Cinnamaldehyde hydrogenation over morphology-controlled Platinum nanoparticles by CO/H_2 pretreatment gas

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Abstract: Morphology of platinum nanoparticles on carbon and SiO_2 supports was controlled using CO gas as a protecting agent in reduction pretreatment of Pt precursor. When only H_2 gas was used for the reduction treatment, Pt nanoparticles did not show a specific morphology. However, when CO gas was mixed with H_2, Pt nanocubes enclosed by (100)-facets were obtained. Cinnamaldehyde hydrogenation was carried out using prepared Pt catalysts. Pt nanocubes prepared with CO/H_2 gas showed higher activity and Cinnamylalchol selectivity than Pt nanoparticles prepared with H_2 gas.
Keywords: pretreatment gas, morphology control, hydrogenation reaction.

1. Introduction

As unique catalysis of morphology-controlled metal nanoparticle catalysts has been revealed, shape control methods of metal nanoparticles have been developed. Generally, a liquid phase reduction method using an organic surfactants such as PVP or CTAB is used. However, this preparation method requires complex experimental procedures such as heat treatment and centrifugation to remove the organic surfactant agents on metal nanoparticle surface. In order to solve the problem of liquid phase reduction method, we focused on morphology control method using gas molecules as protective agents[1]. In this study, we controlled morphology control of Pt nanoparticles is carried out using CO as a protective agent, and applied them to Cinnamaldehyde hydrogenation to investigate the morphology effect on the hydrogenation activity and selectivity.

2. Experimental

Pt/C and Pt/SiO_2 (10 wt% Pt loading) were prepared by an impregnation method. After drying the catalyst, H_2 and CO/H_2 gas were flown into the prepared catalyst at 473 or 573 K for 1 h. The morphology of Pt nanoparticles was analyzed, transmission electron microscopy (TEM) and using X-ray diffraction (XRD).

Toluene solution of Cinnamaldehyde (0.8 M 1 ml) was added to the prepared catalyst and the reaction was carried out under 1 MPa of H_2 in the autoclave at 408 K. For the qualitative and quantitative analysis of the product, GC-FID and GC-MS were used.

3. Results and discussion

The morphology of Pt nanoparticles was analyzed using TEM and XRD. Figure 1a shows the TEM of Pt/C prepared under CO/H_2 and H_2. TEM observation of Pt/C-H_2 did not show Pt nanoparticles with characteristic morphology; however, Pt/C-CO/H_2 exhibited Pt nanocube enclosed by Pt(100)-facet. Figure 1a also shows the XRD of Pt/C prepared under CO/H_2 and H_2. The ratio of the XRD line intensity due to Pt(200) and Pt(111) ($I_{(200)}/I_{(111)}$) was calculated. Pt/C-CO/H_2 showed higher $I_{(200)}/I_{(111)}$ than Pt/C-H_2, which agrees with the formation of Pt nanocubes on Pt/C-CO/H_2, since the cubic morphology has Pt(100) grown relative to Pt(111).

Figure 1b shows the mechanism for formation of Pt nanocube under CO gas. that the exposed surface differs by flowing CO/H_2 gas and the H_2 gas because the CO preferentially adsorbs on the Pt(100)-facet and the growth of the surface is suppressed. It was also confirmed by in-situ IR that CO gas molecules acting as a protective agent can be easily removed by flowing Ar gas at 473 K for 10 min.

Cinnamaldehyde hydrogenation was carried out with the prepared Pt catalysts. As presented in Figure 2, the catalytic activity and Cinnamylalchol selectivity were improved by CO/H_2 pretreatment compared with H_2 pretreatment. According to the literature, the adsorption energies between Pt(100)-facet and the carbonyl bond (di-$\sigma^{C=O}$) of Cinnamaldehyde has a larger than Pt(111)-facet[3]. Therefore, it can be considered that Pt(100) of Pt nanocubes caused the enhanced selectivity of Cinnamylalchol.

