Selective conversion of glycerol to acrolein on W-based solid acid catalysts

Katsuya Asazuma,[a] **Hiroki Miura,**[a,b,c] **Tetsuya Shishido**[a,b,c,*]

[a]*Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan*

[b]*Research Center for Hydrogen Energy-Based Society, Tokyo Metropolitan University, 1-1 minami-Osawa, Hachioji, Tokyo 192-0397, Japan*

[c]*Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8520, Japan*

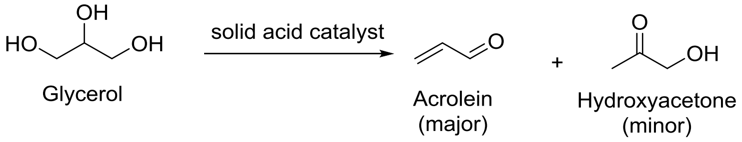
**Corresponding author: +81-42-677-2850, shishido-tetsuya@tmu.ac.jp*

Abstract: Gas-phase dehydration of glycerol to acrolein over W-based solid acid catalysts was examined. WO_3/Al_2O_3 showed a high activity and stability, which were higher than those of WO_3/ZrO_2 and WO_3/TiO_2. The WO_3 loading strongly affected on activity and stability of WO_3/Al_2O_3. 20 wt% WO_3/Al_2O_3 exhibited the highest activity among the catalysts tested. WO_3 was loaded as two-dimensional monolayer domains, which covered most of the Al_2O_3 surface at 20 wt%. The activity of 20 wt% WO_3/Al_2O_3 slightly decreased using N_2 as the carrier. On the contrary, the activity was maintained under O_2 flow and the selectivity to acrolein was remarkably improved.

Keywords: Glycerol dehydration, Acrolein, supported WO_3 catalysts.

1. Introduction

In recent decades, the catalytic conversion of glycerol, which is an unavoidable coproduct of the biodiesel production process, to value-added chemicals has attracted the attention. Among them, the catalytic double dehydration of glycerol to acrolein (Scheme 1) leads to a potentially practical route to transform bio-resources in a sustainable way. In this study, glycerol dehydration by W-based solid acid catalyst was investigated. We found that WO_3/Al_2O_3 showed a high activity for dehydration to acrolein, and characterized structural changes in a series of Al_2O_3-supported WO_3 catalysts with various loadings of WO_3 to clarify the relationship between their acidic properties and local structures around tungsten species.



Scheme 1. Dehydration of glycerol

2. Experimental

A series of W-based catalysts were prepared by impregnation method.[1] The dehydration of glycerol (Gly) was performed in a fixed-bed down-flow glass reactor under atmospheric pressure. Reaction gas composition was Gly/H_2O/carrier gas = 1.0/9.0/9.8, WHSV = 4.70 g_{gly} (h $g_{cat.}$)$^{-1}$. The products were analyzed by FID and TCD-GCs. The characterization was carried out using FT-IR, XRD, Raman, XPS, and XAFS.

3. Results and discussion

The activity of various solid acid catalysts for glycerol dehydration was examined (Figure 1). Acrolein was formed as main product together with a small amount of hydroxyaceton. WO_3/Al_2O_3 showed a high activity and less deactivation. On the other hand, WO_3/ZrO_2 and WO_3/TiO_2 showed less activity and remarkable deactivation. H-ZSM-5 and H-β showed high activity at initial stage, however deactivation took place rapidly. The activity of H-MOR and H-Y was low.

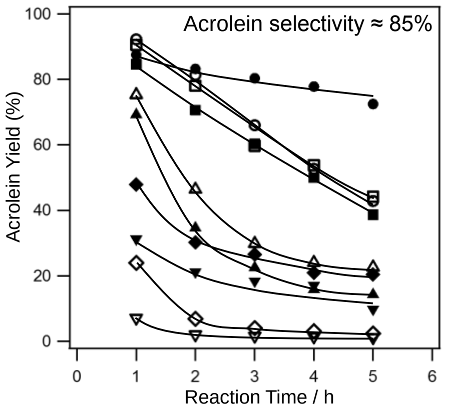


Figure 1. Yield of acrolein over various solid acid catalysts (●:20 wt% WO_3/Al_2O_3, ■:10 wt% WO_3/ZrO_2, ▲:2.5 wt% WO_3/TiO_2, ▼:Nb_2O_5, ◆:Layered Nb_2O_5, ○:$NbOPO_4$, □:H-ZSM-5(90), △:H-β(25), ▽:H-Y(5.5), ◇:H-MOR(20)). WO_3 coverage was 100%. The number in a parenthesis is SiO_2/Al_2O_3 ratio.

