

Reseña Tesis

Catalytic strategies for the upgrading of biomass-derived oxygenated compounds by using Cu/Mg-Al mixed oxides, H-USY zeolites and carbon-based catalysts

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Objectives and Novelty

The main challenge of converting lignocellulosic biomass to hydrocarbon fuels is the removal of oxygen combined with the formation of C–C bonds to control the molecular weight of the final hydrocarbons, and requiring the less amount of H₂ from an external source. Aimed to increase the carbon chain length of some oxygenates, this work evaluated different catalytic strategies to provide some insights about the role of the catalyst properties on the conversion of those oxygenates towards fuel precursors [1,2].

Furfural is one of the most important chemicals derived from the thermochemical decomposition of biomass. The conversion of furfural can produce a wide range of alternative fuels and chemicals, which are traditionally obtained from petroleum-based feedstock. To produce fuel precursors from furfural, a pre-stabilization step into key intermediates is needed. Thus, carbon losses and humins formation are diminished, which are considered the major cause of catalyst deactivation. These intermediate products are still functional, so they can be further upgraded (C-C bond- chain enlarged) to a wide range of desirable products. In this sense, this work describes a selective catalytic route for the synthesis of high-density biofuel with low-temperature properties from biomass-derived furfural (FAL) and guaiacol (GCOL) compounds. This catalytic route involves three-tandem steps. The first step consisted in the hydrogenation of FAL to cyclopentanol (CPOL) over copper supported on Mg-Al mixed oxides. In the second step, the obtained CPOL was used to alkylate GCOL over a series of H-USY zeolites. The aim of this step was to produce molecules of larger carbon chain length. Finally, in the third step, the large oxygenated compounds were hydrodeoxygenated over Ru and Pd catalysts to produce hydrocarbons (C9–C16) in

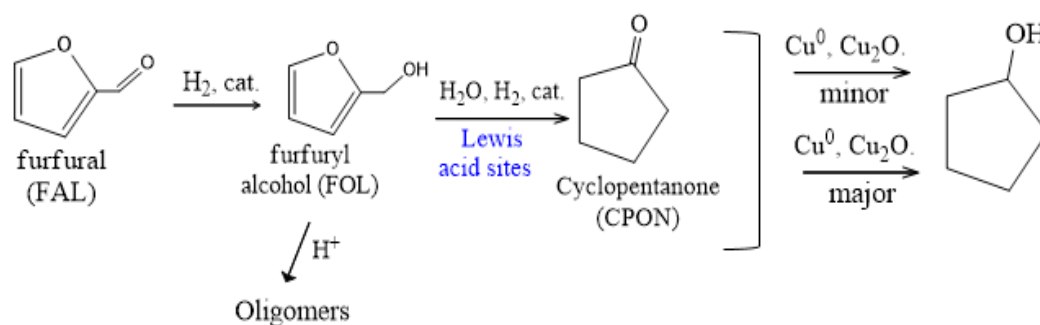
the molecular weight range that is appropriate for transportation fuels.

Catalyst Activity

The conversion of FAL towards CPOL was carried out in a batch reactor at 200 °C, 40 bar of H₂, 8 h and water as solvent. 0.1 g of Cu/MgAl catalysts with different Mg/Al molar ratio (0.5 and 3.0) were employed for the aqueous-phase conversion of FAL. In the alkylation reaction between CPOL and GCOL, a series of commercial H-USY zeolites (CBV780, CBV760, CBV720) with different Si/Al molar ratios were also evaluated. The reaction was conducted in a batch reactor at 160 °C, 20 bar of N₂, 6 h and 0.1 g of catalyst. The ratio of GCOL to CPOL was of 3:1 and decalin was used as solvent. After accomplishing the desired molecular weight via alkylation reaction, the liquid product that exhibited the higher yield of alkylated products was selected to perform the hydrodeoxygenation. Carbon based-catalysts (2%Pd/MWCNT, 2% Ru/MWCNT) and an acidic material (2% Pd/γ- Al₂O₃), were employed in this step. The reaction was carried out at 200 °C, 50 bar of H₂, 8 h and 0.5 g of catalyst.

Results and Discussion

The results of FAL conversion towards CPOL are shown in Figure 1. As observed, at the same reaction conversion (>90%), the yield to CPOL is higher on the Al-rich samples. By incorporating Al, the basicity of the support decreases and Lewis acidity sites are generated. These Lewis acid sites promote the furfuryl alcohol ring-rearrangement to cyclopentanone (Scheme 1). By correlating the catalytic activity with the NH₃-TPD results, it was found that the catalyst with the moderate acid strength (Cu/MgAl-0.5), exhibited the higher CPOL selectivity (Figure 2).



Scheme 1. Pathway for the conversion of FAL to CPOL.

