

Catalytic Deoxygenation of Free Fatty Acids over Pd/C

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Introduction

Environmental concerns and dwindling world petroleum reserves have generated great interest in producing transportation fuels from bio-renewable resources. In this work, we investigate catalytic deoxygenation of free fatty acids (FFAs) [1] to produce linear hydrocarbons for second-generation biofuels. FFAs can be derived from hydrolysis of triglycerides found in edible and non-edible fats and oils. After deoxygenation, the hydrocarbon product can undergo hydroisomerization and hydrocracking to yield fuels in the diesel, kerosene and gasoline boiling ranges. For example, the C₁₇ linear hydrocarbons produced by catalytic deoxygenation of C₁₈ FFAs (stearic, oleic, and linoleic acids) can be used in green diesel after only mild hydroisomerization.

Catalytic deoxygenation of FFAs has been reported to occur via two reaction pathways: decarboxylation and decarbonylation. Recent literature indicates that the decarboxylation pathway is predominant over Pd/C [2]. Catalyst deactivation has been inferred to occur via coking and/or CO poisoning [3]. The research presented here seeks to further elucidate the deoxygenation pathways of saturated and unsaturated FFAs over Pd/C and the factors that influence catalyst lifetime. Deoxygenation of stearic, oleic, linoleic, and palmitic acids in alkane solvents (dodecane, pentadecane, and heptadecane) was investigated under He and 10% H₂ in He.

Materials and Methods

Reagent-grade chemicals were purchased from Sigma Aldrich and Fisher Scientific and used as received. Ultra-high-purity compressed gases were supplied by National Welders. Batch experiments were conducted using a 50-mL stirred autoclave (Autoclave Engineers) and 335 mg of suspended 5% Pd/C catalyst powder (Degussa E117). Pulsed CO chemisorption indicated the Pd dispersion to be 23% assuming a stoichiometry of 2:1 Pd:CO. Typically, the catalyst was reduced prior to reaction at 200°C in solvent under 2 atm H₂. Reaction conditions were 300°C and 15 atm with 60 mL/min of flowing He or 10% H₂. The reactor effluent was analyzed on-line using a quadrupole mass spectrometer (QMS) (Pfeiffer PrismaPlus) with a capillary inlet system. The liquid product was analyzed by gas chromatography (GC) using an HP 5890 FID instrument equipped with an EC-5 capillary column (30 m x 0.32 mm x 1.0 μm).

Results and Discussion

Saturated FFAs, such as stearic and palmitic acids, are readily deoxygenated under a He purge to the corresponding C_{N-1} linear alkanes in high yields (typically >98%). On-line QMS [Fig. 1] revealed the concomitant generation of CO₂ and H₂. Blank experiments with solvent and no FFA confirmed that H₂ is a reaction product. No significant difference in reaction rates was observed for stearic acid deoxygenation under He in dodecane and heptadecane. Additional experiments demonstrated that the decarboxylation rate (as measured by CO₂ evolution) declines markedly with increasing FFA/catalyst ratio. Unsaturated FFAs,

such as oleic and linoleic acids, must be hydrogenated before deoxygenation can proceed at a significant rate. Under flowing 10% H₂, FFA hydrogenation occurs at lower temperatures [Fig. 2], and saturated and unsaturated FFAs yield equivalent rates and product yields. The initial rate of decarboxylation of stearic acid is approximately 3-fold greater under He than under 10% H₂; however, rapid catalyst deactivation occurs under He, as evidenced by repeated batch

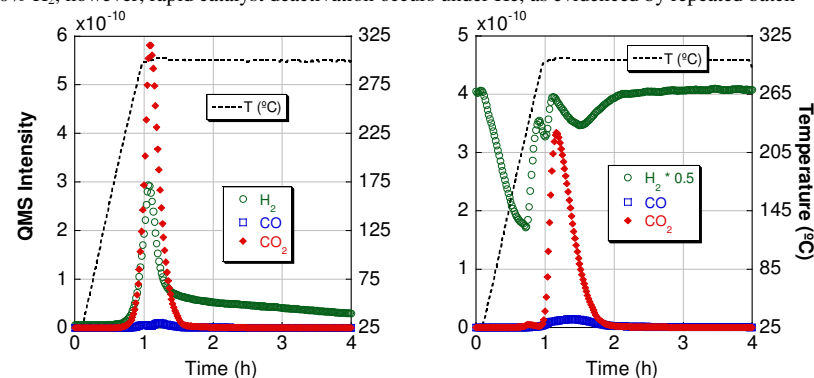


Figure 1. Stearic acid deoxygenation under He evidences co-production of CO₂ and H₂.

Figure 2. Oleic acid deoxygenation under 10% H₂ showing FFA hydrogenation.

experiments using the same catalyst. In 10% H₂, catalyst lifetime is improved approximately 10-fold. This is consistent with previous research which concluded that H₂ was necessary for continuous decarboxylation of FFAs over supported Pd catalysts although H₂ was not consumed in the reaction [1]. In contrast, the decarbonylation rate is not affected by H₂ partial pressure. We infer that H₂ is involved in the decarboxylation pathway but not the decarbonylation pathway. Our results are consistent with decarbonylation as the primary reaction pathway. Moreover, we infer that CO₂ is produced from the decarbonylation products (CO and H₂O) via the water gas shift reaction.

Significance

This work provides further insight into the reaction pathways by which FFAs available from edible and non-edible fats and oils are deoxygenated over supported Pd catalysts to produce hydrocarbons for biofuels.

References

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