

Fine Structural Changes around Pd in Pd/C Employed for the Oxidative Esterification of Propionaldehyde under Pressurized Oxygen

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Introduction

The use of pressurized O₂ greatly enhanced catalytic activity for oxidative esterification of propionaldehyde to methyl propionate with methanol using heavy-metal-free Pd/C demonstrating that doping with heavy metals of Pd catalysts was not needed to achieve comparable activity, which runs contrary to a previous report [1]. To detect fine structure changes in the Pd/C during the reaction, EXAFS was analyzed near the Pd-K edges using the samples obtained before and after the reaction at 1.5 MPa. Based on EXAFS results, the metallic nature of Pd was maintained even after the oxidative esterification of propionaldehyde under pressurized O₂.

Experimental

Into a stainless steel autoclave, a methanol solution containing NaOH, Mg(OH)₂ and propionaldehyde was added [1]. After an autoclave was filled with O₂, the reaction temperature was adjusted to 333 K in the presence of 5%Pd/C and stirred at 700 rpm for 5 h. Analysis of EXAFS near the Pd K-edge was carried out at the High-Energy Accelerator Research Organization (Tsukuba, Japan) with a storage ring current of approximately 400 mA (6.5 GeV). The X-ray was monochromatized with Si(311) at an NW-10A station. The absorption spectra were observed using ionization chambers in transmission mode.

Results and Discussion

It has been already reported that the oxidative esterification of propionaldehyde to methyl propionate in the liquid phase occurs readily using Pd/Al₂O₃ doped with Pb in the presence of Mg(OH)₂ and NaOH in aqueous methanol at 353 K with 0.3 MPa of O₂ gas in a solution with pH of 6-8 [1]. However, using 1.0 g of 5%Pd/C at 333 K with a reaction time of 6 h dramatically improved the yield of methyl propionate from 11.9% at 0.1 MPa to 36.2 % at 0.5 MPa and was kept nearly constant by 2.0 MPa. The highest yield was 38.5% at 1.5 MPa, in which the conversion of propionaldehyde and the selectivity to methyl propionate were 64.7 and 59.5%, respectively. In order to check fine structural changes in 5%Pd/C before and after the employment for the oxidative esterification, EXAFS near the Pd K-edge was employed.

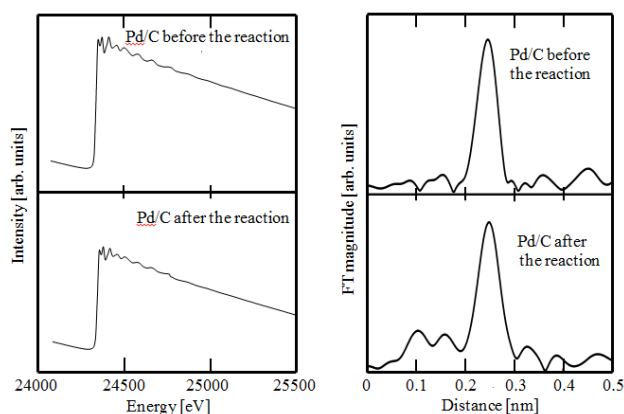


Figure 1. Pd K-edge spectra and the corresponding Fourier transformation of Pd/C before and after the oxidative esterification of propionaldehyde at 1.5 MPa for 6 h.

The Pd-K edge EXAFS spectra (left column in Fig. 1) showed that the absorption due to Pd/C before and after the reaction at 1.5 MPa were essentially identical, which was due to the metallic Pd. The corresponding Fourier transformation near the Pd K-edge for these samples (right column in Fig. 1) showed one signal characteristic metallic Pd; weak or noise-level signals were also detected from Pd/C after the reaction. The nearest-neighbor distance around the Pd increased from 0.274 nm before the reaction to 0.278 nm after the reaction. Furthermore the coordination number increased from 8.18 before the reaction to 9.08 after the reaction. These results are explained by the incorporation of either hydrogen or carbon into Pd bonds [2]. Incorporation of these species might lower the crystallinity of Pd/C during the reaction, which was observed in the XRD. Based on these results, the metallic nature of Pd was maintained even after the reaction under pressurized O₂.

References

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