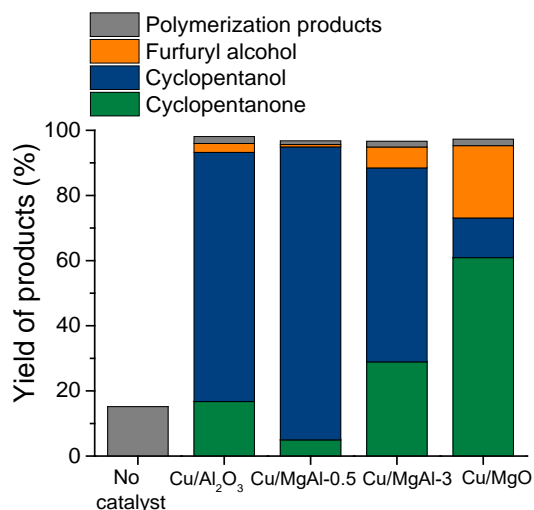


Figure 1. Distribution of products from the aqueous-phase conversion of furfural over Cu/MgAl catalyst [1].

Interestingly, over the Cu/Al₂O₃, the selectivity towards CPOL decreased indicating that a high acid-strength cause the formation of oligomers, which inhibit the cyclopentanone hydrogenation to CPOL. Moreover, the XPS results showed that the composition of the catalytic support not only affects the density and strength of the acid sites, but also the amount of active copper species (Cu⁺ and Cu⁰) on the catalyst surface (Figure 3). Thus, the higher yield of CPOL obtained on the Cu/MgAl-

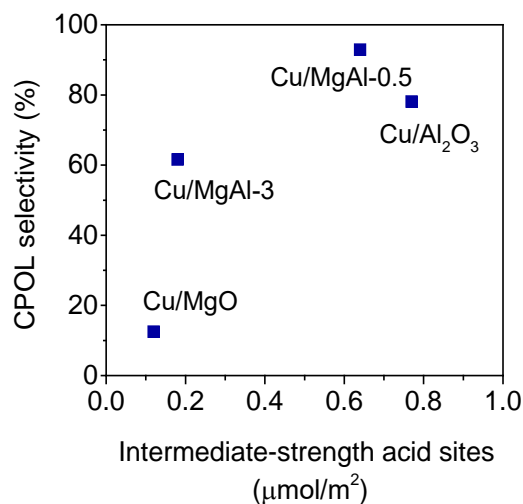


Figure 2. Correlation between intermediate-strength acid sites of the catalysts with CPOL selectivity.

0.5 catalyst (89.9% of CPOL yield) compared to the other materials, can be attributed to the following properties: moderate acidity, higher amount of active Cu⁺ and Cu⁰ sites, and good hydrothermal stability. Considering that CPOL is a potential alkylating agent for the production of cycloalkanes, the second stage of the proposed upgrading process consisted in the alkylation of GCOL with CPOL to produce C9–C16 oxygenates (Scheme 2).

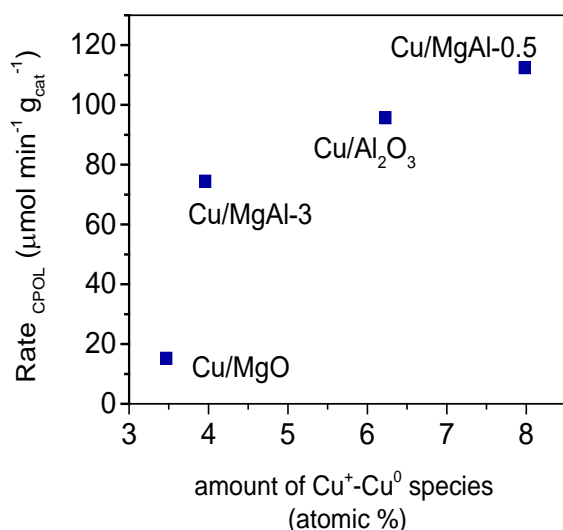


Figure 3. Correlation between active copper species and rate of CPOL.

