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Electrochemical reduction of oxalic acid using TiO_2/ZrO_2 particle

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1. Introduction

Alcohols are regarded not only as an industrially important raw material but also as a transportable fuel. Alcohol production from biomass-derived carboxylic acid using renewable energy, therefore, will make a significant contribution to the realization of low-carbon society. We already found that TiO_2 shows excellent activities in the electroreduction of oxalic acid. Recently, we have reported that oxalic acid, a divalent carboxylic acid, can be electrochemically reduced to glycolic acid, an alcoholic chemical, on anatase-type TiO_2. For the further improvement of catalytic activities, in this study, we prepared anatase-type composite oxide catalysts by introduction Zr into TiO_2 and examined their catalytic activities.

2. Experimental

Complex oxide particles $Ti_{1-x}Zr_xO_2$ were prepared from mixtures of titanium tetraisopropoxide and ziruconium tetrapropoxide with various metal ratios by a solvothermal method. The electrochemical reduction of oxalic acid at a constant potential was performed by chronoamperometry two a conventional three-electrode cell connected to a potentiostat. The modified working electrode was prepared by applying a $Ti_{1-x}Zr_xO_2$ catalyst to Ti foils.

3. Results and discussion

Figure 1 shows yields of chemicals produced in the electrochemical reduction of oxalic acid using $Ti_{1-x}Zr_xO_2$ particles at -0.7 V vs RHE at 50 °C for 2 h. Product yields were significantly increasing with increase of the Zr content up to 10atom%. X-ray diffraction measurements suggested that $Ti_{1-x}Zr_xO_2$ catalysts including small amount of Zr less than 15atom% retain anatase-type crystalline structures. UV–visible diffuse reflectance spectra of complex oxide catalysts revealed that the band gap energy gradually increased from 3.26 eV for the pure TiO_2 to 3.36 eV for the mixed oxide sample including 10atom% of Zr. The blue shift of the absorption onset edge toward a shorter wavelength in the $Ti_{1-x}Zr_xO_2$ catalyst can be attributed to the larger band gap of ZrO_2. These results imply that electrons introduced by the electrode into the conduction band of anatase-type TiO_2/ZrO_2 have higher reduction potentials than those introduced into the conduction band of anatase-type TiO_2.

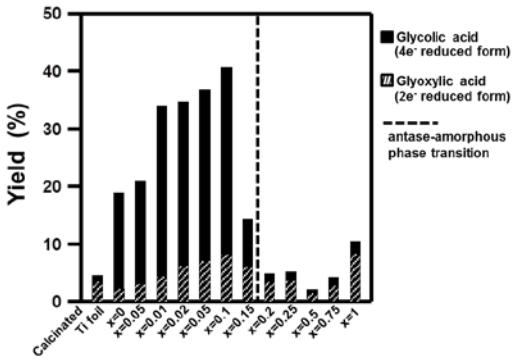

Fig. 1. Yield for products generated in oxalic acid electroreductions using calcinated Ti foil and $Ti_{1-x}Zr_xO_2$.