Fuel 90 (2011) 1155–1165

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Direct conversion of triglycerides to olefins and paraffins over noble metal supported catalysts

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ARTICLE INFO

Article history:
Received 21 March 2010
Received in revised form 6 October 2010
Accepted 13 October 2010
Available online 27 October 2010

Keywords:
Deoxygenation
Methyl esters
Triglycerides
Vegetable oils

ABSTRACT

Deoxygenation of methyl esters and triglycerides was studied for production of either α-olefins or diesel components. The reactions were carried out in a reactive distillation fashion in which products are quickly removed from the reaction mixture in flowing He. The effects of He flow rate, reaction temperature, active component and support were studied. PtSnK supported on silica was found to be the best catalyst for selective production of α-olefins. Palm kernel oil and coconut oil were also deoxygenated to produce α-olefins or diesel components, depending on reaction conditions.

1. Introduction

In the last few years, interest in producing green fuels or chemicals has increased significantly. Natural fats and oils are a potential feedstock for production of surfactants and other chemicals traditionally based on petroleum. Transesterification of triglycerides with methanol is commonly used to convert triglycerides to so-called biodiesel, which consists of fatty acid methyl esters (FAMEs). This conversion method, which uses homogeneous catalysts, is efficient and well understood. However, the FAMEs have some undesirable fuel properties [1–3].

Fungible diesel fuel is produced by conversion of non-petroleum feedstocks to straight chain hydrocarbons comparable to conventional diesel. A selective conversion path to olefins, particularly α-olefins, would also be valuable for the production of starting materials for a variety of specialty chemicals. Production of hydrocarbons from various renewable feedstocks has been extensively studied for many years. More than ten years ago, Delmon et al. [4] and Krause et al. [5] have shown the effectiveness of hydrotreating catalysts in hydrodeoxygenating oxygenates from bio-oils. The products are resulted from direct hydrogenolysis and hydrogenation activity of these catalysts. Recently conversions of triglycerides or vegetable oils to hydrocarbons have been reported over various catalysts in both flow and batch modes. Selective deoxygenations of vegetable oils over supported NiMo and CoMo hydrotreating catalysts have been observed in flow reactions by Kubicka et al. [6,7]. The products are corresponding hydrocarbons of the same nature as hydrocarbons present in diesel fuels. Thermal or catalytic cracking of vegetable oils in batch reactors produces hydrocarbons in the gasoline rather than diesel range; and undesirable oxygenates such as carboxylic acids [8–10]. Thus, catalytic conversion with better product control would be preferred. Hydrogenation of vegetable oils over Ni containing catalyst has been extensively studied [11,12]. In these studies the main products were linear chains of hydrocarbons from either hydrogenation or deoxygenation reactions. However, there are some disadvantages when using these catalysts. In the studies previously mentioned, researchers have showed that unacceptable amounts of cyclic and aromatics products were formed. Another work [13] showed that trace amounts of cyclic and aromatics compounds were present but extremely high H_2 to TG ratio (1000:1) and a long-time sulfidation process were needed to achieve better results. Recently both Murzin et al. [14–16] and Crocker et al. [17] have reported high activity of noble metals (i.e. Ni, Pd, Pt) supported on activated carbon in the deoxygenation of triglycerides under inert atmosphere. High yields of linear corresponding alkanes and alkenes were obtained. The proposed reaction pathway includes formation of fatty acid intermediates accompanied by elimination of CO_2 from the acids.

In the present work we focus on the production of long chain hydrocarbons from methyl esters and/or triglycerides via deoxygenation over a series of supported Pt catalysts. A reactive-distillation process was used to achieve high selectivity to α-olefins in particular. In this process, the primary products (which have higher vapor pressures than the reactant and solvent) are continuously removed as they are formed, minimizing secondary isomerization or oligomerization reactions. At the same time low

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doi:10.1016/j.fuel.2010.10.025

cracking yields were achieved and neither cyclization nor aromatization products were observed. Fig. 1 represents the desirable reaction pathway.

2. Experimental

2.1. Catalyst preparation

Supported platinum catalysts (Pt/Al_2O_3 and Pt/SiO_2) and bimetallic catalysts ($PtSn/SiO_2$, $PtSnK/SiO_2$) were used in this study. Pt/Al_2O_3 and Pt/SiO_2 were prepared by incipient wetness impregnation using aqueous solutions of chloroplatinic acid hexahydrate to obtain a 1 wt.% Pt loading. $PtSn/SiO_2$ catalyst was prepared by incipient wetness impregnation, using the complex method proposed in the literature [18]. Chloroplatinic acid hexahydrate > 99.9%, and Tin (II) chloride, anhydrous, powder, 99.99+% were used as platinum and tin precursors, respectively. The complex method requires, before the addition of active components (and promoters), to dissolve platinum and tin precursors in hydrochloric solution in order to form the bimetallic complex $[PtCl_2(SnCl_3)_2]^{-2}$, indicated by a reddish-purple color. Following the formation of the complex, incipient wetness impregnation was carried out. In this study, silica was used as an inert and non-acidic support for alloy catalysts.

After impregnation, the catalysts were dried overnight in an oven at 383 K. For the K-promoted catalyst (PtSnK), KOH solution was impregnated next followed by drying again at 383 K. Finally, catalysts were calcined under air flow (100 mL/min) for 2 h at 673 K.

2.2. Catalyst characterization

Temperature Programmed Reduction (TPR) was performed on 1% Pt/SiO_2, 1%Sn/SiO_2, 1%Pt–1.3%Sn/SiO_2 (molar ratio = 1:2) and 1%Pt–1.3%Sn–1.5%K/SiO_2 (molar ratio = 1:2:7). One hundred milligrams of catalyst were used in all the cases. The TPR experiments were carried out under 5% H_2 in Ar and a heating ramp of 10 K/min to 973 K. A dry ice/acetone trap was used to condense the water evolved during the experiments. The effluent gases were analyzed using an online SRI 110 thermal conductivity detector (TCD).

2.3. Reactant and solvent selection

Methyl octanoate 99% from Sigma–Aldrich and methyl laurate (methyl dodecanoate) 98% from Procter and Gamble were used in the studies of FAME conversion; *n*-dodecane (C_{12} paraffin) > 99% and *n*-hexadecane (C_{16} paraffin) from Sigma–Aldrich were used as solvents. A feed mixture of 20 mL of reactant and 130 mL of solvent was used for most of the experiments. Trilaurin (1,3-di(dodecanoyloxy)propan-2-yl dodecanoate) 99% and trimyristin (1,3-di(tetradecanoyloxy)propan-2-yl tetradecanoate) 99% from Sigma–Aldrich as well as palm kernel oil (PKO) and coconut oil from Mountain Rose Herbs were used in the studies of triglycerides conversion. The major component of PKO and coconut oil is trilaurin (about 50% and 40%, respectively) while the remainder is a mixture of other triglycerides including trimyristin. For the triglyceride conversion studies, the initial reactant volume was always 150 mL with varying triglycerides to solvent ratios.

