

## Fine Structural Changes around Pd in Pd/C Employed for the Oxidative Dehydrogenation of Sodium Lactate

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### Introduction

The oxidative dehydrogenation of sodium lactate to sodium pyruvate in an aqueous phase at 358 K under pressurized oxygen at 1 MPa proceeded favorably using 5%Pd/C with no adjustment of solution pH, while it had been already reported that the oxidative dehydrogenation of lactic acid to pyruvic acid in an aqueous phase did not proceed with Pd/C at atmospheric pressure and 363 K in an aqueous NaOH solution at a pH of 8. When Pd/C previously employed for the activity test was again used for the reaction, the activity slightly decreased. To clarify a cause on the decrease of the activity in the second run, EXAFS analysis near the Pd K-edge was carried out using 5%Pd/C before and after the activity test.

### Experimental

The typical procedure for the catalytic activity test was as follows. Into a stainless steel autoclave, an aqueous solution containing sodium lactate was added. After an autoclave was filled with O<sub>2</sub>, the reaction temperature was adjusted to 358 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

The oxidative dehydrogenation of sodium lactate to sodium pyruvate using 5%Pd/C and 100% oxygen slightly proceeded at atmospheric pressure. However the activity using Pd/C dramatically improved by increasing the pressure using oxygen and finally reached the sodium pyruvate yield of 45.8 % at 1.0 MPa. In order to check the reproducibility of the catalytic activity of the used catalyst, the catalysts, which was recovered from the first run, was again used for the reaction. Unfortunately the activity decreased by approximately 8%. In order to check fine structural changes in 5%Pd/C before and after the employment for the oxidative dehydrogenation, EXAFS near the Pd K-edge was employed. The Pd K-edge XANES spectra show that the absorption edge observed from Pd/C before and after the oxidative dehydrogenation of sodium lactate at 1.0 MPa and 358 K

was essentially identical (Fig. 1 (A)). Furthermore the corresponding Fourier transformation around the Pd K-edge obtained from these samples shows one signal that is characteristic of metallic Pd (Fig. 1 (B)). However, the nearest-neighbor distance around Pd obtained from EXAFS affords further information on the fine structural changes during the reaction. The nearest-neighbor distance around Pd was extended from 0.274 nm before the reaction to 0.276 nm after the reaction. Furthermore, in contrast, coordination number around Pd was decreased from 7.44 before the reaction to 7.33 after the reaction. This can be explained by the incorporation of either hydrogen or carbon between Pd-Pd, resulting in the lowering of the catalytic activity.

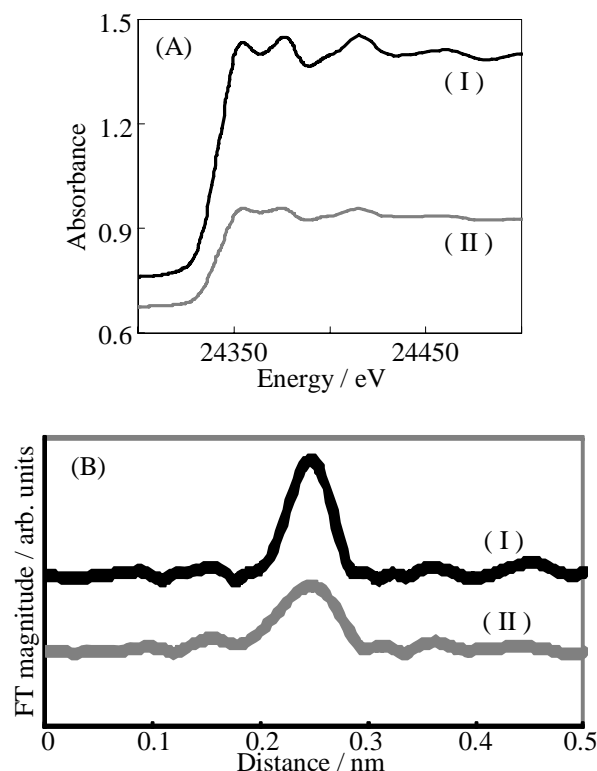


Fig. 1. Pd-K-edge spectra (A) and the corresponding Fourier transformation (B) of EXAFS of Pd/C before (I) and after (II) the oxidative dehydrogenation of sodium lactate at 358 K and 1.0 MPa (100% O<sub>2</sub>).

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