Role of perimeter interfaces between WO_3 monolayer domain and Al_2O_3 in hydrogenolysis of glycerol by $Pt/WO_3/Al_2O_3$ catalysts

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Abstract: The role of perimeter interfaces between WO_3 domain and Al_2O_3 in glycerol hydrogenolysis by $Pt/WO_3/Al_2O_3$ was investigated. The WO_3 loading significantly affected the 1,3-propanediol yield. WO_3 was loaded as two-dimensional monolayer domains below 20 wt.% and these domains covered most of the Al_2O_3 surface at 20 wt.%. We estimated the number of W species at the perimeter interfaces between WO_3 monolayer and Al_2O_3 from H_2-TPR profiles. The estimated value was positively correlated with the 1,3-propanediol yield, suggesting that the W-(OH)-Al sites at the perimeter interfaces between WO_3 monolayer and Al_2O_3 have an important role in hydrogenolysis of glycerol to 1,3-propanediol.

Keywords: Hydrogenolysis of glycerol, Tungsten oxide, Perimeter interface

1. Introduction

The hydrogenolysis of glycerol (Gly) to form 1,3- and 1,2-propanediol (PDO) has attracted a great deal of attention. Although the combination of Pt, WO_3 and alumina-based supports has been one of the most successful systems for Gly hydrogenolysis into 1,3-PDO, the role and structure of WO_3 and alumina-based supports in this catalyst for the selective hydrogenolysis of 1,3-PDO are subjects of controversy. In this study, to reveal the roles of WO_3 in hydrogenolysis of Gly, we investigated the relationship between the number of W species at the perimeter interfaces between WO_3 monolayer domain and Al_2O_3 of $Pt/WO_3/Al_2O_3$ catalysts with various WO_3 loadings and their catalysis in hydrogenolysis of Gly.

2. Experimental

A series of WO_3/Al_2O_3 catalysts was prepared by impregnation of γ-Al_2O_3 (JRC-ALO-8) with an aqueous solution of ammonium tungsten para pentahydrate ($(NH_4)_{10}W_{12}O_{42}$ $5H_2O$), dried at 353 K for 6 h, and then calcined at 1123 K for 3 h in a flow of dry air.[1] $Pt/WO_3/Al_2O_3$ catalysts (Pt loading: 1 wt.%) were also prepared by impregnating WO_3/Al_2O_3 with an aqueous solution of H_2PtCl_6. After the impregnation procedure and drying at 353 K for 6 h, the prepared catalysts were calcined at 573K for 3 h in air. The hydrogenolysis of glycerol was conducted in a Teflon vessel placed in a stainless steel autoclave with magnetic stirring pressurized with 5 MPa of hydrogen. The products were analyzed by FID-GC and TCD-GC. Structural characterization was carried out using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis. The temperature-programmed reduction (H_2-TPR) profiles of the catalysts recorded using an Okura BP-2 instrument were used for determination of H_2 consumption.

3. Results and discussion

Figure 1 shows the effect of WO_3 loading on the activity of $Pt/WO_3/Al_2O_3$ in the hydrogenolysis of Gly. The WO_3 loading significantly affected 1,3-PDO yield. Structural characterization by XRD and XPS revealed that two-dimensional monolayer WO_3 domains (WO_6 units) were loaded on Al_2O_3 surface up to 20 wt.% loadings[2]. The surface coverage of Al_2O_3 with WO_3 monolayer was estimated from the unit size of WO_6 (0.22 nm^2)[3] and the surface area. The surface coverage of $Pt/WO_3/Al_2O_3$ with 6 wt.% WO_3 loading, which showed the highest yield of 1,3-PDO, was ca. 25%. This suggests that the perimeter interfaces between WO_3 monolayer and Al_2O_3 has important role in hydrogenolysis of Gly to 1,3-PDO.

To estimate the number of W species at the perimeter interfaces, H_2-TPR profiles were measured and the amount of H_2 consumption was calculated. The ratio of H_2 consumption below 673 K to the amount of supported tungsten (H_2/W ratio) was much lower than 1 (Fig. 2), indicating that a part of supported WO_3 was reduced. We assumed that H_2 consumption is due to the reduction of W species at the perimeter interfaces between WO_3 monolayer domain and Al_2O_3. Figure 3 shows the effect of H_2 consumption and yield of 1,3-PDO and a positive correlation was observed. It is implied that the perimeter interfaces between WO_3 domain and Al_2O_3 have an important role and the W-(OH)-Al sites at the perimeter interfaces are active sites in hydrogenolysis of glycerol to 1,3-PDO.

