Structure and hydrogenation catalysis of platinum nanosheets between graphite layers

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Abstract: Platinum nanosheets between graphite layers (Pt-GIC) were prepared by the insertion of platinum chloride (IV) into graphite layers under chlorine atmosphere and the following reduction with hydrogen. Pt-GIC was active for cinnamaldehyde hydrogenation in *n*-heptane solvent and more selective to cinnamyl alcohol than platinum nano particles supported on graphite surface (Pt/Gmix).

Keywords: Platinum nanosheet, Graphite intercalated compounds, Selective hydrogenation

1. Introduction

Graphite has a layered structure and each layer stacks with a weak van der Waals interaction. Several metal chloride can be incorporated between the graphite layers to produce graphite intercalated compounds (GIC). It is expected that plate-like metal particles could be formed by the reduction of metal chloride between graphite layers because of the steric hindrance of the layers against the growth of metal particles. In this paper, we report the preparation of platinum metal sheets with 1-3 nm thickness by the reduction of platinum chloride between graphite layers by hydrogen. We also investigated the cinnamaldehyde hydrogenation behavior of Pt-GIC and compared with that of platinum metal particles supported on graphite surface (Pt/Gmix).

2. Experimental

A mixture of solid platinum chloride (IV) and powder graphite, which was treated under 0.3 MPa of Cl_2 at 723 K for 7 days, was reduced at 573 K for 1 h under 40 kPa of H_2 (Pt-GIC). The platinum metal loading was 5wt%. The details of the preparation of Pt-GIC are described in reference 1. A mixture of $H_2PtCl_6 \cdot 6H_2O$ and graphite powder (platinum loading was 5 wt%) was treated at 573 K for 1 h under 40 kPa of hydrogen to give platinum metal particles supported on graphite surface (Pt/Gmix). Cinnamaldehyde hydrogenation was carried out with a 50 ml batch reactor [1].

3. Results and discussion

Figure 1(a) is an image of Pt-GIC, in which platinum rods having 1-3 nm diameter are arranged in parallel with the graphite layers. Also, void spaces are observed at the edge of the platinum. Figure 1(a) shows that platinum sheets are inserted between the graphite layers. Figure 1(b) is an image of Pt-GIC, in which a platinum sheet with hexagonal holes and edge angles of 120° is there. The TEM analysis with the rotation of the sample against the electron beam confirmed that the rod-like platinum as shown in Figure 1(a) is a side image of platinum nanosheets and Figure 1(b) is a top view of the platinum nanosheets.

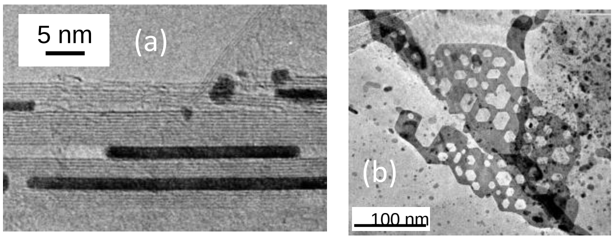

Figure 1. TEM images of Pt-GIC.

Figure 2(a) shows the profile of cinnamaldehyde hydrogenation over Pt-GIC in *n*-heptane. The cinnamaldehyde conversion increased with an increase in reaction time. The reaction rate is not so high; however, 14% of conversion of cinnamaldehyde was obtained within 45 min. Figure 2(b) shows the amounts of the products, in which cinnamyl alcohol (UOL) and hydrocinnamaldehyde (SAL) were formed; however, hydrocinnamyl alcohol (SOL) was not formed. The selectivity to UOL was almost constant at 60% and independent of reaction rate up to 45 min.

Figures 2(c) shows the cinnamaldehyde hydrogenation profile over Pt/Gmix. Higher conversion values were obtained over Pt/Gmix than Pt-GIC; however, the selectivity to UOL over Pt/Gmix was 33%, which was lower than that over Pt-GIC, and those to dehydrogenated products (MS and PB) were higher. The lower conversion of cinnamaldehyde over Pt-GIC would be due to the lower number of exposed platinum metal sites of nanosheets between graphite layers. The higher conversion values obtained over Pt/Gmix shows that cinnamaldehyde molecules would easily access spherical platinum metal particles on graphite surface. In other words, the results of lower activity of Pt-GIC would show that platinum is intercalated into the graphite layers in Pt-GIC samples. On the other hand, Pt-GIC showed higher UOL selectivities compared with those of Pt/Gmix. One probable explanation for the higher UOL selectivity over Pt-GIC is that the preferential adsorption of the terminal carbonyl group of cinnamaldehyde molecule on the exposed platinum sites on nanosheets intercalated in graphite layers because the adsorption of C=C group of cinnamaldehyde molecule was hindered by the steric factors between phenyl group and graphite layers in the Pt-GIC samples.

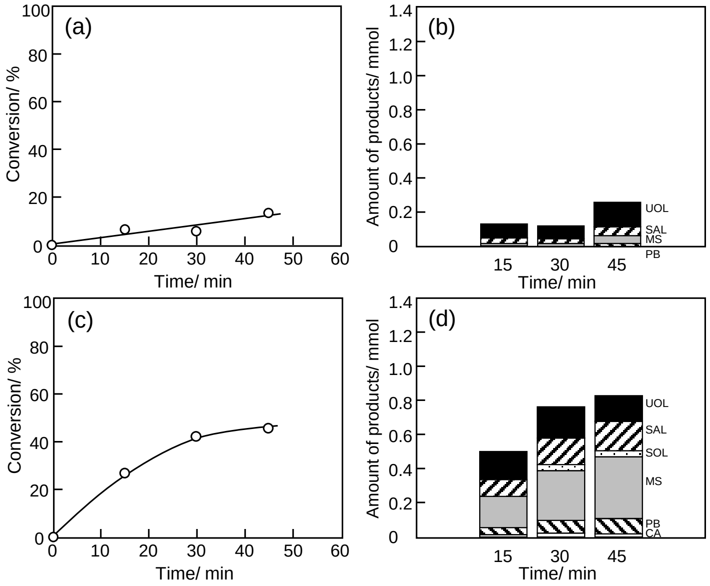

Figure 2. Conversion and product amounts for cinnamaldehyde hydrogenation in *n*-heptane over Pt-GIC (a), (b) and Pt-Gmix (c), (d). Reaction temperature 373 K, Hydrogen pressure 5 MPa, ■cinnamyl alcohol (UOL), ▨ hydrocinnamaldehyde (SAL), ⬚hydrocinnamyl alcohol (SOL), ▒β-methyl styrene (MS), ◩propyl benzene (PB), □cinnamyl acid (CA).

4. Conclusions

Platinum nanosheets with 1-3 nm thickness and hexagonal holes (Pt-GIC) were prepared by the insertion of platinum chloride into graphite layers under chlorine pressure and the following reduction with hydrogen. Pt-GIC was active for cinnamaldehyde hydrogenation in *n*-heptane solvent more selective for cinnamyl alcohol than platinum metal particles supported on graphite surface (Pt/Gmix).

References

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