Liquid-Phase Oxidation of Glycerol over Au-Pd/TiO_2 Catalysts Using Molecular Oxygen as an Oxidant

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Introduction

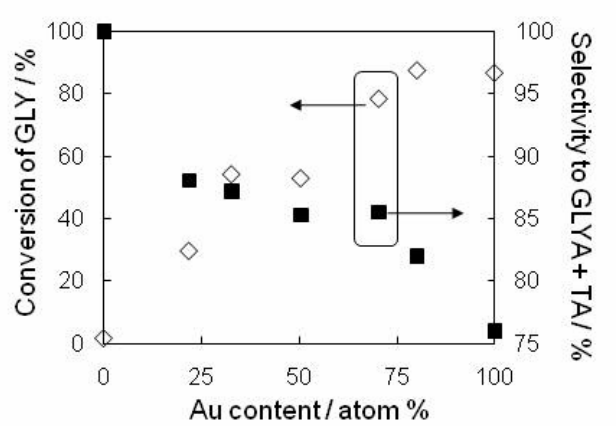
As the amount of bio-diesel production is increasing to reduce the carbon dioxide emission, valorization of glycerol (GLY), which is formed as a by-product from vegetable oil by ester-exchange, is one of the hot topics in the field of biomass utilization. Oxidation of GLY into valuable chemicals has been thus studied recently by using platinum, gold or gold-palladium bimetallic catalysts [1-3]. In this paper, we will present high-performance catalysts for GLY oxidation to glyceric acid (GLYA) and tartronic acid (TA).

Experimental

The Au-Pd/TiO_2 catalysts were prepared by the deposition-precipitation (DP) method [4], which is well-known for standard Au/TiO_2 catalyst for CO oxidation. The source of Au and Pd were $HAuCl_4$ and $PdCl_2$, respectively. After pH of the solution containing both Au and Pd at 6.3–7.0 by addition of dilute NaOH solution, TiO_2 powder (P25) was put into the neutralized Au-Pd solution. Then, the precipitation was washed and calcined at 673 K. GLY oxidation was operated in a stainless-steel batch-type reactor (diameter = 50 mm, depth = 170 mm, volume = 300 mL). The products were analyzed by high pressure liquid chromatography (HPLC).

Results/Discussion

Figure 1 shows the catalytic activities for glycerol oxidation over Au-Pd/TiO_2 catalysts with various Au content. By the addition of Pd, the selectivities to GLYA and TA increased, while the conversions of GLY decreased. The suitable contents of Pd were about 25–30 atomic %. The oxidation without NaOH did not give any catalytic activity, because the formation of $-O^-Na^+$ in the GLY molecule by the reaction between –OH group and NaOH is the important initial step in the GLY oxidation [5]. Also, the stirring speed strongly affected the conversion and selectivity. The suitable stirring speed was 750-900 rpm (The results for 750 rpm are shown in Figure 1). In the case of a slow stirring speed (300 rpm), the catalytic activity was very low (Conversion = 11.6 %, selectivity = 78.4 %).



Reaction conditions, T = 333 K, Initial O_2 pressure = 1.0 MPa, Catalyst = 50 mg, Reaction time = 1.0 h, **Stirring speed = 750 rpm**, GLY solution = 100mL (0.3 mol/L), **NaOH/GLY = 4** (molar ratio).

Figure 1. Effect of Au content in the Au-Pd/TiO_2 catalysts for the glycerol oxidation.

Figure 2 shows TEM images of the Au-Pd/TiO_2 catalyst with the best yield (in the frame in Figure 1). The diameter of the nano-particles was 5–10 nm and the shape was hemisphere-like one, which is similar to Au/TiO_2 catalyst [4].

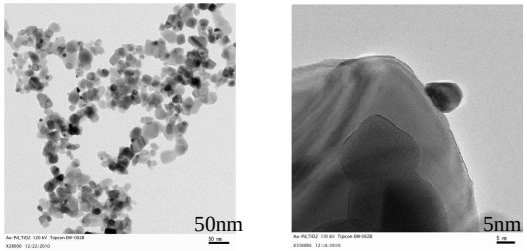


Figure 2. TEM images of Au-Pd/TiO_2 catalyst.

References.

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