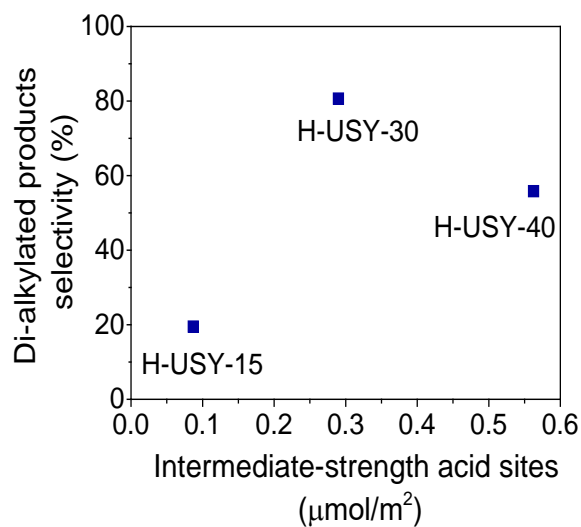
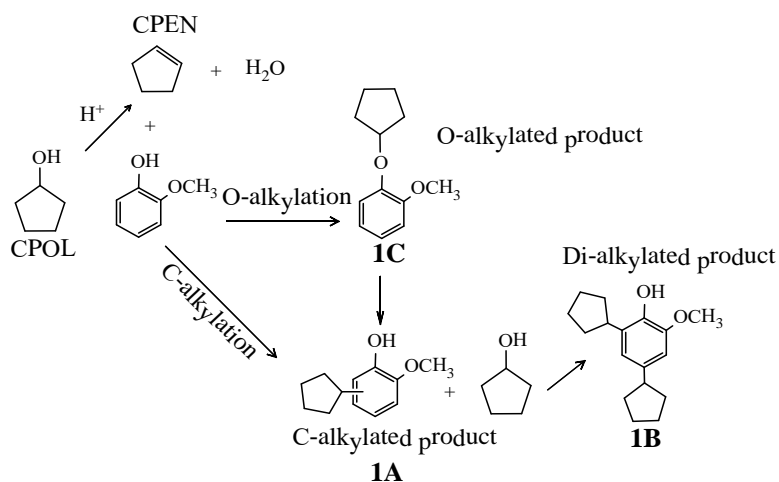


Figure 4. Correlation between the intermediate-strength sites of the zeolites with the selectivity to di-alkylated products.

By correlating the characterization results and the activity of the catalysts (Figure 4), it was observed that the higher acidity of the H-USY-15 could have promoted the formation of oligomers that probably caused the catalyst deactivation. In the case of the H-USY-40 zeolite, its lower Brønsted acidity

decreased the rate of alkylation and therefore, the selectivity to C-alkylated products. Then, the H-USY-30 zeolite exhibited the better activity due to its moderate acidity as compared with the other samples.



Scheme 2. Pathway for the alkylation of cyclopentanol with guaiacol.

Finally, the coupling compounds generated from alkylation would need to be deoxygenated to produce alkanes with properties that can be comparable with liquid fuels derived from petroleum energy sources. To carry out the hydrodeoxygenation of the alkylated products, the resulting liquid obtained over the H-USY-30 zeolite was used. A higher carbon yield of jet-fuel range alkanes (C12-C16) was achieved over the Ru/MWCNT catalyst (75%) compared to the other materials (58% and 45% for the Pd/MWCNT and Pd/Al₂O₃ catalysts, respectively). The better catalytic performance of the Ru/MWCNT

catalyst was associated with the oxophilic character of ruthenium and textural properties of the catalytic support. These results clearly show that carbon nanotubes (e.g., MWCNT) are a suitable support for hydrodeoxygenation reactions due to their intrinsic properties such as chemical inertness, hydrophobicity, and thermal stability. Table 1 shows some fuel properties of the biofuel obtained from the hydrodeoxygenation with Ru/MWCNT catalyst. Notably, the synthesized biofuel has high density and cold-flow properties as compared with those of the conventional jet fuels.

Property	Synthesized jet-fuel	Jet-fuel A1 kerosene based fuel
Density at 20°C (g mL ⁻¹)	0.865	0.775-0.840
Freezing point (°C)	<-40	MAX -47
Viscosity at -20°C (mm ² s ⁻¹)	6.06	MAX 8.0

Table 1. Some fuel properties of the synthesized bio-fuel and a conventional Jet Fuel.

Conclusions

This work demonstrated that it is possible to produce fuel precursors from the simultaneous conversion of two biomass derived oxygenates via different catalytic strategies. In the first strategy, the moderate acidity and higher amount of active copper species (Cu⁰ and Cu⁺) on the Cu/MgAl-0.5 catalyst improved the activity and selectivity towards cyclopentanol. In the second strategy, cyclopentanol was alkylated with guaiacol over different H-USY zeolites. Among the investigated zeolites, H-USY-30 zeolite demonstrated the best catalytic performance and stability, which was attributed to its moderate acid strength. Finally, in the hydrodeoxygenation strategy, the oxophilic nature of Ru combined with the textural properties of the MWCNT support was found to be effective to produce a higher yield of deoxygenated products

under mild reaction conditions. These findings have important consequences for bio-oil upgrading since alkylation become an effective way to enhance the stream of the small oxygenates biomass-derived compounds without loss of carbon.

Related Publications

- [1] N. Pino, G. Hincapié, D. López, Selective catalytic route for the synthesis of high-density biofuel using biomass-derived compounds, *Energy and Fuels* 32 (2018) 561–573.
- [2] N. Pino, T. Bui, G. Hincapié, D. López, D.E. Resasco, Hydrophobic zeolites for the upgrading of biomass-derived short oxygenated compounds in water/oil emulsions, *Appl. Catal. A Gen.* 559 (2018) 94–101.