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Preparation and Cinnamaldehyde Hydrogenation Performance of Platinum Nanosheets Between Graphite Layer

Platinum chloride can be intercalated between the graphite layers and platinum nanosheets with 1-3 nm thickness could be obtained by the reduction of platinum tetrachloride between graphite layers under hydrogen atmosphere [1-3]. Selective hydrogenation of α , β -unsaturated aldehydes to unsaturated alcohols is commercially important. Platinum is one of the active metals for the hydrogenation; however, it is hard to achieve the high selectivity to unsaturated alcohols with the supported monometallic platinum catalysts because carbon-carbon double bond (C=C) is more easily hydrogenated to saturated aldehyde than carbon-oxygen double bond (C=O) to unsaturated alcohol. In this paper, we report that platinum nanosheets located between graphite layers were more selective catalyst for cinnamaldehyde (UAL) hydrogenation to cinnamyl alcohol (UOL) than platinum metal particles on graphite surface in supercritical carbon dioxide (scCO₂) solvent.

A mixture of solid platinum chloride (PtCl₄, Sigma-Aldrich) and powder graphite (KS6, TIMREX) were thermally treated under 0.3 MPa of chlorine at 723 K for 7 days to obtain the platinum chloride intercalated compounds (PtCl₄-GIC). The PtCl₄-GIC sample was reduced at 573 K for 1 h under 40 kPa of hydrogen to produce the platinum metal intercalated compounds (Pt-GIC) [1, 2]. The platinum metal loading for the Pt-GIC sample was 5wt%. The mixture of chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, Wako chemicals) and graphite powder (KS6, TIMREX) were treated at 573 K for 1 h under 40 kPa hydrogen to give platinum metal particles supported on graphite surface (Pt/Gmix).

Figure 1 shows TEM images of the Pt-GIC sample, which were performed JEOL by JEM-2100ExII (200 keV). XMA analysis confirmed that the dark images were composed of platinum. Several rod-like platinum images in parallel are shown in Figure 1(a) and many sheet-like platinum images with hexagonal holes are shown in Figure 1(b). The TEM analysis with the rotation of the Pt-GIC sample against electron beam confirmed that the rod-like images shown in Figure 1(a) was side view and 1(b) was top view of the platinum nanosheets intercalated between graphite layers.

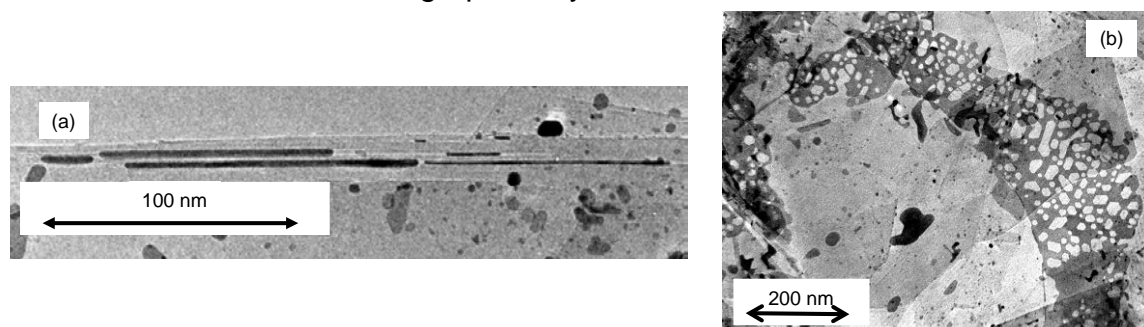


Figure 1 Pt-GIC (a) side view (b) top view

Figures 2(a) and (b) show the hydrogenation profile of Pt-GIC under 5 MPa of hydrogen and 10 MPa of scCO₂ at 323 K. Pt-GIC was active in scCO₂ at 323 K and the UAL conversion increased with an increase in reaction time and 80% of conversion of UAL was obtained at 240 min, in which UOL and hydrocinnamaldehyde (SAL), and hydrocinnamyl alcohol (SOL) were formed. High recovery values more than 90% were obtained up to 120 min and slightly decreased to 80% at 360 min. The UOL selectivity was almost constant at 77% and independent of reaction rate up to 240 min. Dehydroxylation products of β -methyl styrene (MS) and propylbenzene (PB) were not formed at the beginning of the reaction. Total selectivity for hydrogenated compounds (UOL+SAL+SOL) were more than 98% at 360 min. Figures 2(c) and (d) show the hydrogenation profile over the Pt/Gmix catalyst. The conversion increased with an increase in reaction time. 26 and 58% conversion values were obtained at 30 and 90 min over Pt/Gmix, respectively. The recovery value at 15 min was 90%; however, it decreased with an increase in reaction time and became 60% at 210 min. UOL selectivity over Pt/Gmix was low and the values at 30 and 90 min were 48 and 41%, respectively. MS, PB and cinnamic acid (CA) were formed and their selectivities were high. The selectivity values for these undesirable compounds (MS+PB+CA) were 14% at 210 min. One probable explanation for the high UOL selectivity over Pt-GIC than that over Pt/Gmix is the difference of adsorption structure of UAL molecules on active platinum sites between both systems. Carbon dioxide molecules under supercritical conditions would carry CAL molecules into graphite layers with their benzene ring parallel to the graphite layers and the C=O functional groups of UAL molecules preferentially would adsorb on the edge sites of platinum nanosheets. On the other hand, such hindrance of UAL adsorption by graphite layers would not be occurred for Pt/Gmix because platinum metal particles are located on the graphite layers and UAL molecules would randomly adsorb on platinum surfaces to produce thermodynamically stable SAL and SOL molecules.

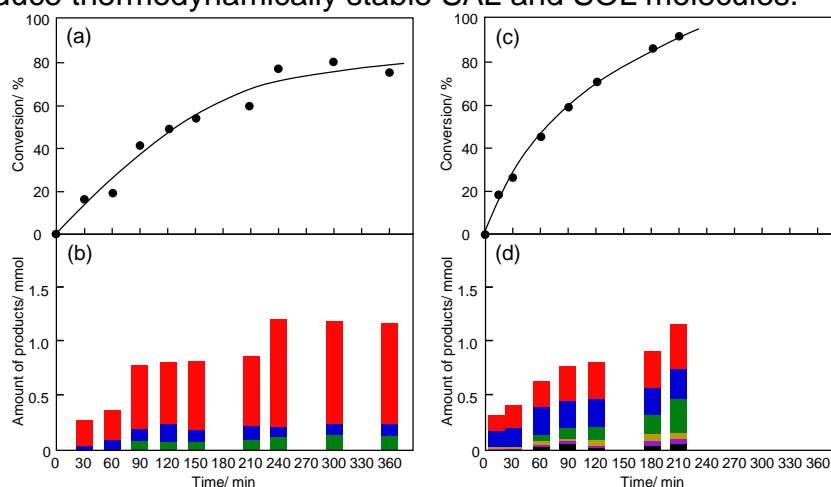


Figure 2 Cinnamaldehyde hydrogenation over Pt-GIC (a, b) and Pt/Gmix (c, d) under 5 MPa of hydrogen in 10 MPa of supercritical carbon dioxide solvent at 323 K. Conversion (a, c) and amounts of recovered reactant and products (b, d) (gray: cinnamaldehyde, red: cinnamyl alcohol, blue: hydrocinnamaldehyde, green: hydrocinnamyl alcohol, brown: β -methyl styrene, purple: propylbenzene, and black: cinnamic acid).

Acknowledgements

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