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

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Abstract: Gas-phase dehydration of glycerol to acrolein over W-based solid acid catalysts was examined. WO3/Al2O3 showed a high activity and stability, which were higher than those of WO3/ZrO2 and WO3/TiO2. The WO3 loading strongly affected on activity and stability of WO3/Al2O3. 20 wt% WO3/Al2O3 exhibited the highest activity among the catalysts tested. WO3 was loaded as two-dimensional monolayer domains, which covered most of the Al2O3 surface at 20 wt%. The activity of 20 wt% WO3/Al2O3 slightly decreased using N2 as the carrier. On the contrary, the activity was maintained under O2 flow and the selectivity to acrolein was remarkably improved.

Keywords: Glycerol dehydration, Acrolein, supported WO3 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 WO3/Al2O3 showed a high activity for dehydration to acrolein, and characterized structural changes in a series of Al2O3-supported WO3 catalysts with various loadings of WO3 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/H2O/carrier gas = 1.0/9.0/9.8, WHSV = 4.70 ggly(h gcat.)-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 hydroxyacetone. WO3/Al2O3 showed a high activity and less deactivation. On the other hand, WO3/ZrO2 and WO3/TiO2 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.
The WO$_3$ loading strongly affected on the activity of WO$_3$/Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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. Bronsted acidity determined by pyridine adsorbed FT-IR increased with increasing WO$_3$ loading up to 20 wt%. Above 20 wt%, Bronsted 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 Bronsted acid site located on WO$_3$ monolayer or at interface between WO$_3$ domains and Al$_2$O$_3$ surface.

The activity of WO$_3$/Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ catalyst showed high catalytic activity and stability toward dehydration of glycerol to acrolein. 20 wt% WO$_3$/Al$_2$O$_3$ exhibited the highest activity, on which WO$_3$ monolayer domains covered most of the Al$_2$O$_3$ surface. Deactivation was inhibited and the selectivity of acrolein was improved by using O$_2$ as a carrier.

References