

Structural characterization of coprecipitated Pd/Co and Pd/Fe catalysts for the selective hydrogenolysis of C-O bond in biomass derived compounds

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1 Introduction

One of the central challenges in biomass utilization is the catalytic, selective deoxygenation of polysaccharides, lignin, lipids, and their derivatives. Hence, the C-O bond hydrogenolysis is of particular significance since it allows the production of certain high value chemicals from biomass derived intermediate compounds (e.g. glycerol, sorbitol, furfural, aryl ethers, etc). [1]

Heterogeneous palladium catalysts were found to be poorly efficient in the hydrogenolysis of biomass derived polyols. [2, 3] However, in the last years, coprecipitated Pd/Co and Pd/Fe catalysts have been investigated for their superior performance in several catalytic reactions including the hydrogenolysis [4, 5] and the transfer hydrogenolysis (CTH) of glycerol. The enhanced catalytic performance shown by Pd/Co and Pd/Fe catalysts can be related to the preparation method used (coprecipitation technique) that ensures a strong metal support interaction (SMSI) between palladium and the cobalt/iron oxide support.

In the present study we show the results of EXAFS analysis on Pd/Co and Pd/Fe catalysts that clearly show the formation of bimetallic Pd-Co and Pd-Fe ensembles that positively promote the C-O bond cleavage.

2 Experiment

Pd/Co and Pd/Fe catalysts were prepared by using the coprecipitation technique and were obtained from aqueous solutions of the corresponding inorganic precursors. Anhydrous palladium chloride (Fluka, purum, 60% palladium) was dissolved in HCl and cobalt(II) nitrate hexahydrate (Fluka, purity $\geq 99\%$) or iron(III) nitrate nonahydrate (Fluka, purity $\geq 98\%$) were added. The obtained aqueous metal salt solutions were added dropwise into a 1 M aqueous solution of Na_2CO_3 . After filtration, samples were washed until complete removal of chloride ions, dried for 1 day at 353 K under vacuum and further reduced at 473 K for 2 h under a flow of H_2 .

Extended X-ray absorption fine structure (EXAFS) of the Pd-based catalysts were measured at the Photon Factory of the High Energy Accelerator Research Organization. Co-K and Fe-K edge XANES/EXAFS spectra for the catalysts were obtained using a Si(111) two-crystal monochromator with beam line BL9A and Pd K-edge spectra were obtained using a Si(311) two-crystal monochromator with beam line NW10A. Analysis of the

EXAFS data was performed using the EXAFS analysis program, REX (Rigaku Co.).

3 Results and Discussion

The extended X-ray absorption fine structure results at Co-K and Fe-K edge show the Co_3O_4 and Fe_3O_4 support structure of Pd/Co and Pd/Fe samples in agreement with XRD and H_2 -TPR analysis that shows a strong promoting effect of palladium on cobalt oxide and iron oxide reduction.

Table 1 reports the main results of extended X-ray absorption fine structure (EXAFS) characterization at the Pd K-edge. In both Pd/Co and Pd/Fe catalysts, the most striking feature is the direct observation of a shorter scattering Pd-Co and Pd-Fe paths of 2.51 Å compared with the Pd-Pd distance of about 2.70 Å confirming the formation of Pd-Co and Pd-Fe bimetallic ensembles.

Table 1: X-ray absorption fine structure characterization at the Pd K-edge for Pd/Co and Pd/Fe catalysts.

Sample	Scattering Pair	CN	BD (Å)	dE (eV)	dW (Å ²)	R (%)
Pd/Co	Pd-Pd	0,93	2,69	-5,81	0,021	0,02
	Pd-Co	3,92	2,51	1,2	0,047	
Pd/Fe	Pd-Pd	2,59	2,71	-4,7	0,91	0,02
	Pd-Fe	0,78	2,51	-3,7		

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