Fig. 2 shows data from Perry's Handbook for vapor pressure as a function of temperature for the reactants (methyl esters/triglycerides), the solvent and possible products. The solvent was chosen so that its vapor pressure is less than that of any expected products. As we have found in previous studies, [19] the deoxygenation reaction occurs readily at 623 K; at this temperature, an operating pressure was chosen greater than the reactant and solvent's vapor pressure but below the products' vapor pressure, such that as the product is formed, it vaporizes readily and preferentially and is carried out of the reactor by the helium stream. Co-products such as CO and CO_2 are also continuously removed.

2.4. Catalyst activity

The reaction system is shown in Fig. 3. The experiments were conducted in a 300 mL high pressure liquid phase stirred reactor (Parr Corporation). The catalyst was initially placed in the reactor and reduced for 2 h at 623 K under H_2 flow. After the reduction, He was passed through to remove any remaining H_2. Then, the liquid feed (either methyl octanoate in *n*-dodecane, methyl laurate in *n*-hexadecane or triglyceride/vegetable oil in n-hexadecane) was added to the reactor using an external unit which prevented air from entering. In order to enhance external mass transfer and suspend the catalyst particles (from 0.15 to 0.20 mm) in the liquid, the stirrer was used at 500 rpm. Pressure and temperature were adjusted according to the desired working conditions. The reaction took place in semibatch mode with continuous removal of product by flowing He. Two different traps were added to the system to collect condensable products. The first trap contained ice water and the second dry ice and acetone. The reactions were conducted for 6 h. Liquid samples were collected in both traps.

Samples were analyzed using a Hewlett Packard 6890 GC, injecting 5 μl of liquid product. Products were identified using gas chromatography/mass spectrometry (Shimadzu GC–MS-P500) and proton NMR. The NMR allowed us to distinguish between α-olefins, internal olefins and saturated hydrocarbons. Gas phase analysis was done using an MKS Cirrus 200 mass spectrometer.

2.5. Mass transfer

Mass transfer-related calculations were carried out to estimate whether external or internal mass transfer would limit the reaction rate under the chosen experimental conditions. Both external and internal mass transfer calculations were based on trilaurin as the reactant.

Diffusion coefficients were calculated using the Stokes–Einstein [20] equation which can be applicable for large molecules such as those used here. Using these estimated diffusion coefficients, the external mass transfer coefficients (k_c) were estimated. We esti-

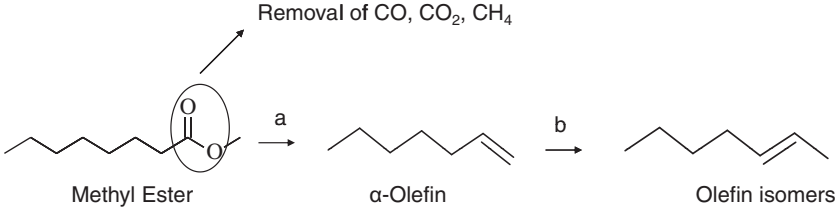
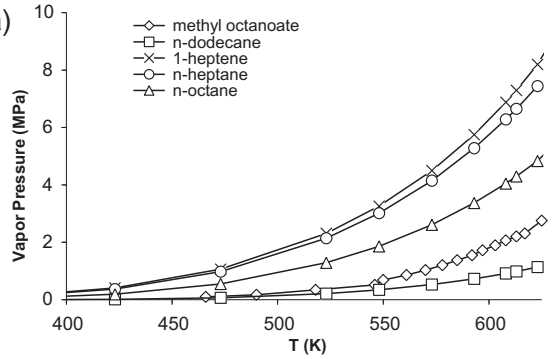


Fig. 1. Schematic representation of the (a) desirable and (b) undesirable pathways from methyl esters.

(a)



(b)

Reactant/Product	T (K)	P (MPa)
n-hexadecane	623	0.34
	593	0.20
methyl laurate	623	0.52
	593	0.32
n-undecane	623	1.58
	593	1.03
n-dodecane	623	1.14
	593	0.73

(c)

Product	T (K)	P (MPa)
n-hexadecane	623	0.34
	593	0.20
n-tetradecane	623	0.61
	593	0.38
n-tridecane	623	0.83
	593	0.52
n-dodecane	623	1.14
	593	0.73

Fig. 2. (a) Vapor pressure curves for methyl octanoate reactant and products, (b) vapor pressure table for methyl laurate reactant and products and (c) vapor pressure table for triglycerides products.

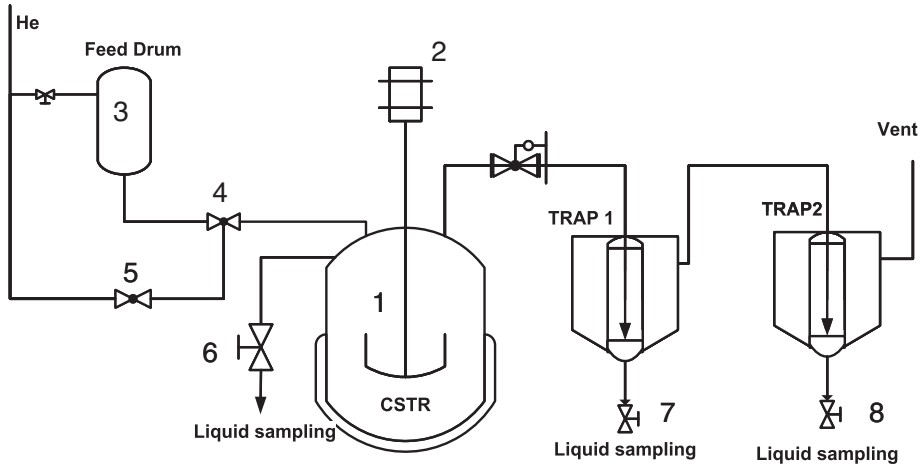


Fig. 3. Experimental setup (1) 300 mL Parr reactor (2) magnetic stirrer (3) feed tank (4–5) needle valves (6–8) on–off valves for liquid sampling from the reactor (6) and the traps (7 and 8).

mated a trilaurin mass flux $N_{\text{Trilaurin}} = 1 \times 10^{-3}$ g/s, which is an order of magnitude greater than the observed reaction rate.

The Weisz-Prater Criterion [21] was used to evaluate internal diffusion limitations. The $C_{\text{wp}} = \left\{-r_A(\text{obs})\rho_p R^2/D_e C_A\right\}$ was found to be $\sim 3 \times 10^{-4}$, which indicates that with the small pellet size used in this study (less than 0.18 mm) there are likely no internal diffusion limitations.

3. Results and discussions

3.1. Temperature programmed reduction

Fig. 4 shows the hydrogen consumption during TPR for the catalysts studied. The Pt/SiO_2 catalyst has only a single reduction peak at just above 400 K corresponding to reduction of platinum oxides to metallic platinum [22]. The peak at high temperature region could correspond to the dehydroxylation activity of silica support, which has been mentioned in the literature [23]. The Sn/SiO_2 catalyst has a broad reduction peak at around 773 K, which corresponds to tin reduction. For the $PtSn/SiO_2$ catalyst there are three hydrogen consumption regions. All these peaks can be associated with different alloys of PtSn (PtSn, Pt_2Sn, $PtSn_4$) as has been proposed based on results from EXAFS, X-ray diffraction, and TEM [24,25] and since no peaks at around 773 K are seen, it can be concluded that unalloyed tin is not present. Finally, when potassium was added, two broad peaks were observed. The first peak at about 550 K can be attributed to PtSn alloy. The second peak at about 750 K matches with tin reduction temperatures and suggests that there is still some unalloyed tin in the catalyst.

