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EXAFS of Palladium in Pd/C and Te-Pd/C Catalysts for the Oxidative Dehydrogenation of Sodium Lactate

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Introduction

In the present study, it was found that the oxidative dehydrogenation of sodium lactate to sodium pyruvate in an aqueous phase proceeded favorably using 5%Pd/C and that doped with Te at 358K with no adjustment in solution pH under pressurized oxygen, although previous reports had stated that this reaction would not proceed using Pd/C while Pd/C doped with either Pb, Bi or Te showed the activity at atmospheric pressure, 363K, and a pH of 8. To confirm whether either the metallic species or the cation species of palladium, analysis of EXAFS near the Pd-Kedge was carried out using 5%Pd/C and 0.19%Te-5%Pd/C before and after the oxidative dehydrogenation.

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_2, the reaction temperature was adjusted to 358 K in the presence of a catalyst (5%Pd/C, 0.19%Te-5%Pd/C; 0.25 g) and stirred at 700 rpm for 5 h. Analysis of EXAFS near the Pd K-edge was carried out at the High-Energy 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 on 5%Pd/C did not proceed at atmospheric pressure. However, the sodium pyruvate yield dramatically improved by increasing the pressure using oxygen and finally reached 63.9% at 0.75 MPa. The beneficial effect of increased pressure was also observed for 0.19%Te-5%Pd/C at 1 MPa. As expected, the yield of sodium pyruvate was improved by the addition of Te to Pd/C and reached a maximum yield of 68.2% on 0.19Te-5%Pd/C.

To confirm whether either the metallic species or the cation species of palladium on those catalysts, analysis of EXAFS near the Pd-Kedge was carried out before and after the reaction. The Pd K-edge XANES spectra show that the absorption edge observed from 5%Pd/C (Figs. 1 (1) and (3)) and 0.19%Te-5%Pd/C (Figs. 1 (2) and (4)) before (Figs. 1 (1) and (2)) and after (Figs. 1 (3) and (4)) the reaction was essentially identical. Furthermore, the corresponding Fourier transformation around the Pd K-edge obtained from all the samples shows one signal that is characteristic of metallic palladium (not shown). Therefore, the formation of Pd-Te binary alloys during oxidative dehydrogenation may be possible. The nearest-neighbor distance around palladium obtained from EXAFS analysis affords further information on the fine structural changes during the reaction. Regardless of the presence of tellurium in the catalyst, the nearest-neighbor distance around palladium was extended from 2.74 nm to 2.76 nm after the reaction, indicating the incorporation of either hydrogen or carbon between the palladium bonds during the reaction together with the formation of Pd-Te binary alloys.

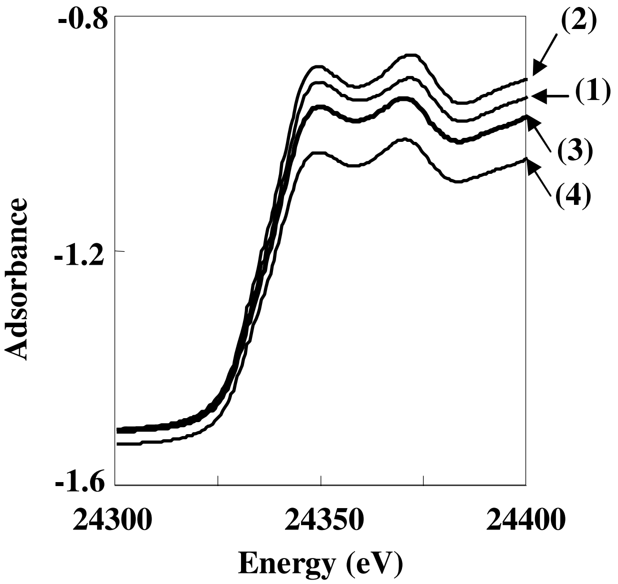

Fig. 1 Pd K-edge XANES of 5%Pd/C and 0.19%-5%Pd/C before and after the reaction.

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