New Pathway for Jet Fuel Production from Bio-derived 2,3-Butanediol

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Introduction

Renewable jet fuel production from biomass is deemed as a key step to decarbonize the aviation sector [1]. This will help to address the challenges of climate change and the declining reserves of fossil fuels. In this work, we will present a new pathway for jet fuel production from biomass-derived 2,3-butanediol (2,3-BDO). The reactant, 2,3-BDO, is first converted to C_3-C_6 mixed olefins, which can be further upgraded to jet range hydrocarbons via oligomerization and hydrogenation reactions. 2,3-BDO is chosen as it can be produced via biomass fermentation at much higher titer owing to the relatively low toxicity of 2,3-BDO to the producing organism [2].

One of the key developments is the one-step conversion of 2,3-BDO to C_3-C_6 olefins via cascade dehydration and hydrogenation as proposed by Zheng *et al.* using Cu/ZSM-5 [3]. To further address catalyst deactivation and improve product selectivity, we developed a new pillared MFI (P-MFI) based catalyst. The presence of two-dimensional lamellar layers of micro- and meso-pores (Figure 1) significantly reduces the diffusion limitation [4], which is hypothesized to be the reason for improved catalyst stability and unique product selectivity.

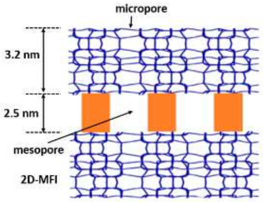

Figure 1: Schematic structure of P-MFI

Materials and Methods

The Cu modified P-MFI catalyst (20 wt.%) (Cu/P-MFI) was prepared by ammonia evaporation method and characterized with different techniques like XAS, STEM, Pyridine IR and NH_3 TPD. The conversion of 2,3-BDO was performed in a fixed bed reactor at ambient pressure. Oligomerization and hydrogenation reactions were carried out in a Parr batch reactor with Amberlyst® 36 and Pt/Al_2O_3, respectively.

Results and Discussion

Cu/P-MFI was shown to be very active and selective for converting 2,3-BDO to butenes and other C_3-C_6 olefins without over saturation to produce alkanes. The catalyst was also very stable with the conversion maintained at 100% for over 80 h and the total olefins selectivity decreased slightly from 90% to ~80%, with butenes as a major fraction. As shown in Figure 2A, this catalyst can be fully regenerated after running over 80 h. When comparing with conventional ZSM-5 (modified with Cu), the total olefins selectivity was similar while butenes selectivity was higher (Table 1). It is proposed that 2,3-BDO is converted to butenes, followed by butenes dimerization and cracking reactions to produce other C_3 and C_5 olefins. The significant reduction of diffusion length in Cu/P-MFI helped to minimize the dimerization and cracking reactions, favoring butenes formation. Since butenes are more active in downstream oligomerization compared with propene [5], the product distribution from Cu/P-MFI is more favorable.

Table 1. Product distributions comparison for Cu/P-MFI and Cu/ZSM-5 at TOS 40 h. Condition: 250 °C, ambient pressure, WHSV=1.0 h^{-1}. Si/Al ratio is 70 for both catalysts.

Catalyst	Propene	Butene	Pentene	Hexene	C_3-C_6 Olefins
Cu/P-MFI	7.4	67.6	9.5	1.3	85.8
Cu/ZSM-5	10.3	57.6	13.8	2.4	84.1

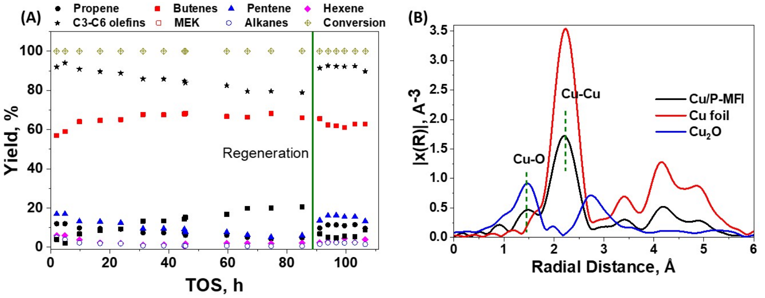

Figure 2: (A) Product distribution from 2, 3-BDO conversion using Cu/P-MFI catalyst.; (B) FT-EXAFS study on Cu/P-MFI catalyst after treatment at 300 °C in H_2 for 1 hr.

In situ XAS revealed (Figure 2B) most of the Cu is in metallic form with a small amount of Cu (I). Based on the estimation of the relationship between particle size and coordination number in FCC structure, the particle size of metallic Cu is in the range of 0.7-1.2 nm. The metallic Cu is proposed to be an active site for selective hydrogenation.

Jet fuel samples were demonstrated by converting C_3-C_6 olefins via oligomerization and hydrogenation. Simulated distillation showed that ~70% of liquid hydrocarbon was in jet fuel range. Preliminary fuel testing suggested the potential to meet Jet A properties.

Significance

Conversion of 2,3-BDO to C_3-C_6 olefins offers a novel pathway for jet fuel production from biomass. Hierarchical Cu/P-MFI enables stable and selective production of butenes.

References

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