_7H_8)) x 100.

The effect of the core-shell structure was examined by FT-IR, $H_2{}^{18}O$ isotopic labeling experiment in toluene steam reforming, H_2-TPR and operando XAFS in C_3H_6 steam reforming. The first two were carried out by similar methods in previous studies [2]. The operando XAFS was conducted at Toyota Beam Line (BL33XU) in SPring-8.

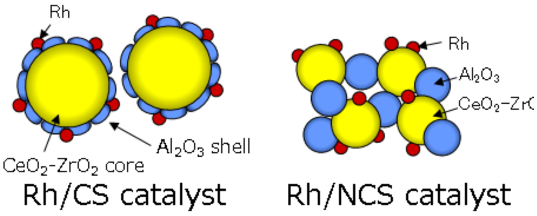

Figure 1. Schematics of the Rh/CS (cross sectional image) and Rh/NCS catalysts.

3. Results and discussion

The results of XPS show that the CS support has much higher surface Al concentration (44 at%) than bulk Al concentration (29 at%) of the support, while the NCS support has almost the same Al concentration as the bulk one. These results demonstrate that the CS support is composed of CeO_2-ZrO_2 core and Al_2O_3 shell structure. Schematic images of the structure are shown in Fig. 1.

The Rh/CS catalyst shows the highest conversion in toluene steam reforming among all catalysts. The order of catalyst in toluene-reforming activity; Rh/CS > Rh/NCS > Rh/CeO_2 has been found.

Table 1. Summary of BET, XPS and toluene conversion results.

Catalyst	Surface Area (m^2/g)		XPS (at%)				Toluene conversion (%)	
	Fresh	Aged	Ce	Zr	Al	Al/(Ce+Zr)	773 K	873 K
Rh/CS	81.2	44.4	46.8	8.9	44.2	79.4	30.2	50.8
Rh/NCS	82.4	36.0	60.3	8.7	31.0	44.9	24.4	46.2
Rh/CeO_2		19.7	-	-	-	-	12.4	26.0

To investigate the effect of the core-shell structure, FT-IR, $H_2{}^{18}O$ isotopic labeling, H_2-TPR and operando XAFS measurements were performed. The intensity of the IR absorbance indicating the decomposition of the adsorbed toluene into carbonated species was in agreement with the catalytic activity. In isotopic labeling experiment using $H_2{}^{18}O$, higher intensity in signal of $C^{18}O$ in the Rh/CeO_2-ZrO_2 catalyst is detected compared to that in the Rh/Al_2O_3 catalyst. This result reveals that H_2O on the CeO_2-ZrO_2 support is activated more highly than that on the Al_2O_3 support, probably due to its higher mobility of lattice oxygen in the CeO_2-ZrO_2.

Fig. 2 shows energy shifts of (a) the Rh K-edge and (b) the Ce K-edge in operando XAFS as a function of temperature for the Rh/CS and the Rh/NCS catalysts. RhO_x species on the Rh/CS catalyst was reduced to Rh metals, accompanied by H_2 generation, at lower temperatures than that on the Rh/NCS catalyst. A part of the CeO_2 in the Rh/CS catalyst is also reduced at lower temperatures but at a smaller extent. These results indicate that the Rh/CS catalyst has smaller amount of Rh-CeO_2 interface compared to the Rh/NCS catalyst, implying that it has larger amount of Rh-Al_2O_3 interface instead. H_2-TPR results showed that RhO_x species on the Al_2O_3 support was reduced more easily than that on the CeO_2 support. Therefore, it is concluded that the core-shell structure in the Rh/CS catalyst promotes reduction of RhO_x through Rh-Al_2O_3 interface and activation of water through Rh-CeO_2 interface, resulting in the high activity.

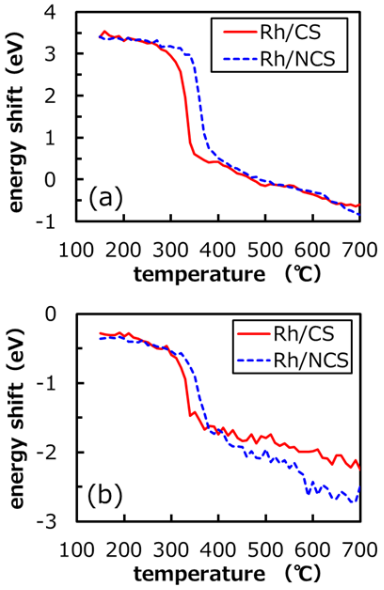

Figure 2. Energy shifts of (a) Rh-K edge and (b) Ce-K edge in C_3H_6 steam reforming as a function of temperature.

4. Conclusions

The catalyst with a core-shell structure, consisting of centered CeO_2-ZrO_2 solid solution and surrounding Al_2O_3 particles, exhibited higher activity for steam reforming of toluene than that without the core-shell structure. The core-shell structure promotes reduction of RhO_x species and activation of H_2O, probably due to formation of its three-phase interface of Rh, CeO_2-ZrO_2 and Al_2O_3 particles, resulting in the high activity.

References

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