Effect of metal amounts for catalytic activity and structure in Pt-MoO_x/TiO_2 for selective hydrodeoxygenation of 2-furancarboxylic acid to valeric acid

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Abstract: We reported that Pt-MoO_x/TiO_2 catalyst is effective for hydrodeoxygenation of 2-furancarboxylic acid (FCA), which is produced by oxidation of furfural, to valeric acid (VA). In this study, we investigated the loading amount dependence of both Pt and Mo for catalytic activity and catalyst structure. The maximum yield of VA was 61% which was obtained over Pt 20wt% - Mo 0.5wt% catalyst. Dispersed Mo species on TiO_2 support seems to contribute to the VA formation.

Keywords: Bimetallic Catalyst, Biomass, Hydrodeoxygenation.

1. Introduction

Biomass conversion is important technique in terms of reducing both the consumption of fossil resources and carbon dioxide emission. Among biomass resources, lignocellulose, which is a structural component of wood, is drawing attention as raw material. Furfural, which is produced from pentose, is an important intermediate compound in conversion of biomass to useful chemicals.[1] There are a lot of reports for the conversion of furfural, such as hydrogenation, hydrodeoxygenation, hydrogenolysis, condensation, rearrangement, and oxidation.[2,3] 2-Furancarboxylic acid (FCA) is easily produced by oxidation of furfural.[3] However, the reports on the use of FCA as an intermediate compound of biomass conversion is very rare. We reported selective hydrodeoxygenation of FCA to valeric acid over Pt-MoO_x/TiO_2 (4 wt% Pt, Mo/Pt molar ratio is 0.25, corresponding to 0.5 wt% Mo) catalyst, and valeric acid yield was 51%.[4] On this catalyst, the exitance of both Pt and Mo on same support is an esential factor for selective hydrodeoxygenation activity. In this study, we investigated the loading amount dependence of both Pt and Mo for catalytic activity and catalyst structure.

2. Experimental

Pt-MoO_x/TiO_2(X, Y) catalysts (X: Pt metal amount in wt%, Y: Mo metal amount in wt%) were prepared by sequential impregnation method using $Pt(NH_3)_2(NO_2)_2$ HNO_3 sol., $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ *aq*, and TiO_2 (P25, pre-calcined at 973 K for 1 h, 29.7 m^2/g), followed by drying at 383 K for overnight and calcination at 773 K for 3 h. Activity tests were performed in a 190 ml stainless-steel autoclave with an inserted glass vessel. The catalyst, solvent, and substrate were loaded in the inserted glass vessel with a spinner. After sealing the reactor, the air content was purged by flushing three times with 1 MPa of hydrogen. Standard reaction conditions are catalyst 0.10 g, water 19 g, FCA, 10 mmol T= 413 K, $P(H_2)$= 1.5 MPa, and t= 4 h. Products in both liquid and gas phases were analyzed with FID-GC.

3. Results and discussion

Figure 1 shows the result of the activity test of Pt-MoO_x/TiO_2 catalysts with various loading amount. At 4 wt% Pt, the valeric acid yield was improved by addition of a trace amount of Mo as reported,[4] and the maximum yield was 51% at 0.5 wt% Mo. At 0.13 and 0.25 wt% Mo, the activity was much lower, and at 1 and 2 wt%, the yield of VA decreased with increasing Mo loading amount. When the Pt amount was less than 4 wt%, conversion and VA yield were significantly decreased in any Mo amount, and when the Pt amount was less than 2 wt%, the VA yield was very low considering the decreased amount of active metal(Pt). When the Pt amount was 20 wt%, the activity was improved by addition of Mo up to 0.5 wt% similarly to the case of 4 wt% and 10 wt% Pt catalysts. The VA yield reached 61% with 20 wt% Pt and 0.5

wt% Mo catalyst, which was the highest yield in the tested catalysts. On the other hand, at 1 wt% Mo and above, the VA yield decreased with increasing Mo loading amount. When the Mo loading amount was 0 wt%, VA was not hardly formed regardless of Pt amount.

