Upgrading of Bio-oil via Acid Removal: Effect of Various Alcohols and Aldehydes on Esterification of Acetic Acid

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Introduction

With growing environmental concerns and the increasing consumption of fossil fuels, which have limited reserves, the use of biomass as an alternative energy source has gained significant attention. Bio-oil derived from the fast pyrolysis of biomass is a potential candidate to replace conventional transportation fuels. However, due to its high oxygen contents and high acidity which make biomass-derived oils corrosive and unstable, bio-oil cannot be used as transportation fuels without being upgraded [1].

Esterification is a possible route to remove acetic acid by utilizing alcohols contained in bio-oil. In this work, the impact of major alcohols (i.e., methanol, ethanol and ethylene glycol) found in bio-oil [1] on the conversion of acetic acid over organic-inorganic mesoporous silicas functionalized with sulfonic acid group (SO_3H-SBA-15) was studied. Since bio-oil also contains a considerable amount of reactive aldehydes, it raises a question as to whether those aldehydes (acetaldehyde, propionaldehyde and glyoxal) can inhibit the esterification of acetic acid. Reported here are the results of those studies.

Materials and Methods

SO_3H-SBA-15 was prepared following the procedures described elsewhere [2]. MPTMS [(3-mercaptopropyl) trimethoxysilane] and H_2O_2 were varied from 0-0.0065 M in order to vary the %loading of SO_3H acid group from 0-15%. Reactions were carried out in a batch reactor at 50-100^{o}C. Reactants were 6 M alcohol/3 M acetic acid for the study of alcohol effects. In the aldehyde effect study, acetic acid and aldehyde were used at 1.5 M representing the amount found in bio-oil and kept constant while the concentration of ethanol was varied in order to obtain a molar ratio of ethanol-to-acetic acid (E/A) of 0.6 and 2.7.

Results and Discussion

The results showing the catalyst activity for the esterification of acetic acid with methanol at 50^{o}C are given in Fig. 1. The conversion of acetic acid increased with increasing %SO_3H loading but only a slight improvement was observed when %loading of SO_3H increased from 10 to 15%. However, 10% SO_3H-SBA-15 was more active than 15% SO_3H-SBA-15 when the activity of catalysts was compared on the basis of SO_3H acid site (activity/site). Therefore, the impact of various aldehydes and other alcohols on acetic acid conversion was performed on 10% SO_3H-SBA-15.

Fig. 2 shows the conversion of acetic acid when the E/A was 0.6. It is clearly seen that at 50^{o}C, the conversion of acetic acid in the presence of acetaldehyde was lower than in its absence. This negative impact of acetaldehyde on the acetic conversion at low temperature (50^{o}C) was also observed even though ethanol was used in an excess amount (E/A = 2.7). A significant amount of acetaldehyde and ethanol were consumed and acetaldehyde diethyl acetal was formed during the reaction. This suggests that acetalization of acetaldehyde with ethanol was taking place and was more favored at low temperature [3]. In contrast, there was no change in the acetic conversion at 100^{o}C, regardless of acetaldehyde addition or amount of ethanol. The impact of other aldehydes and alcohols on the conversion of acetic acid will be discussed.

Significance

Although the study was not performed on real bio-oil, understanding the role of various aldehydes and alcohols on the esterification of acetic acid through the model compound studies can be used to determine the reactivity of those species present in bio-oil thereby leading to the better design of catalysts for bio-oil upgrading via esterification.

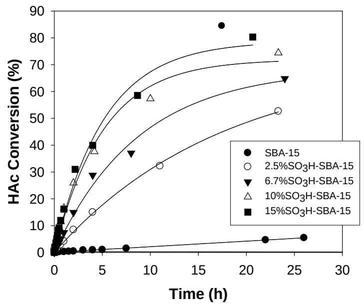

Figure 1. Conversions of acetic acid at 50^{o}C (HAc = 3 M and CH_3OH = 6 M)

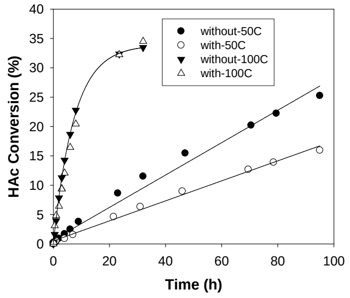

Figure 2. Conversions of acetic acid at EtOH/HAc = 0.6 with and without added acetaldehyde

References

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