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Process Intensification using Catalysis for Renewable Fuels and Chemicals

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Title:

Process Intensification using Catalysis for Renewable Fuels and Chemicals

Extended Abstract: (Your abstract must use Normal style and must fit into the box. Do not enter author details)

1. Introduction:

Rapid depletion of fossil fuels and stringent regulations curbing CO₂ emissions necessitates the use of renewable natural resources for liquid fuel production. In this contest, direct hydrogenation of plant oil based natural triglycerides and fatty acids into valuable hydrocarbons is a potential substitute for production of drop-in biofuels [1-3]. Direct hydrogenation of plant oils to bio fuels is an attractive alternative to transesterification of triglycerides (FAMEs) due to various issues related to stability, unfavourable cold flow properties and engine compatibility issues of FAMEs. However, current manufacturing processes are expensive and hazardous requiring very high pressures and temperatures (200-400 bar hydrogen, 200-400 °C). Under these conditions, control of the selectivity to the desired hydrocarbons is difficult. In this study, we have achieved catalytic hydrogenation of triglycerides at remarkably low temperatures (60-130 °C) and hydrogen pressures (5-30 bars) to corresponding alkanes and alcohols using monometallic Pt/TiO₂ and bimetallic Pt-Re/TiO₂ catalysts. It was possible to tune product selectivity to either hydrocarbons or long chain alcohols. Tristearin was chosen as a model triglyceride, since it is abundant in most vegetable oils, to investigate the reaction pathways and establish reaction kinetics for hydrogenation. Reaction pathways were also explored using stearic acid as the model substrate and the kinetic analysis indicated that a two-site Langmuir-Hinshelwood model with dissociative adsorption of hydrogen and surface reaction as the rate-controlling step fitted well to the experimental data. The kinetic model predicted reaction rates of hydrogenation of acid to alcohol, and subsequent dehydration of alcohol to alkane as well as decarboxylation of acid to alkane with excellent reliability.

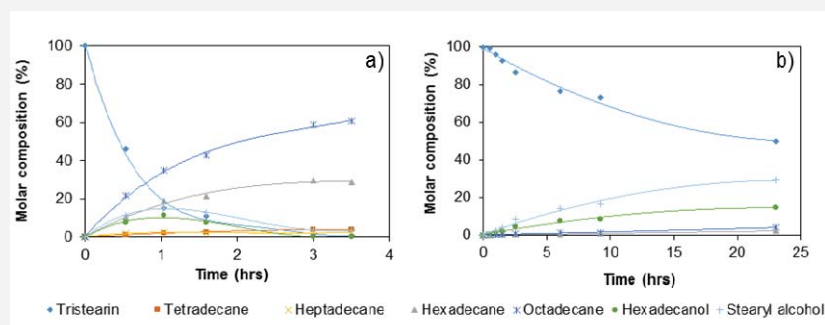


Figure 1. Reaction profile of hydrogenation of tristearin using (a) bimetallic Pt-Re/TiO₂ catalyst and (b) monometallic Pt/TiO₂ catalyst; Reaction conditions: temperature 130 °C, hydrogen pressure 20 bar, speed of agitation 1500 rpm, catalyst loading 0.5g, tristearin 1.4g, cyclohexane 40 cm³.

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2. Material and Methods:

Tristearin (technical grade) and cyclohexane (99.5% pure) were obtained from Sigma-Aldrich and were used without further purification. Pt/TiO₂ and Pt-Re/TiO₂ catalysts were made in house. The liquid-phase hydrogenations were performed in an Autoclave Engineers 100 cm³ stainless steel stirred tank reactor. Samples were taken at regular intervals and analysed by an Agilent 689 GC using an Agilent 145-1001 DB-HT-SIMDIS capillary column and GC-MS (Agilent) using a RTX-5 capillary column.

3. Significant Results and Discussion

A typical reaction profile of the hydrogenation of tristearin using bimetallic Pt-Re/TiO₂ and monometallic Pt/TiO₂ catalysts at 130 °C and hydrogen pressure of 20 bar is shown in **Figure 1**. In presence of bimetallic Pt-Re/TiO₂ catalyst, high selectivity to alkanes (99%) with complete conversion of tristearin was obtained, while in presence of monometallic Pt/TiO₂ catalyst, high selectivity (91%) to corresponding alcohols was achieved. The scope of the liquid phase hydrogenation using both monometallic and bimetallic catalysts was further extended to a variety of plant oil feedstocks such as sunflower, rapeseed, soyabean, olive, coconut, corn and palm oils, as shown in **Table 1**. A broad range of natural triglycerides were successfully hydrogenated to corresponding alkanes in the C10-C18 range, which can be readily exploited for fuel blending purposes. The most notable exception being found with coconut oil which formed mixture of C7-C18 alkanes as the major product irrespective of whether Pt/TiO₂ and Pt-Re/TiO₂ catalysts were employed.

Table 1. Hydrogenation of Plant oils under the reaction conditions in Figure 1.

Plant Oil	Catalyst metal/TiO ₂	Time/h	Plant Oil Conversion/%	Selectivity (%)	
				Alkanes	Alcohols
Tristearin	Pt-Re	3	100	99	1
Palm	Pt-Re	19	99	100	-
Sunflower	Pt-Re	7	73	93.4	6.6
Olive	Pt-Re	23	98	97.2	2.8
Corn	Pt-Re	5	71	86.7	13.3
Soyabean	Pt-Re	5	78	95.2	4.8
Coconut	Pt-Re	22	98	100	-
Rapeseed	Pt-Re	24	100	95.5	4.5
Tristearin	Pt	23	50.1	12.4	87.6
Palm	Pt	90	45.3	12.6	87.4
Sunflower	Pt	20	16.2	25.5	74.5
Olive	Pt	20	23.1	15.1	84.9
Corn	Pt	33	16.3	-	100
Soyabean	Pt	22	74.3	33.3	66.7
Coconut	Pt	90	22.2	100	-
Rapeseed	Pt	20	39.4	21.2	78.8

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4. Conclusions:

In summary, new efficient monometallic and bimetallic catalysts have been established for direct hydrogenation of plant oils to valuable long-chain hydrocarbons and alcohols under mild reaction conditions. At 130 °C and 20 bar hydrogen, high yield of long chain alkanes (95-100%) was achieved. It was possible to tune the product selectivity to obtain alkanes or alcohols by choice of catalysts used.

References

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