

Deoxygenation of Methyl Esters over Supported Noble Metal Catalysts

Phuong T. M. Do,¹ Martina Chiappero,¹ Lance L. Lobban, and Daniel E. Resasco^{1*}
¹Chemical, Biological and Material Engineering Department, University of Oklahoma,
Norman, Oklahoma 73019 (USA)
*resasco@ou.edu

Introduction

In recent years, vegetable oils, which mostly consist of triglyceride compounds, and derived-vegetable-oil products, biodiesel or fatty acid methyl esters (FAME), are one alternative for diesel fuels. Although biodiesels have many advantages, such as being produced domestically from renewable sources and exhibiting high cetane number, they bear some disadvantages as high cloud point and pour point, low thermal and chemical stability, and a heat content 9-13 % lower than conventional diesel that reduces their applicability. Researchers have identified the catalytic conversion of biodiesel to standard diesel via deoxygenation as a viable solution to this problem since no modification in engines or fuel infrastructure would be required.

In this study, we have investigated deoxygenation reactions of pure methyl esters over supported noble metal catalysts both in vapor and liquid phase. First, methyl hexanoate was converted in vapor phase to screen catalysts and understand the various product formation paths. Then, a more realistic FAME feedstock compound, methyl stearate, was used to effect its conversion into standard diesel molecules in liquid phase. Major products from deoxygenation reaction included: light gases, deoxygenated hydrocarbons, deoxygenated oxygenates and condensation/coupling compounds. As we varied the catalysts from monometallic (Pt) to bimetallic (Pt-Sn) and the carrier gas from hydrogen-rich to inert atmospheres, the selectivities of different products were significantly changed.

Materials and Methods

The reactions of methyl hexanoate were carried out in a fixed-bed tubular reactor (1/2" OD stainless steel tube), equipped with a thermo well in the center of the catalyst bed to insert the thermocouple. The catalytic activity measurements were conducted in the gas phase at 653 K, at atmospheric pressure and in the flow of either H₂ or He. The conversion of methyl stearate was conducted in the liquid phase at different temperatures (573 K to 623 K) and 0.69 MPa in a 300 ml stirred reactor (Parr Corporation). The reaction was conducted in semi-batch mode, in which either hydrogen or helium gas was continuously passed through the reactor to remove the light gases produced by the reaction. All of the liquid products were quantified by using a Hewlett Packard 6890 GC. Product identifications were carried out in a Shimadzu GC-MS-P500. Gas products (CO₂, CO and CH₄) were analyzed by online Carle GC.

Pt and Sn were incorporated into silica support by incipient wetness impregnation with aqueous solutions of the corresponding metal precursors. Catalysts were characterized by CO-chemisorption, TPR, FTIR, and XPS techniques.

Results and Discussion

High activity and selectivity toward diesel-like hydrocarbons from both model compound and real vegetable oil feedstock (methyl hexanoate and methyl stearate) can be successfully achieved with all tested supported Pt catalysts. When feeding methyl hexanoate, a mixture of C₅ alkane and alkenes, which results from decarbonylation or decarboxylation of the ester, acid and other 1-oxygen-containing compounds, are dominant products. C₆ hydrocarbons are also

formed in a much smaller quantity. The C₆ compounds are originated from successive removal of oxygen via either oxygen vacancies or direct C-O hydrogenolysis on the metal sites or a combination of dehydration and hydrogenation routes. Under inert atmosphere, formations of heavy products such as dipentyl ketone, hexylhexanoate, and vastly n-undecanone, are dominant at low conversion, then get converted to lighter products at high conversion. Formation of n-undecanone from methyl hexanoate released CO₂, which is detected as a sole gas under He flow in Figure 1.

This also indicates that formation of C₅ hydrocarbons from methyl ester via only *decarboxylation*. Under H₂ atmosphere, CO is the dominant light gas, which indicates that *decarbonylation* is the main mode of deoxygenation in the vapor phase. Likewise, the results from the liquid phase experiments show that the deoxygenation of methyl stearate produces a mixture of heptadecane/heptadecenes with high selectivity. As in the reaction conducted in the vapor phase, in this case the atmosphere also plays an important roll. Under H₂ gas the conversion, stability, and selectivity towards paraffin are increased. However, the light gas compositions do not change as dramatically as in the vapor phase mode. Regardless the carrier gas used, CO is still present as the dominant gaseous product, which indicates that *decarbonylation* is the major deoxygenation reaction path for methyl stearate in liquid phase.

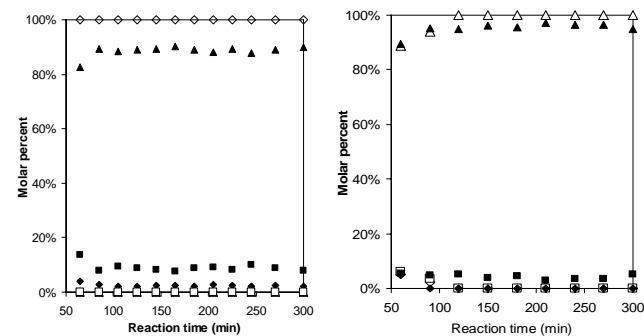


Figure 1. Compositions of light gas products from methyl hexanoate (left) and methyl stearate (right) reactions. Notation: CO₂ (diamond), CO (triangle), CH₄ (square). H₂ atmosphere (filled), He atmosphere (unfilled).

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