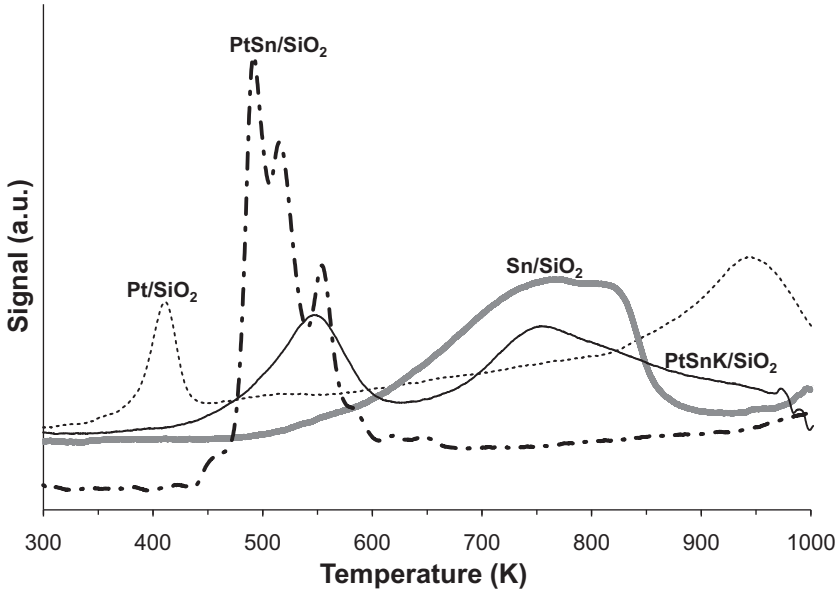


Fig. 4. TPR of Pt/SiO_2, Sn/SiO_2, $PtSn/SiO_2$ and $PtSnK/SiO_2$ catalysts.

3.2. Catalytic conversion of methyl octanoate

Decarboxylation/decarbonylation reactions in both gas and liquid phases produce olefins and/or paraffins with one carbon less than the respective methyl ester. Light gases such as CO, CO_2, and CH_4 are also released. Methanol is also formed from breaking the C–O bond next to the carbonyl group. When unsaturated products are desired, the reaction is carried out in the absence of hydrogen and in a solvent which is not an effective hydrogen donor (e.g., *n*-dodecane or *n*-hexadecane). We have determined through previous flow reaction studies that the highest selectivity to α-olefins is obtained at low conversions since the α-olefin is the primary reaction product. In order to obtain high α-olefins yield, it was decided to use a reactive-distillation process to rapidly remove the primary product from the reactor.

3.2.1. Effect of He flow rate

Reaction products were removed from the reaction mixture by continuously bubbling helium through the reaction mixture. Initial studies to determine the optimal He flow rate were carried out with 1% Pt/Al_2O_3. Fig. 5 shows reaction products from conversion of methyl octanoate at 623 K, 2.41 MPa and at different He flow rates (25, 50 and 100 mL/min). The conversions for these reactions were 69%, 73% and 78%, respectively. Higher volumes were collected in the first trap compared with the second trap (approximately 2–3 times as much).

In the first trap, C_7 α-olefins, internal olefins, paraffins and other products such as hydrogenolysis products were collected. Based on the selectivity to C_7 products, it can be concluded that oxygen is removed by decarbonylation or decarboxylation. Light gases (CO, CO_2, CH_4) and light oxygenates (such as methanol, water, acetaldehyde) are also produced. Mostly methanol and cracking products (light hydrocarbons) were collected in the second trap. As He flow is increased to 100 mL/min product olefin content increases (both α-olefin and isomers at similar rates, with increasing alpha/internal ratio), and paraffin production decreases. These results indicate that the He flow rate plays an important role in product selectivity while conversion is not highly affected. This effect is related to the product residence time. When the He flow is low, the primary product (α-olefin) will remain in the liquid phase and in contact with the catalyst longer and can further isomerize to internal olefins or be hydrogenated by surface hydrogen. Additional studies established the optimum He flow rate range of 75–100 mL/min. At higher flow rates in our system liquid entrainment occurred.

3.2.2. Effect of tin addition

From the results in Fig. 5, Pt is active for deoxygenation but isomerization to internal olefins and hydrogenation to paraffins is significant. In Fig. 6 are compared results of methyl octanoate conversion over the Pt/SiO_2 catalyst and the $PtSn/SiO_2$ catalyst prepared by the chloride complex method. As reported in the literature [26–28], tin can function as both a structural (geometric) and an electronic promoter. The addition of tin modifies catalyst activity by reducing platinum ensemble size and by altering heats of adsorption. Fig. 6 indicates that addition of tin has a positive effect regarding α-olefin content (23% for PtSn vs. 6.5% for Pt) and paraffin (13.5% for PtSn vs. 55.5% for Pt), but undesirable cracking and hydrogenolysis still occur on the bimetallic catalyst. Addition of tin also reduced the methyl octanoate conversion from 50% to 36%. Finally, this conversion reduction positively affects the selectivity.

Cortright and Dumesic [27] used microcalorimetric studies to show that addition of tin decreases the number of sites that strongly interact with hydrogen, CO and ethylene; but the extent of this effect depended on the amount of tin added. Since significant amounts of hydrogenolysis products are still observed in our reactions, it may be that the Pt:Sn ratio was not appropriate to inhibit the formation of hydrogenated species such as 1-octanol and octanal which are intermediates in the hydrogenolysis reaction.

Chloride deposits in the catalyst will also increase the catalyst's cracking activity. This complex preparation method, which uses a hydrochloric solution (chloroplatinic acid hexahydrate), probably leads to chloride residues which enhance the cracking reactions at acid sites.

3.2.3. Effect of temperature

The effect of reaction temperature was investigated on the PtSn catalyst (Fig. 7). Lowering the temperature from 623 K to 593 K decreased the α-olefin selectivity from 23% to 18% and the octanoate conversion from 36% to 19%. Selectivity to paraffins, internal olefins and hydrogenolysis products changed little, but cracking

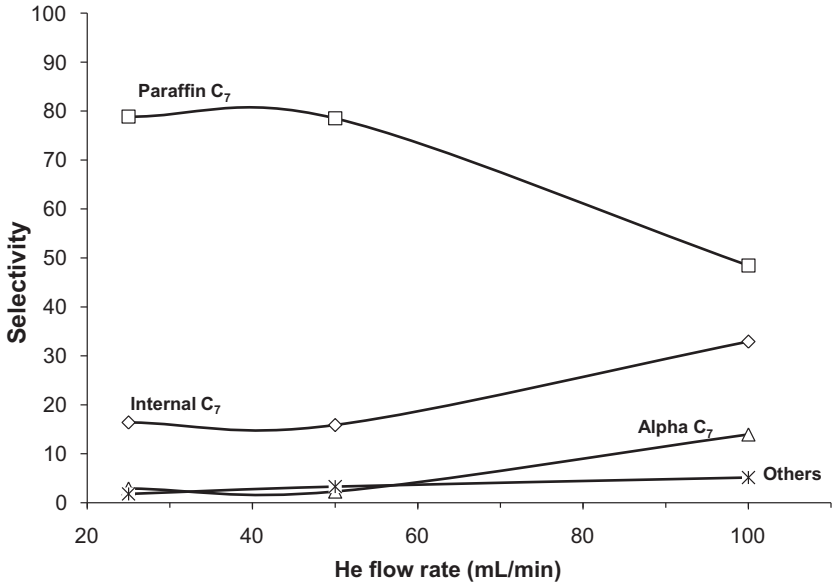


Fig. 5. Effect of He flow rate. Products selectivity for methyl octanoate conversion over Pt/Al_2O_3 catalyst. Reaction occurred at 623 K and 2.41 MPa.

