

EFFECT OF FUNCTIONAL GROUPS ON AUTOTHERMAL PARTIAL OXIDATION OF BIO-OIL

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Summary

In order to probe possible mechanisms for the upgrading of biomass pyrolysis oil (bio-oil), a series of fuels with varying functional groups was subjected to autothermal partial oxidation at varying fuel carbon to oxygen (C/O) ratios over a Pt/Al₂O₃ and Rh/Al₂O₃ catalyst. Additional noncatalytic experiments investigated the role of gas phase chemistry and the effect of oxygen thereon. Dehydration and dehydrogenation appear to be the primary gas phase reactions, while C-C bond cleavage predominates surface chemistry. Oxygen plays a key role in reaction initiation.

Keywords

Sustainability, chemical feedstocks from biomass, alternate energy, biomass processing technologies

Introduction

A shift to sustainable and renewable energy sources is ultimately inevitable as fossil fuel resources become depleted. Many of the current end uses of nonrenewable resources can be fulfilled by non-carbonaceous energy sources such as solar and wind, but a fraction of the nonrenewable resources are used to produce commodity chemicals, solvents, and polymers. For these uses, a source of carbon is required.

The only known renewable source of carbon is biomass, which is highly distributed and has a low energy density. One of the most promising ways to increase the energy density of biomass is pyrolysis, or rapid heating in an oxygen deficient environment. This process produces bio-oil, a viscous, corrosive, highly complex liquid that is prone to further reactions (e.g. polymerization). Because of these shortcomings, the bio-oil must be preliminarily upgraded before transporting to a central refining facility.

Autothermal partial oxidation (APOx), typically employing a noble metal catalyst such as Pt or Rh, is one technology that can potentially improve the characteristics of bio-oil. However, bio-oils contain hundreds of molecular species with a wide variety of functional groups; a comprehensive understanding of how these functional groups react in an autothermal system has been elusive. This work aims to clarify the reactions of some of the functional groups present in bio-oil. Two-carbon molecules with varying functionalities were chosen to investigate the behavior of functional groups during autothermal reforming of bio-oil.

Experimental

Experiments were performed with a 17-mm ID quartz tube. Room-temperature fuels were fed to the tube through a

stainless steel nebulizer, which used high velocity N₂ and O₂ to create a cone of fuel mist. For autothermal experiments, the fuel mist impinged onto a hot catalyst bed, which consisted of three 1-cm α-Al₂O₃ foam monoliths each coated with ~5 wt. % Pt or Rh catalyst, followed by an uncoated α-Al₂O₃ foam monolith. Temperature was measured by a thermocouple inserted between the furthest downstream catalytic monolith and the uncoated monolith. For gas-phase experiments, the three catalytic monoliths were replaced by blank monoliths and external heat was supplied to the reactor by a clamshell furnace. Temperature was adjusted to match the temperature range of the autothermal experiments. The gaseous stream was sampled directly downstream of the uncoated monolith and analyzed via gas chromatography. Residence times were on the order of 100 ms. Aside from the identity of functional groups, the amount of co-fed oxygen was also varied as the parameter C/O ratio:

$$C/O \text{ Ratio} = \frac{\text{mol C in feed}}{\text{mol O in O}_2 \text{ co-feed}}$$

Results

The partial oxidation of ethanol (C₂H₅OH), acetaldehyde (C₂H₄O), ethylene glycol ((CH₂OH)₂), acetic acid (CH₃COOH), methyl formate (HCOOCH₃) and dimethyl ether ((CH₃)₂O) was investigated over a ~5 % Pt/Al₂O₃ or ~5 % Rh/Al₂O₃ catalyst and in the absence of a catalyst. These molecules are shown in figure 1. Conversion ranged from around 85 % to 40 % for temperatures between 700 °C and 400 °C, respectively. It is important to note

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that the low conversion is due largely to heat losses associated with low feed rates (~0.8 mL fuel per minute). Selected results are discussed below.

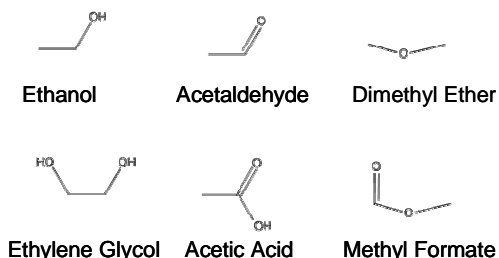


Figure 1. Two-carbon (C_2) molecules with various functional groups investigated in this work.