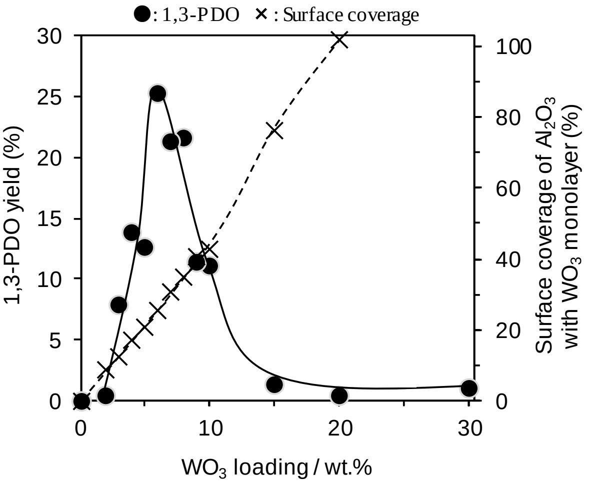

Figure 1. Effect of WO_3 loading on hydrogenolysis over $Pt/WO_3/Al_2O_3$. Conditions: 3 mmol Glycerol, 9 mL H_2O, P_{H2}=5 MPa, T = 453 K, t = 15 h.

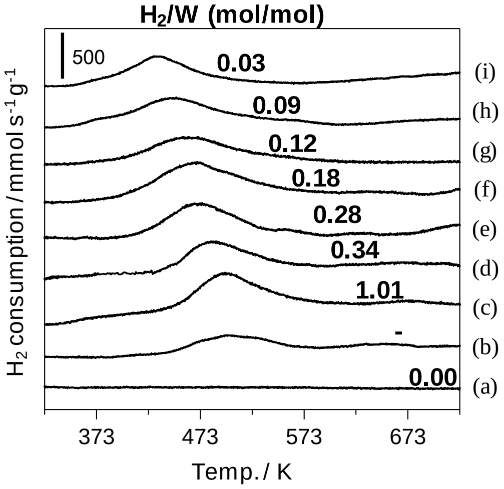

Figure 2. H_2-TPR profiles of $Pt/WO_3/Al_2O_3$ with various WO_3 loadings. (a) 7 wt.% WO_3/Al_2O_3, (b) 0, (c) 2, (d) 4, (e) 6, (f) 8, (g) 10, (h) 15, (i) 20 wt.%.

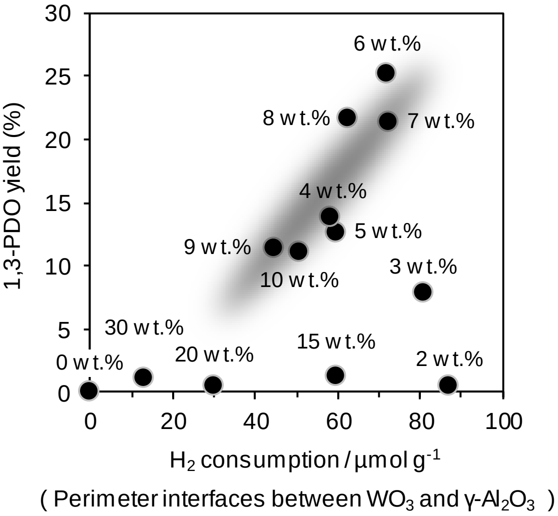

Figure 3. Effect of H_2 consumption on hydrogenolysis over $Pt/WO_3/Al_2O_3$.

4. Conclusions

The effect of WO_3 loading on the activity of $Pt/WO_3/Al_2O_3$ in Gly hydrogenolysis was investigated. The coverage of Al_2O_3 with the WO_3 monolayer strongly affected the yield of 1,3-PDO. H_2 consumption was estimated from H_2-TPR profiles and the estimated H_2/W ratio was much less than 1, suggesting that a part of W species supported on Al_2O_3 was reduced. We assumed that H_2 consumption was correlated with the number of W species at the perimeter interfaces between WO_3 monolayer and Al_2O_3. A positive correlation between H_2 consumption and 1,3-PDO yield was observed. Thus, we conclude that W-(OH)-Al sites at the perimeter interfaces between two-dimensional monolayer WO_3 domain and Al_2O_3 have an important role in selective hydrogenolysis of Gly to 1,3-PDO.

References

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