Gold Nanoparticle-Catalyzed Transfer Vinylation of Carboxylic Acids: Effects of Supports and Gold Particle Size

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Vinyl esters are important compounds that be used for many organic syntheses such as synthesis of vinyl polymers, Claisen rearrangement, Heck reaction, and cycloaddition reactions. Tokunaga et al. reported that a homogeneous Au (I) catalyst shows high activity for transfer vinylation of carboxylic acid to give vinyl esters. On the other hand, supported gold nanoparticle catalysts have been intensively studied for not only gas but also liquid phase reaction. Recently, it has been reported that gold nanoparticles also work as soft Lewis acid catalysts as well as homogeneous Au(I or III) complexes do. Therefore, in this study, we explored transfer vinylation of vinyl esters with carboxylic acids using heterogeneous Au catalysts (Scheme 1).

Scheme 1. Transfer vinylation of benzoic acid with vinyl acetate.

Screening test of metal oxide supports was carried out using 1 wt% Au catalysts. From the screening test, gold on acidic and basic supports showed low catalytic activity. In contrast, Au on amphoteric ones showed moderate to good activity, and the highest activity was recorded by Au/ZrO₂ (Figure 1). Furthermore, a decrease in Au loading to 0.3 wt% improved the yield up to 82%. Mixed metal oxide supports of ZrO₂ were also examined. Although Au/TiO₂-ZrO₂ and Au/SiO₂-ZrO₂ showed low catalytic activity, Au/CeO₂-ZrO₂ exhibited better performance than Au/ZrO₂. Basic sites of metal oxide supports were evaluated by temperature-programmed desorption of carbon dioxide (CO₂-TPD). There was no significant difference in basicity between CeO₂-ZrO₂ and ZrO₂. According to HAADF-STEM, Au/ZrO₂ contained Au single atoms and large Au nanoparticles (average 5.6 nm), while only smaller Au nanoparticles (average 2.9 nm) were observed on CeO₂-ZrO₂. This result suggests that high activity of Au/CEO₂-ZrO₂ was ascribed to small gold nanoparticles, and the gold single atoms do not play a major role for this reaction. In addition, Au/CEO₂-ZrO₂ also catalyzed the transfer vinylation of carboxylic acids other than benzoic acid (Figure 2).

Figure 1. Relationships between electronegativity of metal oxide supports and yield of vinyl benzoate.

Figure 2. Substrate scope of carboxylic acids.

References

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