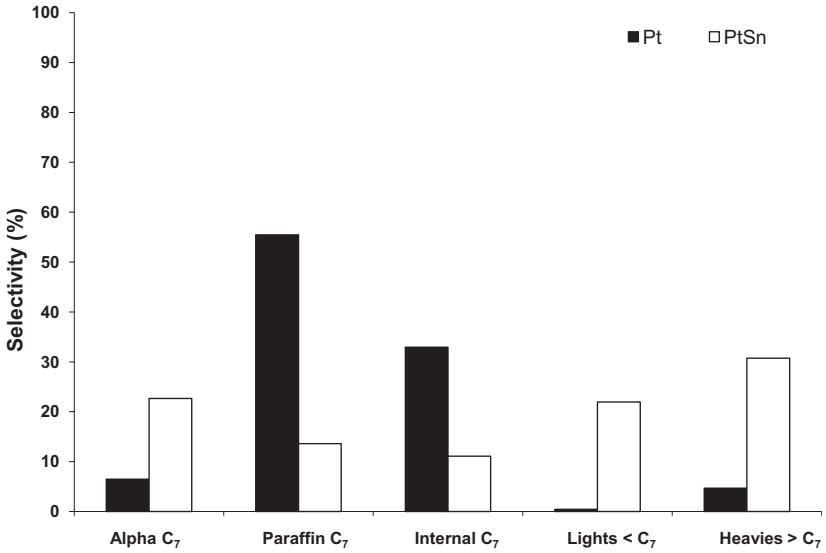


Fig. 6. Effect of catalyst alloying. Products selectivity for methyl octanoate conversion over Pt/SiO_2 (X = 50%) and $PtSn/SiO_2$ (X = 36%) catalysts. Reaction occurred at 623 K, 2.41 MPa, and 100 mL/min.

products were significantly reduced at 593 K due to temperature effect.

3.2.4. Effect of potassium addition to PtSn catalyst

Fig. 8 shows the effect of adding potassium to the PtSn catalyst. It was shown in the literature [29] that when potassium was added in excess in order to neutralize acid sites on supported PtSn catalysts, cracking reactions were significantly decreased. Even though silica is an inert support and has no acid sites to neutralize, some chloride residues that remain from the catalyst synthesis could be still present in the catalyst. Such chlorides residues could generate acidity and cause cracking. In fact, the XPS results of reduced PtSn and PtSnK samples have shown that the chlorine content is higher in the latter sample. However, most of chlorine is retained in the form of KCl, consequently not causing undesirable acidity as in the case of PtSn catalyst. Fig. 8 shows that the addition of K significantly reduces the cracking from 9% to trace amount. In the meantime, it helps to increase both α-olefin (from 18% to 47%) and internal olefin (from 9% to 31%) selectivities. The TPR results in Fig. 4 suggest that potassium withdraws tin from the PtSn alloy, altering the remaining PtSn alloy. Such phenomena apparently have positive impacts on the total olefin content in our reaction system when compared with the many PtSn phases observed with bimetallic PtSn catalyst. There is also lower selectivity to hydrogenation/hydrogenolysis products (denoted as heavies) on the PtSnK catalyst. On the K-doped catalyst, less hydrogen is available; therefore the selectivity to hydrogenation/hydrogenolysis compounds is decreased. According to Dumesic et al. [30], the added potassium could also further reduce the size of Pt ensembles, which would inhibit double-bond isomerization reactions in gas phase. In this study, while selectivity to both α-olefin and internal olefins increased, the ratio of alpha to internal olefins actually decreased. The cause for the different behavior may be related to effects of reaction in the liquid phase (e.g., longer

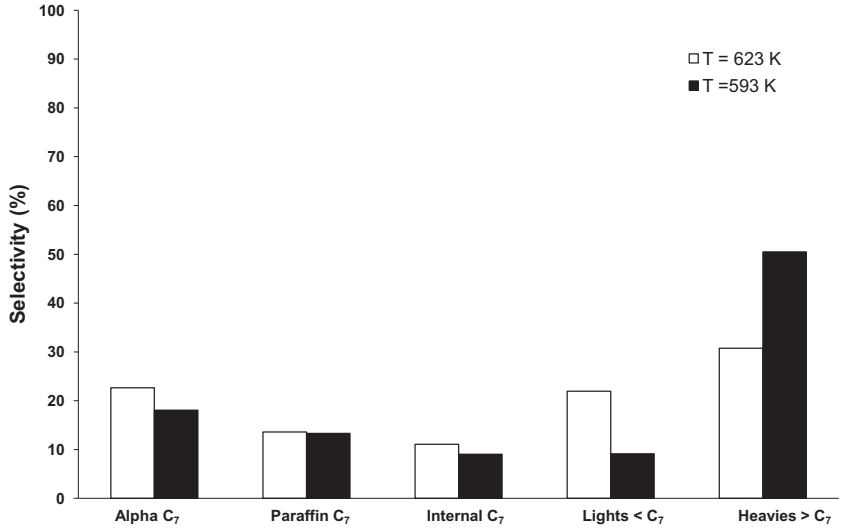


Fig. 7. Effect of reaction temperature. Products selectivity in the first trap for methyl octanoate conversion over $PtSn/SiO_2$ catalyst at 623 K (X = 36%) and 593 K (19%). Reaction occurred at 2.41 MPa and 100 mL/min.

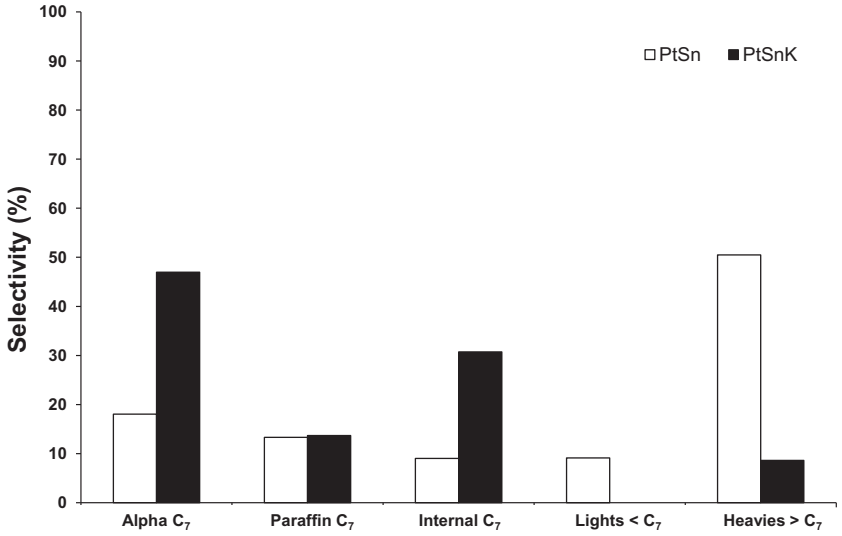


Fig. 8. Effect of potassium addition. Products selectivity in the first trap for methyl octanoate conversion over $PtSn/SiO_2$ catalyst (X = 19%) and PtSnK/SiO2 catalyst (X = 13%). Reaction occurred at 593 K, 2.41 MPa, and 100 mL/min.

diffusion times from the catalyst pores) or due to some diffusion inhibition caused by K deposits. Detailed analysis on the effect of K on the gas-phase reaction will be addressed in the future publication [31].