On Pt, major products were CO and H_2O , although acetaldehyde, CO_2 , CH_4 , and H_2 were also produced in significant amounts. Figure 2 shows selectivity (defined as the ratio of moles of carbon converted to a particular product to total moles of converted fuel carbon) to carbon monoxide (a) and acetaldehyde (b) for ethanol, ethylene glycol, and acetaldehyde. For ethanol, the correlation coefficient (R) for acetaldehyde and CO selectivity is $R = (-0.99)$, suggesting that acetaldehyde is an intermediate in CO production from ethanol. Selectivities to CH_4 and H_2 were also highly correlated with CO and

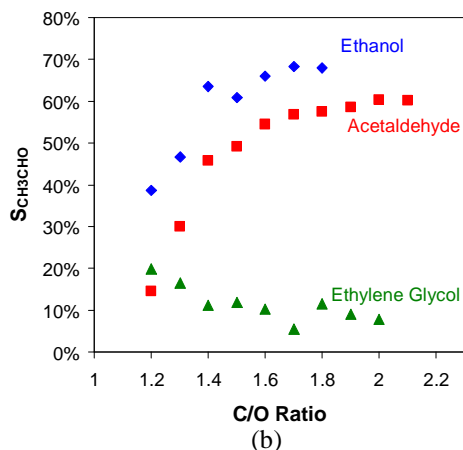
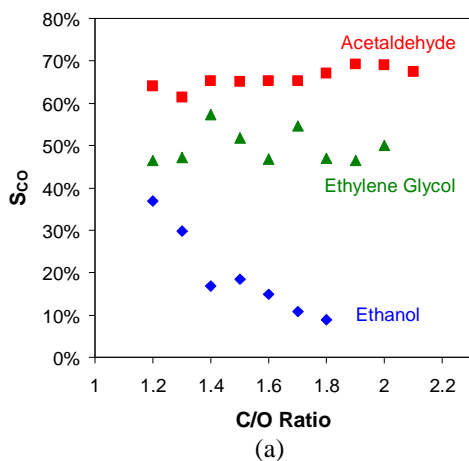


Figure 2. Selectivity to CO (a) and acetaldehyde (b) over a Pt catalyst. For acetaldehyde, selectivity to acetaldehyde is calculated as 100 % minus conversion.

acetaldehyde. Aside from acetaldehyde, the Pt catalyst produced almost exclusively C_1 compounds.

Acetaldehyde, which can be produced via gas-phase or surface dehydrogenation of ethanol or dehydration and rearrangement of ethylene glycol, appears to be a stable C_2 oxygenate at high temperatures, but appears to react rapidly in the presence of oxygen as suggested below. Figure 3 shows conversion of ethanol (a) and selectivity to acetaldehyde (b) as a function of temperature in the presence and absence of a Pt catalyst and O_2 . The presence of a small amount of O_2 markedly increases ethanol conversion but decreases selectivity to acetaldehyde, suggesting that O_2 plays a key role in reaction initiation and that much of the acetaldehyde observed may be formed after O_2 has been consumed.

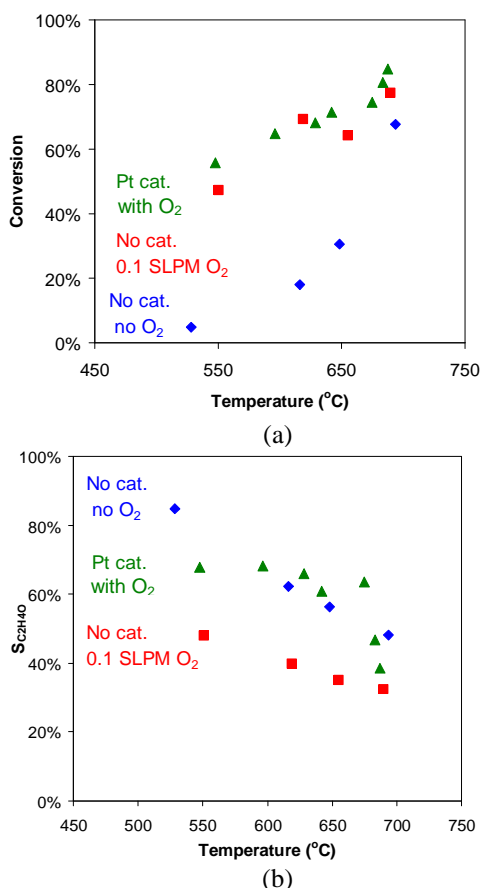


Figure 3. Conversion of ethanol (a) and selectivity to acetaldehyde (b). The presence of O_2 increases conversion but decreases selectivity to acetaldehyde. SLPM = Standard Liters per Minute. Pt cat. data has 0.2-0.3 SLPM O_2 co-feed.

Implications

These results suggest that functional group identity and O_2 co-feed both significantly affect APOx chemistry. Thus, this work may be useful in tuning selectivity to specific products given bio-oil of a certain composition, e.g. by altering O_2 co-feed, residence time, or amount of catalyst.