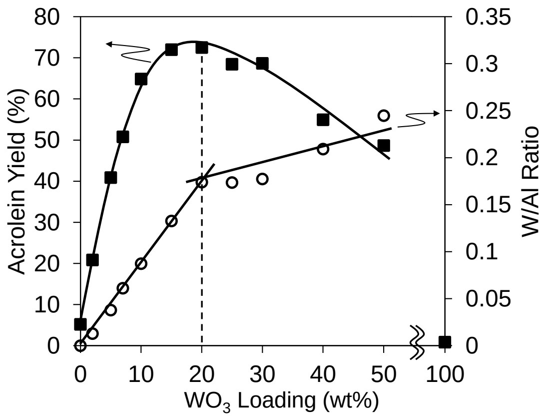


Figure 2. Effect of WO_3 loading on the yield of acrolein over WO_3/Al_2O_3 catalysts. Surface W/Al ratio was estimated by XPS.

The WO_3 loading strongly affected on the activity of WO_3/Al_2O_3 catalysts (Figure 2). The activity increased with increasing WO_3 loading up to 20 wt%, then decreased. XRD patterns indicated that amorphous WO_3 were supported on the Al_2O_3 surface up to 20 wt%. Surface W/Al ratio estimated by XPS was linearly increased up to 20 wt%. These results indicate that 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%. When the WO_3 loading was sufficient to form two-dimensional WO_3 overlayers (> 20 wt%), WO_3 domains were aggregated. Brønsted acidity determined by pyridine adsorbed FT-IR increased with increasing WO_3 loading up to 20 wt%. Above 20 wt%, Brønsted acidity gradually decreased. On the other hand, Lewis acidity was decreased with increasing WO_3 loading. These results suggest that glycerol was dehydrated to acrolein on the Brønsted acid site located on WO_3 monolayer or at interface between WO_3 domains and Al_2O_3 surface.

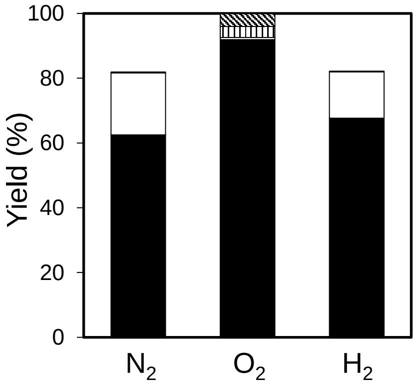


Figure 3. Effect of Reaction Conditions on Activity over 20 wt% WO_3/Al_2O_3 (■:Acrolein, □:Hydroxyacetone, ▥:Acetaldehyde, ▧:CO_2). Yield are presented at time on stream of 4-5 h

The activity of WO_3/Al_2O_3 slightly decreased with reaction time under N_2 and H_2, however, the activity recovered to the initial level by treatment with O_2 at 823 K. On the contrary, the activity maintained up to 5 h under O_2 flow. Moreover, the selectivity to acrolein was improved, whereas hydroxyl acetone was not formed (Figure 3). After the reaction, supported WO_3 on the Al_2O_3 surface is maintained amorphous regardless of carrier. The change in valence of surface of W was not observed in spite of carrier. The amount of coke deposited on 20 wt% WO_3/Al_2O_3 after the reaction under O_2 flow was much larger than that under N_2 flow. Moreover, Brønsted acidity is quite smaller than the amount of coke, and the crystalline of the coke was independent on carrier. These results implied that coke deposition was not main reason for deactivation.

4. Conclusions

WO_3/Al_2O_3 catalyst showed high catalytic activity and stability toward dehydration of glycerol to acrolein. 20 wt% WO_3/Al_2O_3 exhibited the highest activity, on which WO_3 monolayer domains covered most of the Al_2O_3 surface. Deactivation was inhibited and the selectivity of acrolein was improved by using O_2 as a carrier.

References

1. T. Kitano, T. Hayashi, T. Uesaka, T. Shishido, K. Teramura, T. Tanaka, ChemCatChem 6 (2014) 2011–2020