

Deoxygenation of Methyl octanoate and Isomerization of Paraffins over Supported Pt-Pd Catalysts

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Introduction

The use of renewable vegetable oils to produce biodiesel has drawn considerable public attention. However, as-produced biodiesel has some drawbacks such as low stability and fungibility with regular diesel. An interesting additional process to biodiesel production is conversion to alkanes, which can be used as normal diesel. Triglyceride molecules in vegetable oils contain fragments of C14 to C20 straight chains, which can be converted to long paraffins that bear a potentially high cetane number (CN), but at the same time they may result in increased cloud point (CP). In order to be used in regular diesel, these molecules have to undergo mild isomerization to produced mono-branched isoparaffins with still acceptable CN and lower CP. In this work, methyl octanoate (MeOct) has been used as a model compound to study the conversion of biodiesel-like oxygenates to paraffins and isoparaffins, which meet the above requirements. To achieve this goal we have investigated two consecutive catalytic steps: first, deoxygenation of oxygenates to paraffinic compounds and second, mild isomerization of straight-chain products to slightly branched isoparaffins.

Materials and Methods

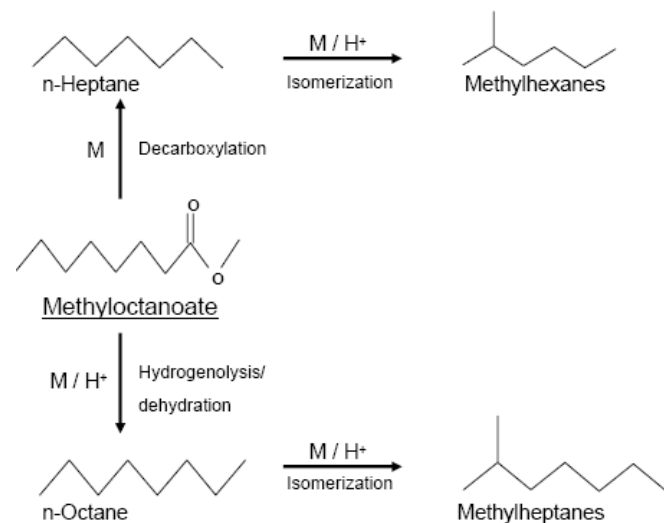
The reaction studies were carried out over various noble-metal catalysts (Pt-Pd) under three different conditions: a) in pure H₂, b) in pure He and c) in 5% H₂/He. In all cases, the operating pressure and temperature were kept at 500 psig and 300°C, respectively. The products were analyzed and identified by HP 6890 GC and Shimadzu P500 GC-MS.

Results and Discussion

We have found that the deoxygenation of MeOct readily occurs over bimetallic 0.4%Pt-0.6%Pd/ γ -Al₂O₃ as well as monometallic 5%Pd/C catalysts in the flow of either H₂ or He (see Scheme 1). Interestingly, it was observed that the Pd/C catalyst deactivates much faster than the bimetallic Pt-Pd/ γ -Al₂O₃ under both carrier gases. Under He, the main products from the two catalysts were n-heptane (n-C7) and n-heptenes, which result from decarboxylation and decarbonylation/dehydration of MeOct, respectively. Due to rapid hydrogenation, under H₂ flow, the main product was n-C7. Interestingly, the selectivity to n-C8 (a product of C-O bond hydrogenolysis) greatly increased when acidic supports such as W-ZrO₂, 3%F-Al₂O₃ and HY (Si/Al=15) were used. The product ratio n-C8/n-C7 (which can be taken as the ratio of hydrogenolysis-to-decarboxylation) increased for the different supports in the following order: F-Al₂O₃ << HY < W-ZrO₂. Although this trend does not correspond with the acid density, it might be related to acid strength of the acidic supports.

The formation of n-C8 can be explained in three steps: C-O hydrogenolysis on metal sites, dehydration of oxygenate intermediate on acid sites to alkene, and hydrogenation of alkene to

alkane on metal sites. The double hydrogenolysis of C-O bonds to directly convert MeOct to n-C8 is less likely since n-C8 was not observed on monofunctional metal catalysts (e.g. bimetallic Pt-Pd/ γ -Al₂O₃). This result opens the possibility for catalyst tailoring both metal and acid functions to achieve desired product selectivities.



Scheme 1: Reaction pathway of methyl octanoate on metal and acid functions.

We have also observed isomerization of n-C7 and n-C8 to branched isoparaffins over two of the bifunctional catalysts, Pt-Pd/W-ZrO₂ and Pt-Pd/HY, but not on Pt-Pd/F-Al₂O₃. Isomerization products were mainly mono-branched isomers: methylheptanes and methylhexanes when the carrier was pure H₂ flow. Some additional methylheptenes and methylhexenes were formed with a 5% H₂/He carrier. This is a desirable outcome since mono-branched alkanes have CP lower than normal paraffins, while keeping an acceptable CN. On both catalysts, isomerization selectivity was seen to increase five times when partial H₂ was used instead of pure H₂. This can be explained by the well-know effect of increasing the surface residence time of the alkene intermediates at low H₂ partial pressure, which leads to higher isomerization selectivity. The order of isomerization selectivity was W-ZrO₂ > HY, which indicates that the isomerization may depend more strongly on the acid strength than density.