3.3. Catalytic conversion of methyl dodecanoate

Methyl octanoate was the initial reactant used to develop the reactive distillation procedure due to its easier handling. Helium flow, temperature and catalyst type were studied with that ester. Larger FAMEs and triglycerides (methyl laurate, triglycerides and vegetables oils) were subsequently tested. Temperature and He flow conditions were chosen according to the best conditions found with methyl octanoate. Pressure was selected using the results shown in Fig. 2(b) and (c). In this section, results of reaction of methyl laurate over Pt supported on both alumina and silica, and PtSnK supported on silica, will be presented.

Fig. 9(a–d) show the α-olefin, internal olefin, paraffin and cracking yields respectively for the three catalysts studied as a function of catalyst amount. The reaction time for all the experiments was 6 h. When increasing the amount of catalyst, and thus increasing the 6-h conversion, α-olefin yield remains approximately constant only with $PtSnK/SiO_2$ catalyst (Fig. 9(a)). With less catalyst (0.5 g), similar α-olefin yields were observed on both Pt/Al_2O_3 and $PtSnK/SiO_2$ but when the amount of catalyst was increased, the α-olefin yield decreased significantly for Pt/Al_2O_3. Results of the reactions carried out using Pt/SiO_2 showed relatively low α-olefin yields for all catalyst weights, while secondary products' yields increased rapidly with catalyst amount. Internal olefin yield increased with catalyst weight for all catalysts, as did paraffin yield (Fig. 9(b) and (c)), with the highest yields for both internal olefins and paraffins observed on Pt/Al_2O_3.

Paraffin yield seems to increase much faster with conversion over alumina-supported catalysts. Even though the reactions were carried out in He atmosphere, there are two possibilities for hydrogen generation that is participating in the hydrogenation of the olefins. H_2 can be produced from either coking reactions or from methanol decomposition. Methanol decomposition to produce H_2

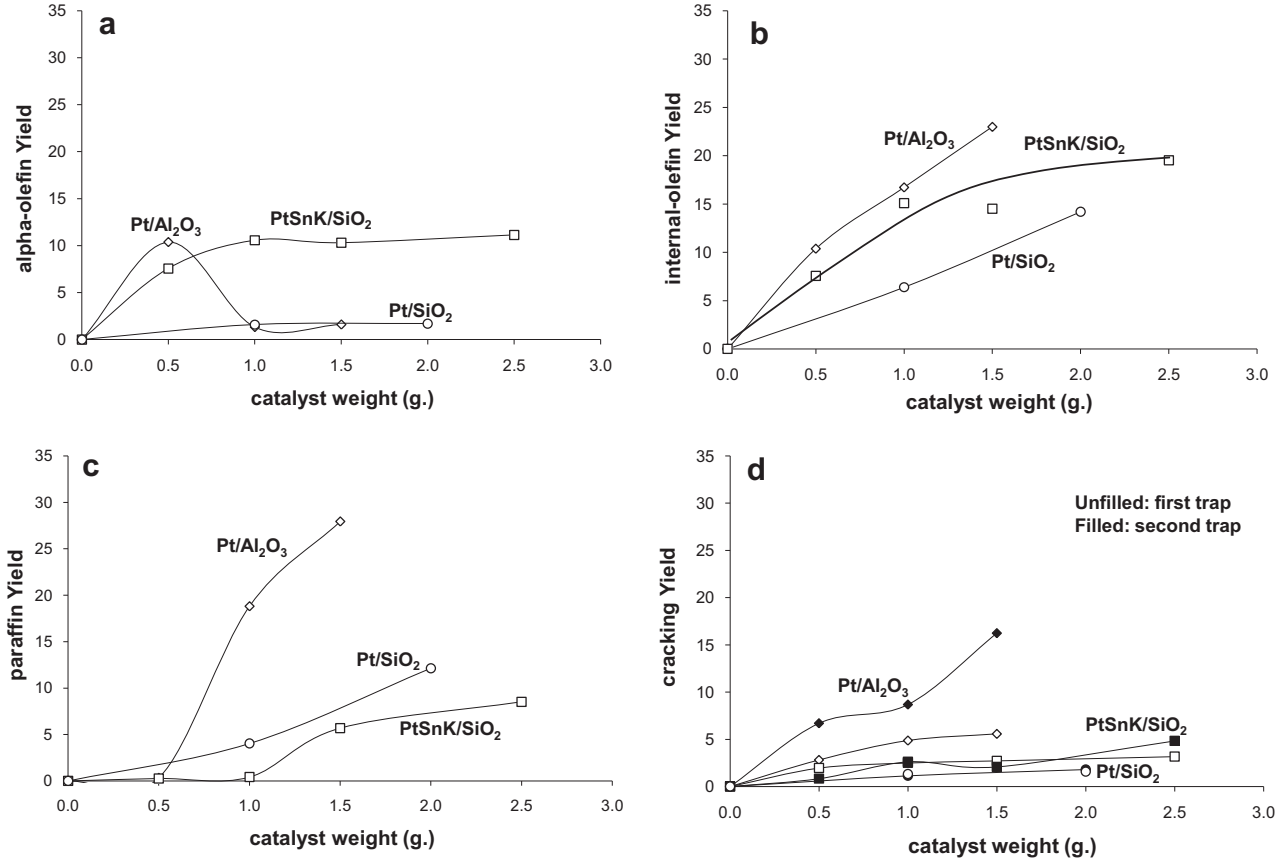


Fig. 9. (a) alpha olefin, (b) internal olefin, (c) paraffin and (d) cracking yields over different amounts of Pt/Al_2O_3, Pt/SiO_2 and $PtSnK/SiO_2$ catalyst. Reaction of methyl dodecanoate occurred at 593 K, 0.52 MPa, and 100 mL/min. Reaction time:6 h.

and CO is known to occur on alumina [32]. Indeed the analysis of the gas phase shows more H_2 when the reactions were carried out over alumina-supported catalyst than over silica-supported catalysts.

Cracking increases with increasing conversion on all catalysts (Fig. 9(d)), with highest yields observed over Pt/Al_2O_3. These results can be understood in terms of alumina acid sites catalyzing both isomerization and cracking.

