Role of perimeter interfaces between WO$_3$ monolayer domain and Al$_2$O$_3$ in hydrogenolysis of glycerol by Pt/WO$_3$/Al$_2$O$_3$ catalysts

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Abstract: The role of perimeter interfaces between WO$_3$ domain and Al$_2$O$_3$ in glycerol hydrogenolysis by Pt/WO$_3$/Al$_2$O$_3$ 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$_2$O$_3$ surface at 20 wt.%. We estimated the number of W species at the perimeter interfaces between WO$_3$ monolayer and Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ of Pt/WO$_3$/Al$_2$O$_3$ catalysts with various WO$_3$ loadings and their catalysis in hydrogenolysis of Gly.

2. Experimental

A series of WO$_3$/Al$_2$O$_3$ catalysts was prepared by impregnation of γ-Al$_2$O$_3$ (JRC-ALO-8) with an aqueous solution of ammonium tungsten para pentahydrate ((NH$_4$)$_{10}$W$_{12}$O$_{42}$ 5H$_2$O), dried at 353 K for 6 h, and then calcined at 1123 K for 3 h in a flow of dry air. Pt/WO$_3$/Al$_2$O$_3$ catalysts (Pt loading: 1 wt.%) were also prepared by impregnating WO$_3$/Al$_2$O$_3$ with an aqueous solution of H$_2$PtCl$_6$. After the impregnation procedure and drying at 353 K for 6 h, the prepared catalysts were calcined at 573 K 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$_2$O$_3$ 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$_2$O$_3$ surface up to 20 wt.% loadings. The surface coverage of Al$_2$O$_3$ with WO$_3$ monolayer was estimated from the unit size of WO$_6$ (0.22 nm$^2$) and the surface area. The surface coverage of Pt/WO$_3$/Al$_2$O$_3$ 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 WO3 monolayer and Al2O3 has important role in hydrogenolysis of Gly to 1,3-PDO.

To estimate the number of W species at the perimeter interfaces, H2-TPR profiles were measured and the amount of H2 consumption was calculated. The ratio of H2 consumption below 673 K to the amount of supported tungsten (H2/W ratio) was much lower than 1 (Fig. 2), indicating that a part of supported WO3 was reduced. We assumed that H2 consumption is due to the reduction of W species at the perimeter interfaces between WO3 monolayer domain and Al2O3. Figure 3 shows the effect of H2 consumption and yield of 1,3-PDO and a positive correlation was observed. It is implied that the perimeter interfaces between WO3 domain and Al2O3 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 WO3 loading on hydrogenolysis over Pt/WO3/Al2O3.](image)

4. Conclusions

The effect of WO3 loading on the activity of Pt/WO3/Al2O3 in Gly hydrogenolysis was investigated. The coverage of Al2O3 with the WO3 monolayer strongly affected the yield of 1,3-PDO. H2 consumption was estimated from H2-TPR profiles and the estimated H2/W ratio was much less than 1, suggesting that a part of W species supported on Al2O3 was reduced. We assumed that H2 consumption was correlated with the number of W species at the perimeter interfaces between WO3 monolayer and Al2O3. A positive correlation between H2 consumption and 1,3-PDO yield was observed. Thus, we conclude that W-(OH)-Al sites at the perimeter interfaces between two-dimensional monolayer WO3 domain and Al2O3 have an important role in selective hydrogenolysis of Gly to 1,3-PDO.

References