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FINAL ANALYSIS

Platinum Group Metal Catalysts for the Development of New Processes to Biorenewables

There is a growing move away from so called first generation biorenewables (which use food crops as the feedstock) towards second generation biorenewables which use non-food sources of biomass. Biorenewable products have the potential to support growing resource needs while addressing concerns regarding climate change and energy security.

Examples of second generation biorenewable feedstocks include:

- Wood from natural forests and woodlands;
- Forestry plantations and residues;
- Agricultural residues such as straw and corn stover;
- Algae;
- Municipal solid wastes (MSWs);
- Industry processing wastes.

Process developers have been looking to utilise lower cost biofeedstocks, including those traditionally classified as waste streams. The use of cheaper biomass feedstocks and waste streams, which are often accompanied by higher impurity levels, do however present additional purification and processing challenges such as the need for new feedstock pretreatment steps and the solving of catalyst deactivation issues. Catalysis is playing a leading role in addressing and solving these conversion and purification challenges.

Key Reactions for Biorenewables Processes

Some of the key reactions being targeted in biorenewables processes include hydrogenation, dehydration, decarbonylation, dehydrogenation and oxidation. Each of these processes covers a number of important potential reaction steps which are necessary to achieve efficient renewable processes. For some processes, the removal of oxygen and water and addition of hydrogen are key to success, and there are a range of base and precious metal catalysts to address this.

As can be seen from **Figure 1**, each of these conversions can lead to important products for industries and end consumers. Bioplastics, for example, find many applications in consumer goods and household items. Biochemicals can themselves be consumed in or converted into products for industry, such as fibres, coatings, automotive components and many more. Therefore by integrating biorenewable analogues of chemical intermediates into manufacturing processes through the use of chemical catalysis or otherwise, the sustainability of all products in the supply chain can be enhanced.

In many cases, using low cost biorenewable raw materials reduces the overall production costs of the end chemical product. However, it is important to note that many of the processing steps required in this expanding field are new and this presents exciting challenges for the development of new, custom designed catalysts.

The unique properties of the platinum group metals (pgms) can be applied to these complex challenges, such as catalyst deactivation and low-temperature operation. One of the problematic features of biorenewable feedstocks is the level and type of impurities they contain. Consequently, work is being focused on exploiting the resistance of pgms

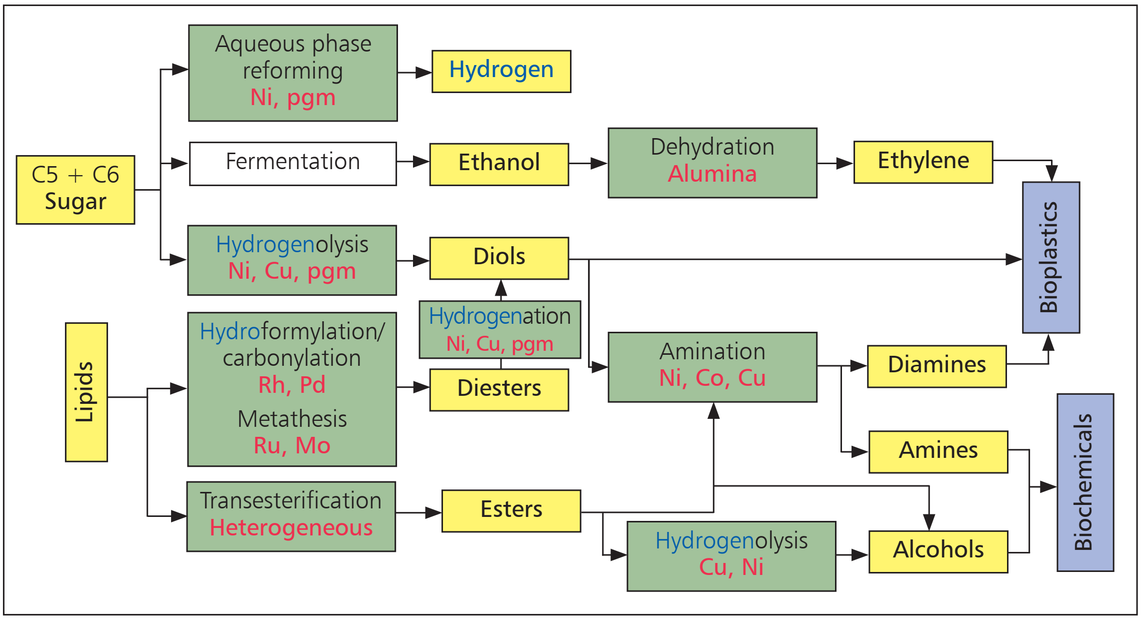

Fig. 1. Reaction scheme showing the conversion of lipids and carbohydrates to biorenewable products by a variety of pgm- and base metal-catalysed processes

to common poisons, such as sulfur, encountered in biomass processing and seeking to take advantage of their high activity to enable milder operating conditions (1).