The α-olefin/internal olefin ratio as a function of conversion is shown in Fig. 10. At low conversions the $PtSnK/SiO_2$ and the Pt/Al_2O_3 show similar ratios, but as the conversion increases, the ratio over Pt/Al_2O_3 decreases rapidly compared to the $PtSnK/SiO_2$

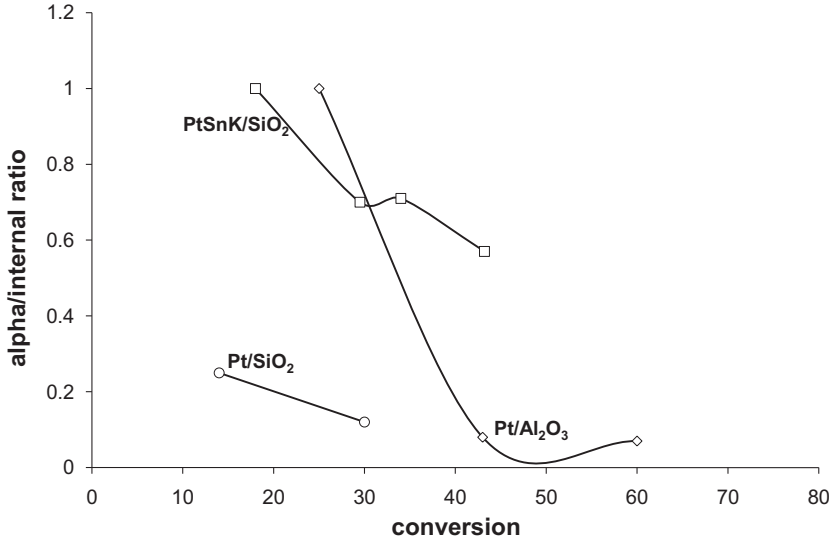


Fig. 10. Alpha/internal olefin ratio versus conversions obtained by varying amounts of Pt/Al_2O_3, Pt/SiO_2 and $PtSnK/SiO_2$ catalysts. Reaction of methyl dodecanoate occurred at 593 K, 0.52 MPa, and 100 mL/min.

catalyst. Even at very low conversion, Pt/SiO_2 shows poor alpha to internal ratio results. These results support the reaction pathway shown in Fig. 1.

3.4. Catalytic conversion of triglycerides and vegetable oils

Results of trilaurin and trimyristin conversion vs. time are shown in Fig. 11. The figure also shows the fit of the data for each reactant to 1st order reaction rate expressions, i.e.,

$$\text{Rate} = -\frac{dC_{TGs}}{dt} = k'C_{TGs}$$

where, k' is the rate constant and C_{TGs} is the concentration of either the trilaurin or trimyristin. Rates of trilaurin and trimyristin conversions are very similar, with rate constants of 1.20E−02 min^{-1} and 1.16E−02 min^{-1} respectively. Despite the differences in carbon number of trilaurin and trimyristin, they present virtually the same kinetics behavior.

Interestingly, in this reaction, two new peaks appeared in the chromatogram between the trilaurin and trimyristin peaks (Fig. 12). GC chromatograms of the feed and of a sample after 2 h of reaction are shown in Fig. 12(a) and (b). As reaction time advanced, these new compounds together with the reactant were consumed (Fig. 12(c)). According to the literature [33–35], transesterification is likely to occur over potassium or tin loaded catalysts. Trilaurin and trimyristin are triglycerides with three C_{12} and three C_{14} hydrocarbon legs, respectively. It is believed that "scrambling" of the hydrocarbons legs occurs in the presence of the PtSnK catalyst generating two new peaks as seen in Fig. 12. The first new peak (elution time of 27.5 min) can be attributed to a triglyceride containing two C_{12} legs and one C_{14} leg. The second new peak (elution time of 28.5 min) can be attributed to a triglyceride composed of one C_{12} leg and two C_{14} legs. However, no mono- or di-glycerides are observed during the reaction. Pospisil et al. [13] showed that when reactions were carried out at temperatures above 583 K, no intermediates were seen because at such higher temperatures, the mono- or di-glycerides either reacted

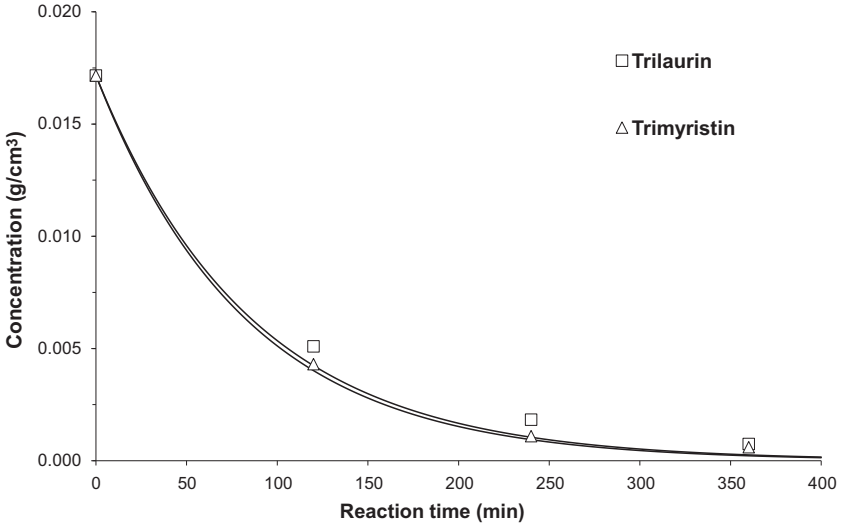


Fig. 11. Triglycerides concentration versus time. Reaction occurred at 598 K, 0.31 MPa, and 100 mL/min. Feed composition: 50/50 trilaurin to trimyristin over $PtSnK/SiO_2$ catalyst. Lines represent kinetic model fittings.

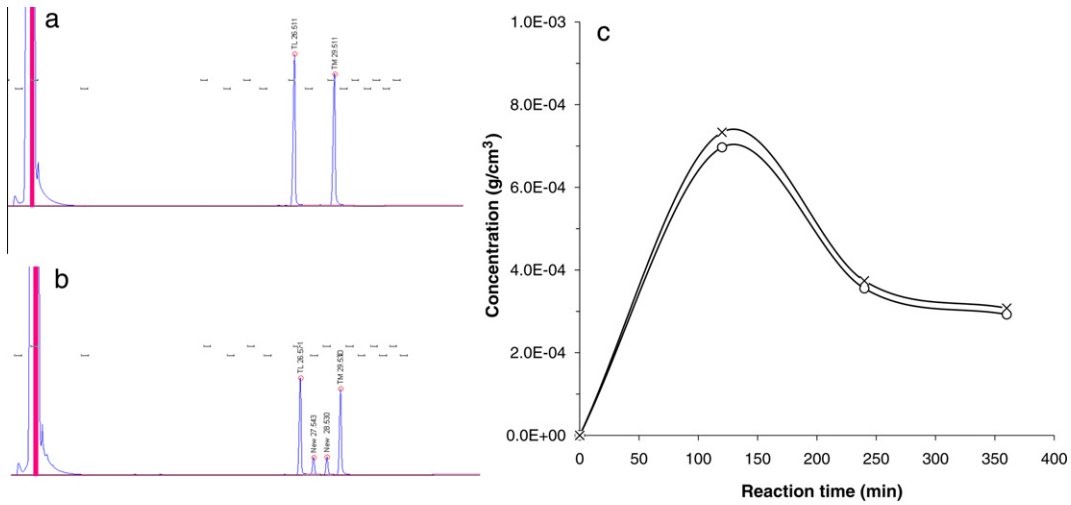


Fig. 12. GC chromatograms from an experiment with feed mixture 50/50 trilaurin to trimyristin over $PtSnK/SiO_2$ catalyst. Reaction occurred at 598 K, 0.31 MPa, and 100 mL/min. (a) Feed (b) Sample after 2 h of reaction (c) Concentration of new triglycerides in the product, peak #1 at elution time 27.5 min (○), and peak #2 at elution time 28.5 min (□).

very fast, and thus their concentrations remained below detection limits, or they do not desorb from the catalyst surface.

