DEOXYGENATION OF FATTY ACIDS FOR PREPARATION OF HYDROCARBONS

FIELD

Disclosed herein are embodiments of fatty acid deoxygenation (decarboxylation/decarbonylation/dehydration) catalysts and methods of making and using the same.

BACKGROUND

The terms "green diesel" and "renewable diesel" broadly refer to diesel-quality, non-FAME (fatty acid methyl ester) fuels derived from renewable resources (e.g., plant and/or animal sources) that are suitable for direct use in most ordinary compression ignition diesel engines. Renewable diesel is chemically distinguishable from biodiesel, which is primarily composed of fatty-acid-derived mono alkyl esters. The oxygen content of biodiesel is too high to be suitable as a direct replacement for conventional petroleum diesel. In contrast, renewable diesel is substantially oxygen-free and is indistinguishable from petroleum diesel. Thus, renewable diesel can replace petroleum diesel and/or be used in blends with petroleum diesel. Renewable diesel also has higher energy content per volume compared to biodiesel. Renewable diesel may be used or blended in aircraft fuel where oxygen-containing fuels are not allowed.

Conventional processes for converting renewable oils or fats, such as vegetable oil or animal fat, to renewable diesel include catalytic or thermal decarboxylation (removal of carbon dioxide), catalytic decarbonylation (removal of carbon monoxide) and catalytic hydrocracking. The products are expected to be simple hydrocarbons or olefins. The feed for these processes can be a triglyceride or a free fatty acid.

Commercially available deoxygenation catalysts suffer from several disadvantages such as poor stability, low activity, undesirable side reactions, and/or a need to operate under high pressure conditions in the presence of hydrogen gas.

SUMMARY

Embodiments of methods for making renewable fuel (such as renewable gasoline, renewable diesel, or renewable aviation fuel) by deoxygenating fatty acids to produce hydrocarbons are disclosed. Embodiments of highly active, selective catalysts for deoxygenating fatty acids and embodiments of methods for making and using the catalysts also are disclosed. The disclosed catalysts comprise a Group VIII metal, a support material, and a transition metal oxide or a non-transition metal. In particular embodiments, the Group VIII metal is platinum. The support material is carbon, a metal oxide, or a metalloid oxide. In some embodiments, the support is a metal oxide, and the catalyst further includes a transition metal oxide. In other embodiments, the support is carbon, and the catalyst further includes one or more non-transition metals (e.g., Ge, Sn, Pb, Bi).

In certain embodiments, the catalyst is $MO_3/Pt/ZrO_2$ where M is W, Mo, or a combination thereof, Pt/Ge/C, Pt/Sn/C, or a mixture thereof. In some embodiments, the catalyst comprises 0.1 wt % to 1.5 wt % Pt and 6 wt % to 30 wt % MO_3 on ZrO_2, relative to the total mass of catalyst. In one embodiment, the catalyst comprises 0.7 wt % Pt and 12 wt % WO_3 on ZrO_2. In another embodiment, the catalyst consists essentially of 0.7 wt % Pt and 12 wt % WO_3 on ZrO_2. In one embodiment, the catalyst comprises 0.7 wt % Pt and 7.8 wt % MoO_3 on ZrO_2. In another embodiment, the catalyst consists essentially of 0.7 wt % Pt and 7.8 wt % MoO_3 on ZrO_2. In other embodiments, the catalyst comprises 1 wt % to 5 wt % Pt and 0.1 wt % to 5 wt % Ge and/or Sn on carbon. In certain embodiments, the catalyst comprises a) 5 wt % Pt and b) 0.5 wt % Ge, 0.5 wt % Sn, or 0.5 wt % of a combination of Ge and Sn, relative to the total mass of the catalyst. In particular embodiments, the catalyst consists essentially of a) 5 wt % Pt and b) either 0.5 wt % Ge or 0.5 wt % Sn on carbon, relative to the total mass of the catalyst.

Embodiments of methods for deoxygenating fatty acids with the disclosed catalysts are also disclosed. In one embodiment, fatty acids are exposed to a catalyst selected from a) Pt and MO_3 on ZrO_2 where M is W, Mo, or a combination thereof, or b) Pt/Ge or Pt/Sn on carbon, and the catalyst deoxygenates at least 10% of the fatty acids in a fatty acid composition. Some embodiments of the disclosed catalysts deoxygenate at least 80% of the fatty acids.

The fatty acids are obtained from a plant oil, a plant fat, an animal fat, or any combination thereof. In some embodiments, at least 90% of the fatty acids in the fatty acid composition are saturated fatty acids. In certain embodiments, the catalyst comprises 0.1-1.5 wt % Pt and 6-30 wt % MO_3 on ZrO_2, where M is W, Mo, or a combination thereof, relative to a total mass of the catalyst. In one embodiment, the catalyst consists essentially of 0.7 wt % Pt and 12 wt % WO_3 on ZrO_2, relative to the total mass of the catalyst. In another embodiment, the catalyst consists essentially of 0.7 wt % Pt and 7.8 wt % MoO_3 on ZrO_2, relative to the total mass of the catalyst.

In other embodiments, at least some of the fatty acids are unsaturated fatty acids having one or more double and/or triple bonds. In certain embodiments, the catalyst comprises a) 1-5 wt % Pt and b) 0.1-5 wt % Ge, 0.1-5 wt % Sn, or 0.1-5 wt % of a combination of Ge and Sn on carbon, relative to a total mass of the catalyst. In particular embodiments, the catalyst consists essentially of a) 5 wt % Pt and b) 0.5 wt % Ge or 0.5 wt % Sn on carbon, relative to the total mass of the catalyst. In some embodiments, exposing the unsaturated fatty acids to the catalyst results in cyclization and/or aromatization of up to 10% of the fatty acids. In certain embodiments, exposing the unsaturated fatty acids to the catalyst results in isomerization, cracking, alkylation, cyclization and/or aromatization of greater than 10% of the fatty acids.

In some embodiments, the fatty acids in the composition are free fatty acids, fatty acid esters, fatty acid monoglycerides, fatty acid diglycerides, fatty acid triglycerides, or any combination thereof. In certain embodiments, at least 90% of the fatty acids in the fatty acid composition are free fatty acids. The free fatty acids can be obtained, for example, by hydrolyzing triglycerides or fatty acid esters. In some embodiments, triglycerides are hydrolyzed to produce free fatty acids and glycerol. In certain embodiments, the free fatty acids are separated from the glycerol, and the glycerol is recovered. In some embodiments, the fatty acids include unsaturated fatty acids, and the unsaturated fatty acids are hydrogenated before exposure to the catalyst. In particular embodiments, triglycerides comprising unsaturated fatty acids are hydrogenated before hydrolyzing the triglycerides to produce free fatty acids and glycerol.

In certain embodiments, deoxygenation is performed at a temperature of at least 250° C. In one embodiment, the fatty acid composition is preheated to a temperature of at least 50° C. before exposure to the catalyst. In another embodiment, the composition is not preheated before exposure to the catalyst. In yet another embodiment, the composition is heated in the presence of the catalyst at a temperature of at least 50° C., and deoxygenation is performed subsequently at a temperature of at least 250° C. In another embodiment, the composition is exposed to a first catalyst in a first catalyst bed at a