

Kinetics of Tungstated Zirconia Catalyzed Transesterification and Esterification for Biodiesel Synthesis

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Introduction

Due to global environmental concerns, alternative fuels developed from renewable sources are gaining popularity. Biodiesel (mono alkyl esters), derived from vegetable oils through transesterification, is recognized as a “green fuel” because it is biodegradable, non-toxic, and exhibits a low emission profile. Low quality feedstocks such as yellow grease, containing high free fatty acid (FFA) concentrations, can be used to reduce the biodiesel cost. However, current homogeneous alkali-catalyzed transesterification can not tolerate the presence of water and FFAs that exist in these cheaper feedstocks, requiring acid catalyzed preesterification.

The use of solid acid catalysts can suppress the drawbacks found in liquid acids, such as separation problems and vessel corrosion. Solid acid catalysts such as tungstated zirconia (WZ) show a good promise in catalyzing both transesterification of oils and esterification of FFAs [1, 2]. Few studies have emphasized the use of solid acid catalysts for transesterification, and the reaction pathway of esterification on solid acid catalysts is still debated [3].

In this study, WZ was studied in gas-phase esterification of acetic acid (HAc) and transesterification of ethyl acetate (EtOAc) with methanol. HAc and EtOAc were used as model compounds for FFAs and triglycerides, respectively, in general. Kinetic parameters such as apparent activation energies and reaction orders were determined. The catalyst deactivation/regeneration was examined to evaluate the potential use for biodiesel production.

The objective of this study was to establish a better fundamental insight for solid acid catalyzed transesterification and esterification using model compounds, and to assess the possibility of using WZ for biodiesel synthesis.

Materials and Methods

Transesterification of EtOAc and esterification of HAc with methanol (MeOH) over WZ were carried out in a fixed-bed flow differential reactor at 120°C and atmospheric pressure. The molar ratios of reactants were 1. WZ was characterized by elemental analysis, BET, XRD, and TPD of NH₃.

Results and Discussion

Apparent activation energies determined for both reactions were in the range of 65-76 kJ/mol, suggesting that WZ has a similar capability for catalyzing both reactions. Reaction profiles (Figure 1) shows that WZ exhibits a comparable sustained catalytic activity as SZ over 120 min TOS for both transesterification and esterification. After re-calcination of the used

catalyst at 315°C, the reaction profiles resembled with minor differences those obtained using the fresh catalyst, showing the ease of regeneration. However, the used catalyst treated with He at 315°C, thereby eliminating moisture but leaving carbonaceous species on the catalyst surface, did not regain the initial activity. The evidence suggests that catalyst deactivation occurs due to the formation of carbonaceous deposits.

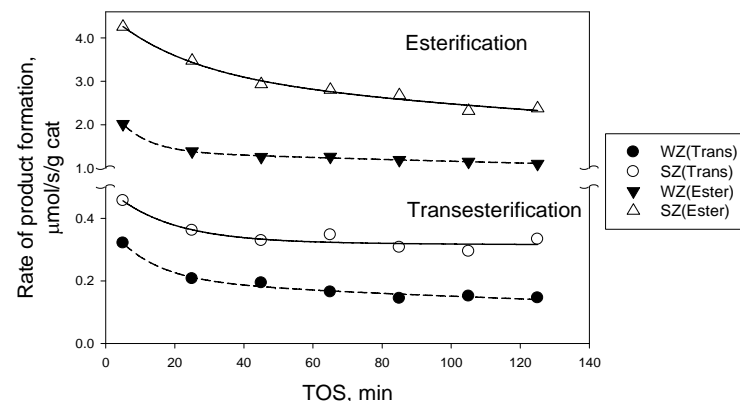


Figure 1: Reaction profiles of WZ for transesterification of EtOAc and esterification HAc with MeOH at 120°C.

Selective poisoning experiments showed that both reactions primarily took place on Brønsted acid sites. The catalyst pretreated with water showed higher initial reaction rates; however, the activity reached the same plateau as the fresh catalyst. The results obtained from determined apparent reaction orders and pre-adsorption experiments can explicitly explain the reaction pathway for the reactions, as will be discussed.

Significance

This study provides fundamental insight into transesterification and esterification, important reactions for biodiesel synthesis on solid acid catalysts.

Acknowledgments

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References

1. Lopez, D.E., Goodwin, J.G., Jr., Bruce, D.A., and Lotero, E. *Appl. Catal. A: General* 295, 97 (2005).
2. Suwannakarn, K., Lotero, E., and Goodwin, J.G., Jr. In preparation.
3. Koster, R., Van der Linden, B., Poels, E., and Blik, A. *J. Catal.* 204, 333 (2001).