

Upgrading of biomass-derived resources to liquid transportation fuels on Cu-base bifunctional catalysts

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Introduction

Lignocellulose, the most abundant carbohydrate in nature, is an inexpensive feedstock that can be transformed in sugars. Then, conversion of sugars in the biorefinery may

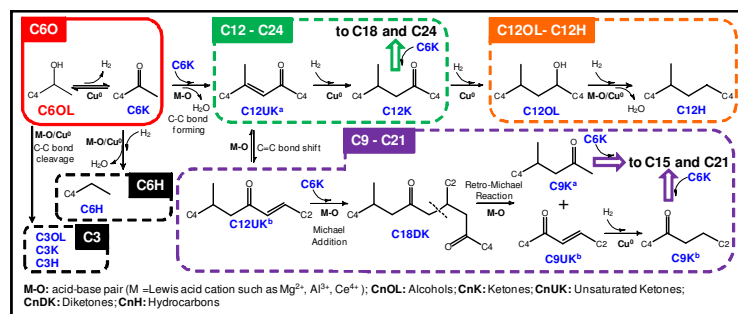


Figure 1: Pathways for conversion of 2-hexanol (C6OL) on bifunctional metal-base catalysts

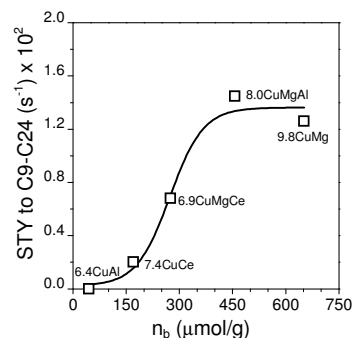


Figure 2: STY to C9-C24 products as a function of n_b on $ZCuM_l(M_{II})$ catalysts

result in the production of second generation biofuels. Liquid transportation fuels consist of nonoxygenated hydrocarbons in the range of C9-C16 for jet fuel and C12-C20 for diesel [1]. Thus, several strategies have been postulated for removal of oxygen from sugar-derived feedstocks [2,3]. In this work we investigate the synthesis of liquid transportation fuels from 2-hexanol (C6OL), a model molecule of the primary conversion of sugars. Formation of C9-C24 compounds from C6OL involves tandem dehydrogenation/C-C coupling/dehydration/hydrogenation reactions, Figure 1. Catalysts are mixed oxides that combine metallic Cu⁰ sites with moderate acid-base properties. The bifunctional nature of the catalytic process is discussed as well as the role played by each active site and also, the effect of cofeeding H₂ on the shift of the reaction pathway. The rate-limiting steps operating in catalysts with different relative abundance of metal and acid-base sites are postulated.

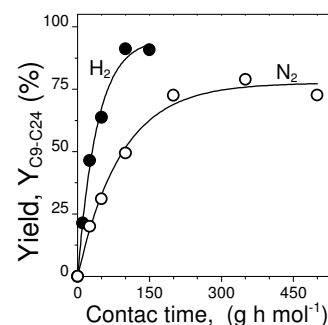


Figure 3: Yield to C9-C24 products at different reaction atmospheres (N₂ or H₂) and contact times on 8.0CuMgAl

Materials and Methods

Cu-free and Cu-containing $ZCuM_l(M_{II})$ mixed oxides (M_I, M_{II} : Mg²⁺, Al³⁺, or Ce⁴⁺; Z: wt. %Cu) were prepared by coprecipitation. Catalyst base and acid site numbers (n_b and n_a , μmol/g) were measured by TPD of CO₂ and NH₃. Cu⁰ dispersion was measured by combining TPR and N₂O decomposition. Vapor-phase conversion of C6OL was carried out at 573K and 101.3 kPa in a fixed-bed reactor on previously reduced catalysts. C6OL (4.1 kPa) was vaporized into N₂ or H₂.

Results and Discussion

$ZCuM_l(M_{II})$ oxides were more active and selective than their Cu-free homologues. Selectivity toward C9-C24 compounds increased with n_b/n_a site ratio on both kinds of catalysts. Thus, besides the need of base sites, the presence of dispersed Cu⁰ species improved formation of C9-C24 products because Cu⁰ promotes the C6OL dehydrogenation step at high rates. In Figure 2, the shape of the curve of the site time yield per metal site (STY) suggests a change of the rate-limiting step (r.l.s) as n_b increases: for $n_b < 400$ μmol/g, the r.l.s is a base-catalyzed reaction (the C-C bond forming step) whereas the rather constant values for $n_b > 400$ μmol/g indicates the Cu⁰-promoted hydrogenations as r.l.s, Figure 1. Thus, participation of surface Cu⁰ or base species in the r.l.s of C9-C24 product formation depends on the relative abundance of these sites in the bifunctional catalysts.

The most promising catalyst was 8.0CuMgAl. On this catalyst, the rate and yield to C9-C24 products was higher in H₂ (91%) than in N₂ (73%), Figure 3, thus confirming participation of hydrogen in the r.l.s. of the most basic bifunctional catalysts (Figure 2). The availability of hydrogen atoms determines the oxygenate/hydrocarbon ratio in the products and the predominant reaction pathway. Products with odd carbon atom number are formed through a distinct reaction pathway compared to products with even number. C9, C15 and C21 products are more likely formed in N₂ because their formation pathway starts from the C=C bond shift of the unsaturated ketone C12UK^a, Figure 1. This bond is rapidly reduced in presence of molecular H₂, thereby inhibiting that pathway. The O/C atom ratio is 1 in sugars, 0.17 in C6OL and can be decreased by applying the present strategy to 0.05 in N₂ or 0.024 in H₂.

Significance

Cu-Mg-Al(Ce) catalysts efficiently catalyze 2-hexanol upgrading to liquid fuels. Yields to branched C9-C24 compounds reach 91% on a Cu(8wt%)MgAl oxide at 573K and 101.3 kPa.

References

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