Preparation and Characterization of the Ni/CeO₂/Al₂O₃ Catalyst for

Steam gasification of Biomass

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Introduction

Conversion of biomasses to hydrogen and synthesis gas becomes more and more important in terms of the utilization of renewable sources. Our group has been reported that Rh/CeO₂/SiO₂ was very effective to the gasification of biomass [1]. However, the catalyst has problems in high cost and limited availability originated from the usage of Rh. Recently, we have investigated various oxide supported Ni catalysts in steam gasification. As a result, it is found that CeO₂ support played an important role on the decrease of coke deposition. Here we show the results of the EXAFS analysis of the Ni/CeO₂/Al₂O₃ catalysts prepared by co-impregnation and sequential impregnation methods and we discuss the relation between the results and catalyst activity for steam gasification of real biomass.

Experimental

Ni/CeO₂/Al₂O₃ catalysts were prepared by two different methods. One was co-impregnation method, and the other was sequential impregnation method. In the coimpregnation method, an Al₂O₃ support (JRC-ALO-1) was impregnated with the aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $Ce(NH_4)_2(NO_3)_6$ (Wako) mixture by the incipient wetness method. In the case of the sequential impregnation, the CeO₂ was loaded on the Al₂O₃ and after the calcination at 773 K for 3 h, Ni was loaded on this CeO₂/Al₂O₃. After the impregnation, both catalysts were dried at 383 K for 12 h, followed by the calcination at 773 K for 3 h under air atmosphere. The loading amount of Ni was 4 wt%, and that of CeO₂ was 30 wt%. The catalysts prepared by the co-impregnation method and the sequential impregnation method are denoted as Ni/CeO₂/Al₂O₃ (CI) and Ni/CeO₂/Al₂O₃ (SI), respectively. EXAFS spectra were measured by transmission mode at 77 K. After back ground subtraction, k^3 weighted EXAFS functions were Fourier transformed into R space and the one or two-shell fitting were analyzed by curve fitting.

Results and Discussion

The Fourier transforms of k^3 -weighted Ni K-edge EXAFS oscillations for reduced Ni/CeO₂/Al₂O₃ (CI), Ni/CeO₂/Al₂O₃ (SI) and Ni/Al₂O₃ catalyst are shown in Fig. 1 and the fitting results are summarized in Table 1. From the fitting results of EXAFS data, we could fit the spectrum only Ni-Ni species. The coordination number of Ni-Ni on the Ni/CeO₂/Al₂O₃ (SI) was similar to that of Ni/ Al₂O₃. On the other hand, Ni/CeO₂/Al₂O₃ (CI) gave much lower coordination number of Ni-Ni than other catalysts. This result indicates that the Ni particles were highly dispersed on the CeO,/Al,O, by co-impregnation and the particle size of Ni on the Ni/CeO₃/Al₃O₃ (CI) was much lower than that of Ni/CeO₂/Al₂O₃ (SI) and Ni/Al₂O₃ due to the strong interaction of CeO2 and Ni. And this can be related to the high performance of Ni/CeO₂/Al₂O₃ (CI) on the steam gasification of biomass.



Fig. 1. Results of Ni K-edge EXAFS analysis of Ni catalysts

Reference

[1] K. Tomishige, et al. *Appl. Catal. A: Gen.* **246** (2003) 103 *tkmyzw@ims.tsukuba.ac.jp

Table1	Curve fitting	g results of Ni-k	K edge EXAFS	of various Ni	catalysts aft	er reduced at 7	73 K

Catalyst	Shells	CN^{a}	$R / 10^{-1} \rm{nm}^{b}$	ơ⁄ 10 ⁻¹ nm ^c	$\Delta \! E_0 / eV^d$	$R_{\rm f}/\%^{\rm e}$
NiAl ₂ O ₃ (4-0)	Ni-Ni	10.4±0.2	2.49±0.001	0.082±0.002	-3.8±0.3	0.54
Ni/CeO ₂ /Al ₂ O ₃ (SI) (4-30)	Ni-Ni	10.5±0.3	2.49±0.001	0.088±0.002	-0.7±0.3	0.88
Ni/CeO2/Al2O3 (CI) (4-30)	Ni-Ni	8.3±0.3	2.48±0.002	0.089±0.003	-3.7±0.4	0.74
Ni Foil	Ni-Ni	12.0	2.49	0.06	0	

^aCoordination number. ^bBond distance. ^cDebye-Waller factor. ^dDifference in the origin of photoelectron energy between the reference and the sample. ^eResidual factor. Fourier filtering range: 0.129-0.295 nm.