Catalytic deoxygenation of tristearin to hydrocarbons over supported nickel alloy catalysts

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Introduction

Biodiesel (fatty acid methyl esters) has shortcomings as a renewable fuel that can be attributed to its oxygen content. Consequently, there is a strong impetus to develop processes for the conversion of fatty acid and triglyceride feeds to hydrocarbons that can serve as fully fungible fuels. Hydrodeoxygenation (HDO) processes can be employed but these require high pressures of hydrogen and the use of sulfided metal catalysts. To avoid these issues, the removal of oxygen from fats and oils via decarboxylation/decarbonylation (deCO_x) has begun to attract interest. Work by several research groups has shown that supported Pd and Pt catalysts are effective for the removal of oxygen via deCO_x [1]. Given the high price of these metals, we [2] and others [3] have sought to develop cheaper alternatives and have shown that supported Ni-based catalysts can exhibit good activity for the catalytic upgrading of model fatty acids and triglycerides. The present study focused on improving the activity and selectivity of supported Ni catalysts by incorporating Cu as a promoter, Ni-Cu catalysts having been shown to outperform their monometallic (Ni) counterpart in similar reactions [4].

Materials and Methods

The supported catalysts were prepared by incipient wetness impregnation using Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·3H₂O as the metal precursors and γ -Al₂O₃ as the support. The fresh catalysts (particle size less than 150 µm) were calcined *ex situ* at 500 °C for 3 h under air and then reduced *in situ* at 350 °C under 10% H₂ in N₂ for 3 h. The deCO_x experiments were performed in a mechanically stirred 100 mL stainless steel autoclave using tristearin as the model feed. After the addition of the feed, the autoclave was pressurized with H₂ to 580 psi and a continuous flow of H₂ (60 mL/min) was maintained for the duration of the experiment. Liquid products were analyzed using simulated distillation GC.

Results and Discussion

The yields of the liquid products from the $deCO_x$ of tristearin are shown in **Table 1** for the various catalysts tested.

Table 1. Liquid 1	product vie	lds obtained	from tristear	in at 260 ° (C and 6 h	reaction time.
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Catalyst	Metal particle size (nm)	Conversion (%)	C10-C17 Yield (%)	C17 Yield (%)
20% Ni/Al ₂ O ₃	7.4	26	23	11
20% Ni-2%Cu/Al ₂ O ₃	6.4	85	80	56
20% Ni-5%Cu/Al ₂ O ₃	10.7	>99	98	71

At 260 °C the bimetallic catalysts showed superior activity and selectivity to diesel range hydrocarbons (~C10-C17) as compared to the monometallic Ni catalyst. Notably, the selectivity to C17 (heptadecane) was much higher for the Cu-promoted catalysts, indicating a reduction in cracking activity. As shown in **Figure 1**, the entire liquid product obtained using the 20%Ni-5%Cu/Al₂O₃ catalyst boiled in the diesel fuel range. Similar results were obtained at a reaction temperature of 300 °C (data not shown). Small differences in the weight loss of the spent catalysts during thermal gravimetric analysis (TGA) indicate that the observed promotion effects are not the result of decreased coke formation. The improved catalytic performance also appeared to be independent of the metal particle size. Temperature programmed reduction (TPR) results for the fresh catalysts showed that the increased Cu loading caused a decrease in the reduction temperature of the Ni. This suggests the increased activity is a consequence of the lower reduction temperature of the bimetallic catalysts, resulting in a higher concentration of active sites under the reaction conditions.



Figure 1. Boiling point distribution plot of the liquid products from tristearin deCOx catalyzed by 20%Ni-5%Cu/Al₂O₃ at 260 °C.

Significance

Promotion with Cu is a promising approach for improving the activity and selectivity (to long chain hydrocarbons) of supported Ni catalysts in the $deCO_x$ of triglycerides.

References

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