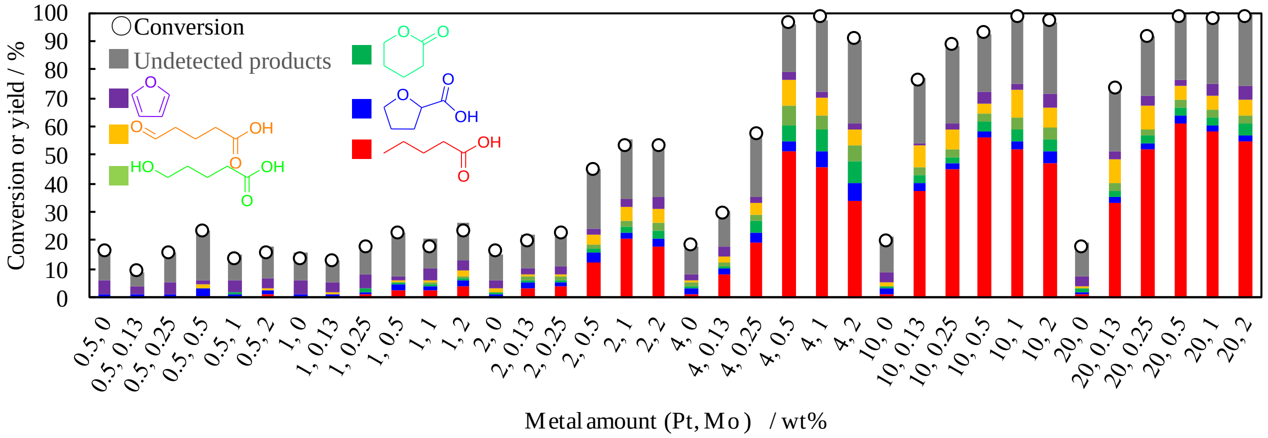

Figure 1. Effect of metal amount on Pt-MoO_x/TiO_2 catalysts for selective hydrodeoxygenation when standard reaction conditions.

From these results, it is considered that the selectivity to VA is almost determined by Mo loading amount rather than Mo/Pt ratio when Pt is sufficiently loaded(>2 wt% Pt). According to the literature, the interaction of Mo species and TiO_2 surface is very strong, and at small Mo loading amount the Mo species are mainly monomeric ones.[5-7] We carried out CO adsorption and XRD measurements for Pt-MoO_x/TiO_2 and Pt/TiO_2, and the results of calculated Pt dispersions suggest that the Pt particles were not covered with Mo species. Therefore, we propose that the structure of Pt-MoO_x/TiO_2 has Pt particles located on Mo-dispersed TiO_2. Based on the surface area of support, the surface concentration of Mo is about 1 Mo atom/nm^2 at 0.5 wt% Mo, and most Mo species are supposed to be monomeric. On the other hand, at 2 wt% Mo, the oligomeric species will predominate. Based on the proposed structure and performance, the active site for VA production can be the interface between dispersed Mo species and Pt particle surface. The interface between oligomeric Mo species and Pt is not active, and the catalysts with too much Mo have low activity.

Mo *K*-edge XANES spectra of reduced Mo 0.5 wt% catalysts were similar to that of MoO_2, which suggests that Mo(VI) species in the calcined catalyst were reduced to Mo(IV). In Mo *K*-edge EXAFS of reduced catalysts with Mo 0.5 wt% and any Pt amount, bonds due to Mo-O and Mo-Mo were observed. On catalysts with 4 wt% or more Pt amount, the bond between Mo and heavy atom such as Pt was observed.

4. Conclusions

The yield of valeric acid reached 61% with 20 wt% Pt-0.5 wt% Mo catalyst, and the value is higher than the originally reported yield (51%) with 4 wt% Pt- 0.5wt% Mo catalyst. The Mo concentration of 0.5 wt% Mo catalyst on the support surface is calculated to be 1 Mo atom/nm^2 and the monomeric species contribute to the activity. Covering of Pt particle with Mo species was negligible, and the active site can be the interface of dispersed Mo species on TiO_2 and Pt particle surface.

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