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Effect of the Supports on the Oxidative Esterification of Propionaldehyde on Supported Palladium Catalysts

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1 Introduction

Recently, Pd catalysts doped with a heavy metal supported on various oxides and active carbon have attracted attention, particularly for industrial application. However, recent reports state that the use of pressurized O_2 resulted in great activity for the reaction of sodium lactate to sodium pyruvate using heavy-metal-free Pd/C, indicating that loading by heavy metals is not needed for the catalytic reaction, which is important for green chemistry and suggests the potential use of heavy-metal-free Pd catalysts for other catalytic reactions [1]. The direct oxidative esterification of propionaldehyde (PA) to methyl propionate (MP) in the liquid phase attracts attention in our laboratory [2]. Earlier studies have established that the oxidative esterification of PA to MP in the liquid phase occurs readily using Pd/Al_2O_3 doped with Pb [3]. In the present study, Pd/C and Pd/Al_2O_3 without heavy-metal doping were used for the direct oxidative esterification of PA to MP in the liquid phase under at 0.1 MPa of O_2 to examine the unnecessary of heavy-metal doping and the effect of the supports.

2 Experiment

Pd/C and Pd/Al_2O_3 (both with Pd of 5% by weight) were used as supplied. The BET surface areas of Pd/C and Pd/Al_2O_3 were 946 and 94.0 m^2/g, respectively. Catalytic activity was tested in a magnetically-stirred stainless steel autoclave (85 ml) reactor. The catalyst (0.5 g, Pd/C or Pd/Al_2O_3) was added into a 25 mL methanol solution containing 75 mmol of propionaldehyde in the reactor. Then, 25 μL of aqueous 5M NaOH and 0.025 g of $Mg(OH)_2$ were added to keep the solution pH at 6–8. Reactions were carried out at 333 K and oxygen pressure of 0.1 MPa. Analysis of EXAFS near the Pd-K edge was carried out at the High Energy Accelerator Research Organization with a storage ring current of 400 mA (6.5 GeV). The X-rays were monochromatized with Si(311) at an NW-10A station. The absorption spectra were observed using ionization chambers in the transmission mode. Since it was impossible to compress Pd/C and Te/Pd/C into a disk with diluents, the catalysts were carefully placed into a hand-made sample holder with two polypropylene windows. The photon energy was scanned in the range of 24,080–25,600 eV for the Pd-K edge.

3 Results and Discussion

At first, the oxidative esterification of PA with methanol was examined at 333 K and oxygen pressure of 0.1 MPa. After 2 h, the conversion of PA and the yield of to MP using Pd/C were 1.5 and 0.5% while 12.8 and 1.9 using Pd/Al_2O_3, indicating that Al_2O_3 support seems to be suitable support for the present system. Although the situation of Pd in both supported catalyst was checked using XRD, any evident differences of Pd species on those supported catalyst did not obtained. Therefore EXAFS analyses were employed to this catalyst system. Figure 1 shows the Pd-K edge EXAFS spectra of Pd/C (A) and Pd/Al_2O_3 (B), indicating that Pd nature on Pd/C was evidently different from that on Pd/Al_2O_3.

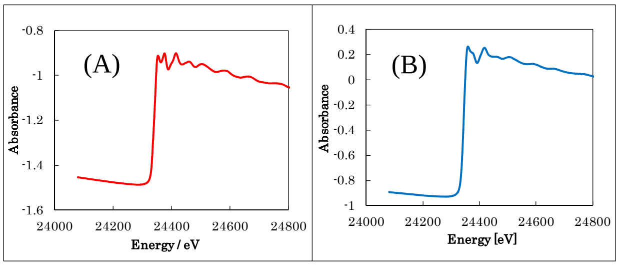

Figure 1. Pd-K edge EXAFS spectra of (A) Pd/C and (B) Pd/Al_2O_3.

Figure 2 shows the Fourier transformation of EXAFS of both supported catalysts. Single signal due to metallic Pd was detected from Pd/C while complex signals due to metallic and oxidized Pd species was detected from Pd/Al_2O_3. Therefore it may be concluded that the ease redox nature of PD species in Pd/Al2O3 results in the better activity that that using Pd/C

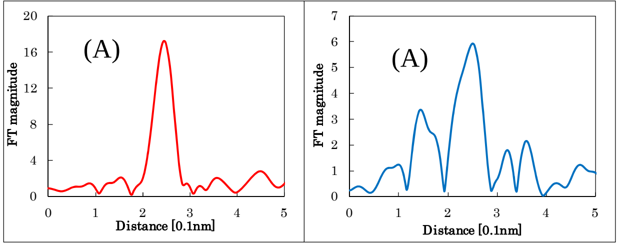

Figure 2. Fourier transformation of Pd-K edge EXAFS spectra of (A) Pd/C and (B) Pd/Al_2O_3.

References

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