Probing structure and selectivity relationships for one-step biofuel production on bi-functional catalyst

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Introduction

According to the Department of Energy's report, 20-30% of the petroleum consumed in US could be replaced sustainably with biomass.[1] To fulfill this goal, a massive amount of biomass needs to be processed efficiently into hydrocarbons with chain length longer than C8. While many approaches have been recently developed to convert the biomass, the energy efficiency is still far from ideal. Currently, biofuel is priced at more than 15 USD per gallon compared with less than 4 USD per gallon for gasoline.[2] This is partially because the state-of-the-art biofuel production requires complex and energy-inefficient processes.

Our recently work using 2-methylfuran and butanal as model reactant has shown that biofuel can be efficiently produced from biomass-derived chemicals on bi-functional catalysts.[3] Levulinic acid is an up-stream biomass derived chemical, and is commonly considered as a platform chemical for biofuel generation.[4] In this study, Levulinic acid will be adopted as the feedstock for biofuel production. This work explores the structure and selectivity relationships to improve the biofuel yield.

Materials and Methods

Levulinic acid (LVA) (98%), butanal (98%), MCM-41mesostructured aluminosilicate (Si/Al ratio of 40), and ammonium tetrachloroplatinate (II) (99%), were purchased from Sigma-Aldrich, and used as-received. 0.1-0.3 wt% Pt/MCM-41 catalysts used in this work were prepared by incipient wetness impregnation of MCM-41 with a methanol solution of ammonium tetrachloroplatinate. The MCM-41 was mixed with the platinum solution at room temperature and the methanol naturally evaporated. The mixture was then dried in an oven at 373 K for 10 h, and calcined at 823 K for 3 h with temperature ramping from room temperature to 823 K at the rate of 5 K min⁻¹.

The reaction was performed in a plug-flow stainless-steel reactor. Before reaction, the catalyst was activated under hydrogen flow of 60 mL min⁻¹ at 673 K and 3.5 MPa for 1 h. After activation, the system was cooled down to the desired reaction temperature (between 503–623 K), and a mixture of LVA and butanal (molar ratio of LVA: butanal of 1:1 with total weight of 19 g) was pumped into the system with a flow rate of 0.02 mL min⁻¹. The reaction was run continuously for 20 h and the products were collected and analyzed using GC-MS.

Results and Discussion

Figure 1 shows the TEM image of Pt supported on mesoporous MCM-41. The mesoporous MCM-41 has average pore size of 2.6 nm in the TEM image, which is consistent with the results from nitrogen adsorption and desorption experiments. On the MCM-41, the Pt particles appear darker due to higher electron density, and have a size between 2-5 nm.



Figure 1. TEM image of platinum supported on mesoporous MCM-41.

On the as-synthesized Pt/MCM-41, the rection was carried out using LVA, butanal, and H₂ as feedstocks. While the conversion of LVA and butanal is above 96% on all the bifunctional catalysts, the final liquid composition depends on the loading of Pt on the MCM-41. With low loading of Pt at 0.1 wt%, C_{8+} hydrocarbon selectivity is 38%, and carbohydrate selectivity is 52% with C_7 as the balance. Increasing the Pt loading to 0.3 wt% will lead to products composed of 98% of C_{8+} and only 2% of C_7 . These results show that selectivity is sensitive to the structure of the bi-functional catalyst, and more detailed investigation will be presented.

Significance

Bi-functional catalysts can produce biofuels in an energy efficient manner. Our results indicate that the biofuel selectivity is sensitive to the catalyst structure. Detailed catalyst structure to selectivity relationships will be presented.

References

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