Enhanced Hydrogenation of Cinnamaldehyde by Twin Au Nanoparticles

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Supported Au nanoparticles show unique catalysis depending on their size and morphology [1,2]. In this study, we demonstrate effect of crystal structure of Au nanoparticles on catalysis for hydrogenation of an unsaturated aldehyde.

Metal-oxide (MO_x) supported Au catalysts (Au/MO_x) were prepared by a deposition precipitation method using TiO_2 and Nb_2O_5 as supporting materials and $HAuCl_4$ as a precursor (Au loading: 1 wt%). Au/MO_x were treated under 4% CO/N_2 at room temperature (Au/MO_x-CO). For comparison, Au/MO_x were also treated under conventional conditions: air at 473 or 573 K (Au/MO_x-A). Hydrogenation of cinnamaldehyde (CAL) was carried out in a stainless autoclave. To the autoclave were added Au/MO_x (10 mg) and CAL solution (0.66 M CAL in toluene 1.0 mL; water 0.5 mL). The hydrogenation of CAL was conducted under 1.0 MPa of H_2 at 393 K. The reaction solution was analyzed by gas chromatograph. The catalysts were characterized using HAADF-STEM.

Table 1 presents the results of hydrogenation of CAL on Au/MO_x-CO and Au/MO_x-A. Au/TiO_2-CO showed higher conversion of CAL than Au/TiO_2-A. As is the case with Au/TiO_2, Au/Nb_2O_5-CO exhibited higher CAL conversion compared to Au/Nb_2O_5-A. Therefore, the CO treatment enhanced the hydrogenation activity in comparison with the conventional heat treatment under air. On the other hand, the selectivity of cinnamylalchol (COL) and hydrocinnamaldehyde (HCAL) was not affected by the catalyst preparation conditions. Rather, the hydrogenation selectivity is strongly affected by supporting materials. Actually, we confirmed that acid-base property of metal-oxide support have a significant influence on the selectivity (data not shown).

The particle size of Au nanoparticles was analyzed using HAADF-STEM. The average particle sizes of Au/MO_x are listed in Table 1. The particle sizes of all Au catalysts were about 2 nm. On the other hand, atomic scale observation revealed two types of crystal structure in Au nanoparticles: twin and single crystal (Fig. 1). Au/MO_x-CO contained twin particles at higher percentage than Au/MO_x-A (Fig. 2). Twin Au nanoparticles inherently have strained structure [3], which can cause stronger hydrogen adsorption and consequently higher hydrogenation activity than single crystal Au nanoparticles. Therefore, we concluded that twin structure of Au nanoparticles induced by CO treatment enhances hydrogenation activity.

Table 1. Results of hydrogenation of CAL and average particle sizes of Au/MO_x.

Catalyst	Conv. (%)[a]	Select. (%)[b]	Size (nm)[c]
Au/TiO_2-CO	38	48/46	2.1
Au/TiO_2-A	23	52/44	2.3
Au/Nb_2O_5-CO	23	19/80	2.2
Au/Nb_2O_5-A	16	23/76	2.2

[a] CAL conversion. [b] COL/ HCAL selectivity.
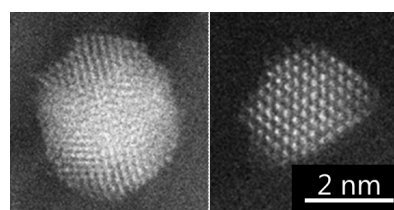[c] Based on TEM observation.

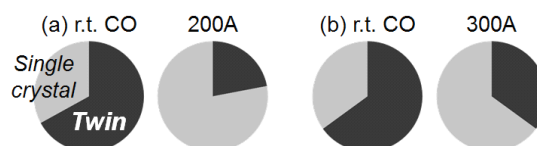**Fig. 1** HAADF-STEM image of a twin Au nanoparticle (left), and a single crystal one (right).

Fig. 2 Crystal-structure distributions of (a) Au/TiO_2 and (b) Au/Nb_2O_5.

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[3] M. J. Walsh, K. Yoshida, and E. D. Bpyes, et al., Nano Lett., 12 (2012) 2027.