Results of deoxygenation of trilaurin and trimyristin in separate experiments are shown in Table 1(a) and (b), respectively. Primary products from trilaurin deoxygenation are C_{11} olefins and paraffins, with small amounts of cracking products from the hydrocarbon chains, and small amounts of C_2 and C_3 oxygenates from the glycerol head group of the triglyceride. Some light hydrocarbons (cracking products) are also observed. Primary products of trimyristin deoxygenation are C_{13} olefins and paraffins.

Table 1
Product selectivities and conversion (%) from conversion of (a) trilaurin and (b) trimyristin over PtSnK/SiO2 catalyst. Reaction occurred at 593 K, 0.31 MPa, and 100 mL/min.

Products	PtSnK/SiO_2
(a)	
C11 Alpha olefins	28
C11 Internal olefins	51
C11 Paraffins	11
Light oxygenates	0.70
Lights < C11	3.0
C12 range	6.0
Alpha/internal olefins	0.64
Total olefins	79
Conversion	96
(b)	
C13 Alpha olefins	25
C13 Internal olefins	58
C13 Paraffins	1.3
Light oxygenates	0.25
Lights < C13	14
C13 range	1.5
Alpha/internal olefins	0.43
Total olefins	83
Conversion	93

Table 2
Product selectivities (%) for PKO and coconut oil conversion over PtSnK/SiO2 catalyst. Reaction occurred at 598 K, 0.31 MPa, and 100 mL/min.

Products	PKO	Coconut
Alpha olefins	47	53
Internal olefins	25	19
Paraffins	12	15
Light oxygenates	0	0
Lights < C11	5.6	6.7
Heavies > C11	11	6.4
Alpha/internal	1.8	2.8
Total olefin	72	73
Conversion	78	46

Deoxygenation of PKO or coconut oil is more complex than deoxygenation of trilaurin or trimyristin mixtures since these real oils comprise many triglycerides ranging from C_{10} triglycerides up to C_{18} triglycerides, with C_{12} triglycerides being the most abundant (48% for PKO, 40% for coconut oil). For this study, selectivities to α- and internal olefins are of interest. Since there is some degree of mono-unsaturation and poly-unsaturation in the triglycerides, prior to deoxygenation a mild hydrogenation treatment at 523 K for 1 h was carried out to saturate these bonds. In agreement with previous studies [12], experimental results confirmed that this pretreatment also decreases cracking during deoxygenation.

Results of deoxygenation of PKO and coconut oil over PtSnK/SiO_2 are shown in Table 2. As was observed with FAMEs and triglycerides, deoxygenation remains the main reaction. Products from either oil consist of about 50% α-olefin content with lesser amounts of internal olefins and paraffins. Light hydrocarbons and hydrogenolysis products are observed as well; and C_2–C_3 light oxygenates were collected. Despite similar initial triglycerides composition, the ratio of alpha to internal olefins was significantly higher for deoxygenation of coconut oil compared to PKO (2.8 vs. 1.8). One possible reason is that the overall conversion of coconut oil was lower, which results in a higher α-olefin selectivity as previously observed. The compositions of PKO and coconut oil differ [36,37], and the differences in conversion may be due to greater competitive adsorption by some species in the coconut oil.

Finally, the effect of varying initial PKO concentration was studied. Figs. 13 and 14 shows the results from six experiments with varying initial oil concentrations. Each reaction was run for 6 h. As initial oil concentration increased, the 6-h fractional conversion decreased, consistent with a reaction order less than one. These apparent kinetics are consistent with an adsorption inhibition effect, especially at higher oil concentrations. In Fig. 13, α-olefin, internal olefin and paraffin yields are shown as a function of oil conversion. Fig. 14 shows the alpha to internal ratio as a function of conversion. Although this is the same trend as for methyl esters (increasing conversion decreases the ratio) the values of the ratio were much higher than for methyl esters, reaching values as high as 6 (the highest ratio for methyl laurate was 1). The higher

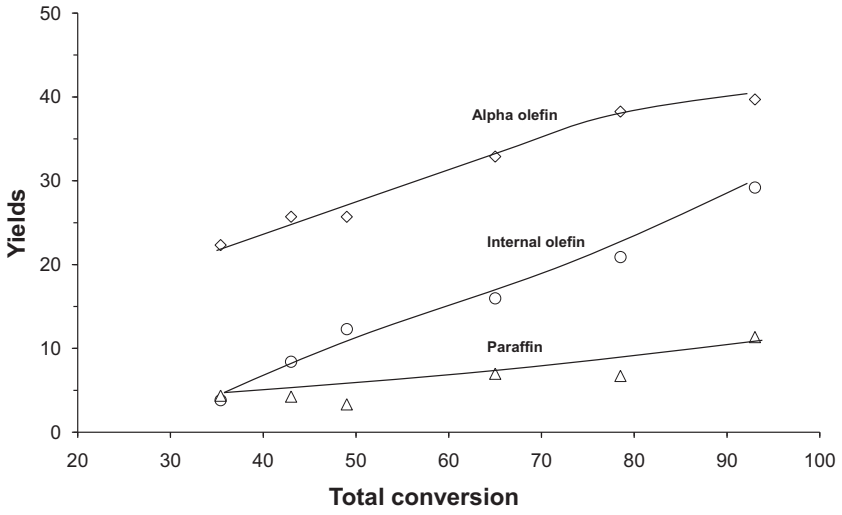


Fig. 13. Alpha olefin, internal olefin and paraffin yields from reaction of PKO over PtSnK/SiO2 catalyst. Reaction occurred at 593 K, 0.31 MPa, and 100 mL/min.