Bio-Based Routes to Valuable Chemicals

There is interest in using biomass as a raw material for the production of a range of valuable chemical building blocks including diols, oxygenates such as ethanol and biosyngas (a mixture of hydrogen and carbon oxides). Three main processes can be identified:

1. **Conversion of lignocellulose (dry plant matter) to high value chemicals.** The biochemical conversion of biomass, such as sugars, *via* fermentation is well established but thermochemical conversion of cellulosics may offer alternative pathways to valuable chemicals such as diols. In particular the focus on lignocellulosic feedstocks such as wood and agricultural waste avoids the 'food to fuel' dilemma.
2. **Conversion of bioderived syngas to oxygenates.** Although oxygenates (such as ethanol) are already commonly produced from biomass *via* fermentation routes, the thermochemical synthesis of C2 oxygenates from syngas using rhodium-on-silica-based catalysts with a range of promoters is being investigated as an alternative route.
3. **Hot conditioning of syngas derived from gasified biomass.** Gasification of biomass consists of reacting biomass with steam/oxygen to produce a mixture of carbon monoxide, carbon dioxide and hydrogen. This route offers a more efficient way of producing power (as an alternative to combustion) or syngas (which can be used as a building block for many other chemical products). Biomass gasification at a relatively small scale produces tar (aromatic condensable hydrocarbons) and light hydrocarbons, in particular methane. These hydrocarbons make up a significant proportion of the carbon content of the gas and need to be converted or 'reformed' into syngas to improve the economics of the process and prevent downstream fouling (2). Biomass derived syngas also contains sulfur as an impurity and promoted rhodium catalysts have been found to work better for reforming methane than conventional nickel-based steam reforming catalysts in this environment.

Conversion of Biomass to Liquid Fuels

With continued focus on the availability of oil and gas and interest in alternative energy sources it is not surprising that the feasibility of producing hydrocarbon fuels from biomass is a topic of much research.

Triglycerides and fatty acids are naturally occurring molecules that have attracted much interest. They have the potential to be catalytically converted into long chain hydrocarbons which can be used as a drop-in replacement for traditional fuels. These compounds occur in feedstocks such as palm oil, soya oil and algae. The molecular structure of the triglycerides and acids found in algae in particular makes them an excellent starting point for the production of long chain hydrocarbons, such as those found in diesel fuel. This conversion can be carried out catalytically in high yield, over pgm-based catalysts, as illustrated in **Figure 2** for a palmitic acid feed.

Recent catalyst developments have demonstrated the potential of more complex, bifunctional catalysts for the single step conversion of fatty acid feeds to the branched and aromatic molecules that are important constituents of aviation fuel. **Figure 3** compares the performance of a 5% palladium-on-carbon catalyst with a novel bifunctional catalyst, 0.3% platinum-on-ferrierite (3), for the conversion of a palmitic acid feed. The palladium on carbon catalyst gives high yields of linear hydrocarbons suitable for diesel fuels, while the bifunctional catalyst gives a product that contains good levels of branched and aromatic hydrocarbons in the C9 to C16 chain length range, in addition to linear hydrocarbons.