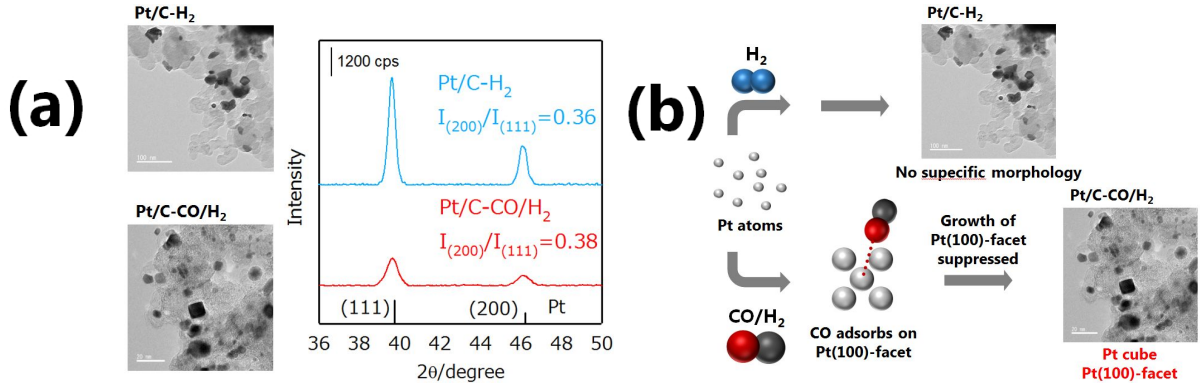

Figure 1. (a)TEM and XRD pattern of Pt/C prepared by H_2 and CO/H_2 pretreatment. (b)Morphology control mechanism of Pt nanoparticles by gas adsorption.

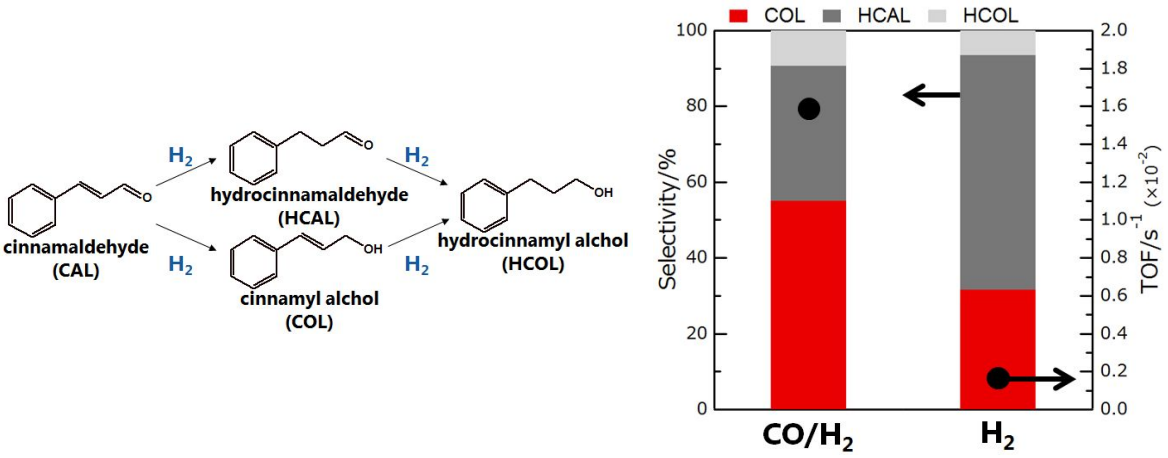

Figure 2. Activity and product selectivity of Cinnamaldehyde hydrogenation (Pt/C).

4. Conclusions

Morphology of platinum nanoparticles on carbon and SiO_2 supports was controlled using CO gas as a protecting agent in reduction pretreatment of Pt precursor. The morphology of Pt nanoparticles was analyzed using TEM and XRD. When CO/H_2 gas was used for the reduction treatment, Pt nanocubes enclosed by (100)-facets were obtained. Moreover, It was also confirmed by in-situ IR that CO gas molecules acting as a protective agent can be easily removed. Cinnamaldehyde hydrogenation was carried out using prepared Pt catalysts. Pt nanocubes prepared with CO/H_2 gas showed higher activity and Cinnamylalchol selectivity. it can be considered that Pt(100) of Pt nanocubes caused the enhanced selectivity of Cinnamylalchol.

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