

Catalytic Partial Oxidation of BioEsters to yield Syngas and Olefins

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Introduction

Catalytic partial oxidation is an effective method of producing olefins or syngas. Recently, our group has autothermally reformed bio-fuels: ethanol, biodiesel, vegetable oil, and small carbohydrates [1,2,3]. The multiple oxygen groups in these molecules have high sticking coefficients, which could result in surface oxametallacycles, resulting in complete decomposition of surface bound molecules. [4] We have observed conversions of > 99% in the reforming of small carbohydrates, which convert almost entirely to syngas. [5] This paper explores the autothermal reforming of two renewable esters: ethyl lactate and ethyl propionate, which differ only by a hydroxyl group.

Each fuel reacted autothermally over four different catalysts: Rh, Rh-Ce, Rh-La, and Pt. The observed product selectivities were tunable from syngas to olefins by varying the fuel to oxygen feed ratio (C/O).

Materials and Methods

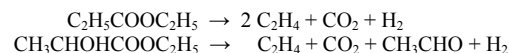
Ceramic α -alumina foams were loaded with noble metal salts and then calcined at 600 °C. In all cases, the final catalyst loadings were 5 wt % of the original support. The foams were then placed in a quartz reactor. Fuel was sprayed by a fuel injector onto the walls of the reactor which were heated to just above the fuel's boiling point. O₂ and N₂ were fed at air stoichiometry through a port above the catalyst, and product was sampled through a port below the catalyst for analysis on a GC. This experimental apparatus and procedure have been described elsewhere. [2,3]

Results and Discussion

At C/O~1 (defined as carbon in the fuel to oxygen from O₂), high selectivities to syngas were observed on all catalysts and fuels. This is consistent with heterogeneous catalysis, which decomposes the fuel completely to CO, H₂ [6]. CO₂ production stayed nearly fixed at about 20% for all C/O ratios, suggesting a decarboxylation of the ester, both on the surface of the catalyst and homogeneously. This decarboxylation limits the CO selectivity to about 75-85% on the best syngas catalysts, Rh-Ce and Rh-La.

At higher C/O, syngas production declined in favor of ethylene and acetaldehyde. Selectivity to ethylene from ethyl propionate was approximately double that from ethyl lactate, suggesting that the ethyl group produces ethylene from both esters. However, ethyl propionate produced almost no acetaldehyde, while ethyl lactate produced ~1:1 acetaldehyde to ethylene. These results, in combination with decarboxylation, suggest a homogeneous decomposition of the ester at high C/O. The groups on either side of the ester linkage from ethyl propionate become

olefins while the respective groups on the ethyl lactate with the hydroxyl group yield acetaldehyde and ethylene.



Selectivity to ethylene from ethyl propionate at high C/O was nearly 50% with high conversion. Endothermic homogeneous decomposition is driven by exothermic surface oxidation which consumes some of the fuel, thus limiting gas phase product selectivity. We will describe results comparing these esters with the methyl esters and with acetates, and other esters and organic acids to further confirm these mechanisms.

Significance

Individual bio-derived oxygenates are simple model components which lend insight into how more complex bio fuels will reform. Esters are common reactive groups in bio fuels. With increasing demand for alternative energy and chemical feed stocks, detailed understanding of the catalytic reforming of basic bio fuels allows for more efficient renewable technology.

References

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