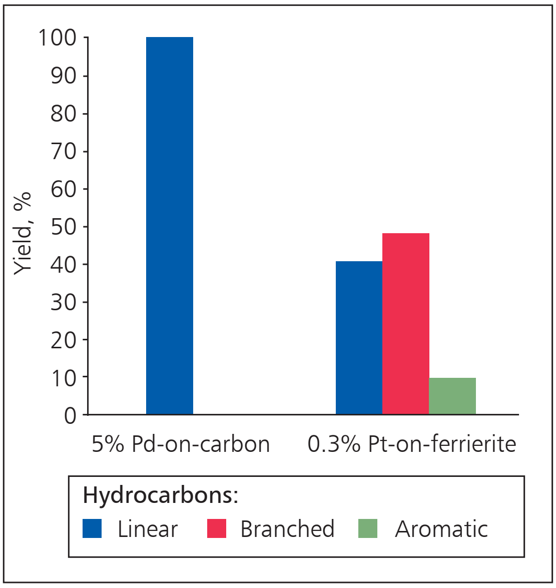

Fig. 3. Performance of palladium-on-carbon compared to a novel, bifunctional platinum-on-ferrierite catalyst for the conversion of palmitic acid to hydrocarbons

This technology is being investigated within projects that are developing the biology and fermentation systems to produce a fatty acid feed from CO_2 and H_2 which can then be converted to an infrastructure-compatible fuel using catalysts. An example of the composition of the product from one project is shown in **Figure 4** where complete conversion of the fatty acid feed has been achieved with high selectivity to a range of linear hydrocarbons in the range C11 to C18, as would be found in diesel fuel.

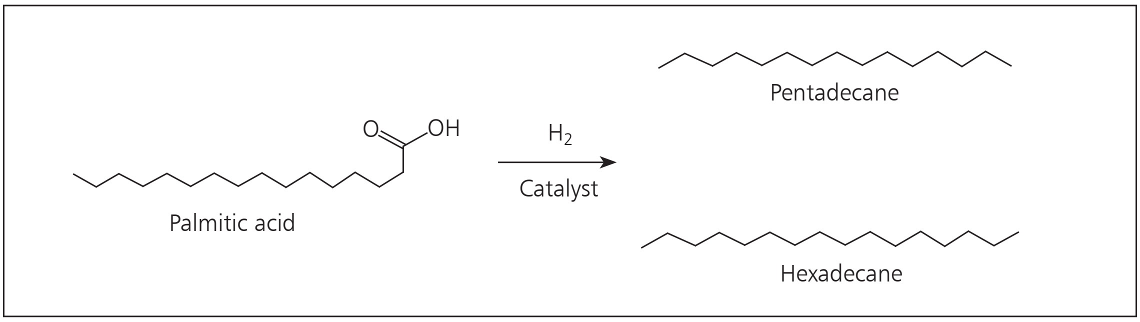

Fig. 2. The pgm-catalysed conversion of palmitic acid to long chain (C15 and C16) linear hydrocarbons such as those found in diesel fuel

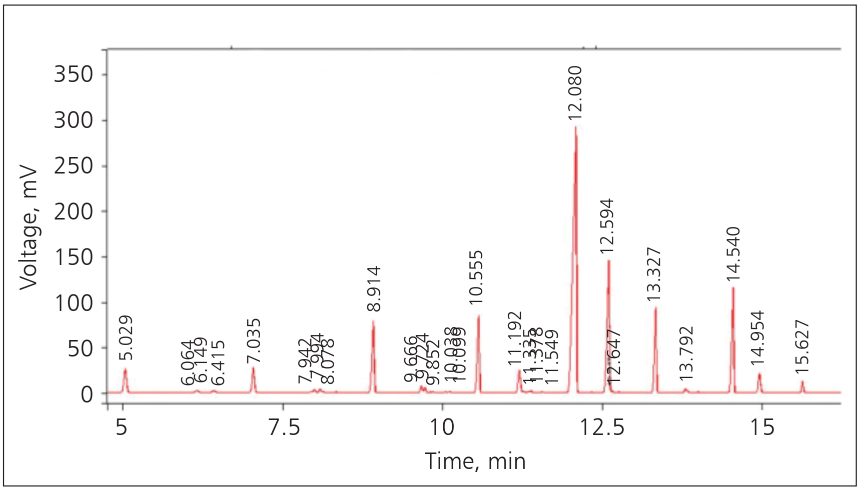

Fig. 4. Linear hydrocarbons produced via catalytic transformation of fatty acids

Conclusion

The move to second-generation biorenewables will require innovative solutions in terms of both catalyst and process technology capabilities. Catalysts based on pgms can provide both high selectivity and good resistance to the poisons typically found in biomass. They are set to play a leading role in providing cost effective solutions to manufacturing biorenewable products. By opening up access to milder operating conditions and pathways to new, valuable products, they will contribute to environmental stewardship and sustainability.

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