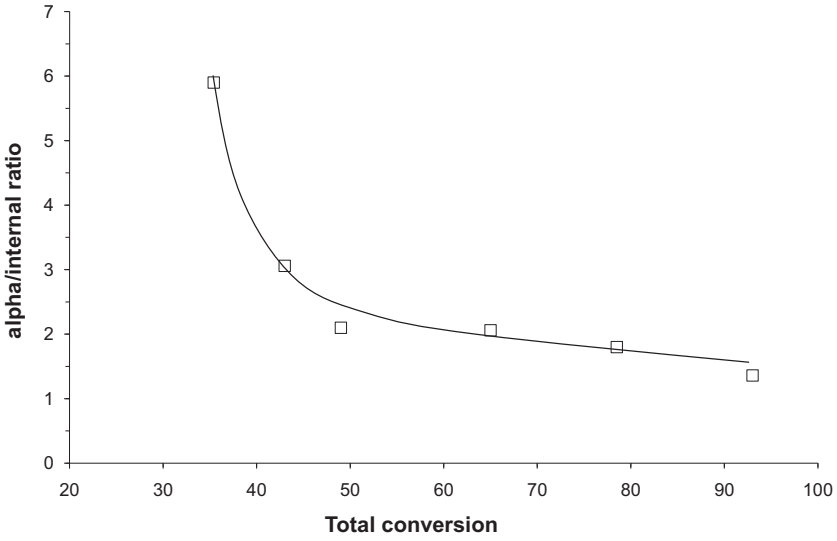


Fig. 14. Alpha to internal olefin ratio as a function of PKO conversion over PtSnK/SiO2 catalyst. Reaction occurred at 593 K, 0.31 MPa, and 100 mL/min.

alpha/internal ratios for triglycerides conversion are also consistent with adsorption competition – the stronger adsorption by triglycerides inhibits adsorption and subsequent reaction of the α-olefins. Also, since the reaction pressure for triglycerides conversion was lower than for methyl laurate (0.31 MPa vs. 0.52 MPa), the primary α-olefin products may be removed more quickly from the reaction mixture in the case of triglycerides conversion.

4. Conclusions

Catalytic deoxygenation of methyl esters and triglycerides (vegetable oils) is a promising route for production of "green" diesel fuel or hydrocarbons which can substitute for petrochemical feedstocks for specialty chemicals. $PtSnK/SiO_2$ was found to be the best catalyst of those tested for yields of primary reaction products. Reactive distillation improved α-olefin yields for both methyl esters and triglycerides (vegetable oils) reactants. Reactive distillation also enables easy removal of products from the reaction mixture. Olefin yield was increased by use of He (instead of hydrogen) as a carrier gas, but some hydrogenation still occurs. No cyclic or aromatic products were observed under these conditions. These results suggest that this catalyst shows good promise for conversion of FAMEs and vegetable oils to hydrocarbons.

Acknowledgment

This work has been supported by Procter and Gamble, the Oklahoma Center for the Advancement of Science and Technology, and the Oklahoma Bioenergy Center. This work has been supported in part by the NSF EPSCoR award EPS 0814361.

References

[1] Geyer SM, Jacobus MJ, Lestz SS. Comparison of diesel engine performance and emissions from neat and transesterified vegetable oils. Trans ASAE 1984;27:375–81.
[2] Peterson CL, Korus RA, Mora PG, Madsen JP. Fumigation wit propane and transestrerification effects on injector coking with vegetable oils. Trans ASAE 1987;30:28–35.
[3] Demirbas A. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. Energy Convers Manage 2003;44(13):2093–109.
[4] Laurent E, Delmon B. Influence of oxygen-, nitrogen-, and sulfur-containing compounds on the hydrodeoxygenation of phenols over sulfide $CoMo/\gamma\text{-}Al_2O_3$ and $NiMo/\gamma\text{-}Al_2O_3$ catalysts. Ind Eng Chem Res 1993;32(11):2516–24.
[5] Senol OI, Ryymin EM, Viljava TR, Krause AOI. Reactions of methyl heptanoate hydrodeoxygenation on sulphided catalysts. J Mol Catal A Chem 2007;277:107–12.
[6] Kubicka D, Aluza L. Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts. Appl Catal A Gen 2010;372(2):199–208.
[7] Kubicka D, Bejblova M, Vlk J. Conversion of vegetable oils into hydrocarbons over CoMo/MCM-41 catalysts. Top in Catal 2010;53(3–4):168–78.
[8] Lima DG, Soares VCD, Ribeiro EB, Carvalho DA, Cardoso ECV, Rassi FC. Diesel-like fuel obtained by pyrolysis of vegetable oils. J Anal Appl Pyrolysis 2004;71:987–96.
[9] Alencar JW, Alves PB, Craveiro AA. Pyrolysis of tropical vegetable oils. J Agric Food Chem 1983;31:1268–70.
[10] Schwab AW, Dykstra GJ, Selke E, Sorenson SC, Pryde EH. Diesel fuel from thermal decomposition of soybean. J Am Oil Chem Soc 1988;11:1781–6.
[11] Da Rocha Filho G, Brodzki D, Djega-Mariadassou G. Formation of alkanes, alkycycloalkanes and alkylbenzenes during the catalytic hydrocracking of vegetable oils. Fuel 1993;72:543–9.
[12] Gusmao J, Brodski D, Djega-Mariadassou G, Frety R. Utilization of vegetable oils as an alternative source for diesel-type fuel: hydrocracking on reduced Ni/SiO2 and sulphided $Ni–Mo/\gamma\text{-}Al_2O_3$. Catal Today 1989;5:533–44.
[13] Simacek P, Kubicka D, Sebor G, Pospisil M. Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel. Fuel 2009;88:456–60.
[14] Kubickova I, Snare M, Eranen K, Maki-Arvela P, Murzin DY. Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. Catal Today 2005;106:197–200.
[15] Snare M, Kubickova I, Maeki-Arvela P, Eranen K, Murzin DY. Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel. Ind Eng Chem Res 2006;45:5708–15.
[16] Maeki-Arvela P, Kubickova I, Snare M, Eranen K, Murzin DY. Catalytic deoxygenation of fatty acids and their derivatives. Energy Fuels 2007;21:30–41.
[17] Morgan T, Grubb D, Santillan-Jimenez E, Crocker M. Conversion of triglycerides to hydrocarbons over supported metal catalysts. Top in Catal 2010;53(11–12):820–9.
[18] Baronetti GT, de Miguel SR, Scelza OA, Fritzler AA, Castro AA. $Pt–Sn/Al_2O_3$ catalysts: studies of the impregnation step. Appl Catal A: Gen 1985;19:77–85.
[19] Do P, Chiappero M, Lobban LL, Resasco DR. Catalytic deoxygenation of methyl–octanoate and methyl-stearate on Pt/Al_2O_3. Catal Lett 2009;130:9–18.
[20] Satterfield CN. Mass transfer in heterogenous catalysis. MIT Press; 1970.
[21] Fogler HS. Elements of chemicals reaction engineering. second ed. Pentice-Hall; 1986.
[22] De Miguel SR, Román-Martınez MC, Cazorla-Amorós D, Jablonski EL, Scelza OA. Effect of the support in Pt ans PtSn catalysts used for selective hydrogenation of carvone. Catal Today 2001;66:289–95.
[23] Vansant EF, Voort P, Vrancken KC. Characterization and chemical modification of the silica surface. Amsterdam: Elsevier; 1995.
[24] Chojnacki TP, Schmidt LD. Microstructures of supported Pt–Sn and Rh–Sn particles on SiO_2. J Catal 1991;129:473–85.
[25] Meitzner G, Via GH, Lytle FW, Fung SC, Sinfelt JH. Extended X-ray absorption fine structure studies of Platinum–Tin catalysts. J Phys Chem 1988;92(10):2925–32.
[26] Arteaga JG, Anderson JA, Rochester CH. Effects of catalyst regeneration with and without chlorine on heptane reforming reactions over Pt/Al_2O_3 and $Pt–Sn/Al_2O_3$. J Catal 1999;187:219–29.

[27] Cortright RD, Dumesic JA. Microcalorimetric, spectroscopic and kinetic studies of silica supported Pt and Pt/Sn catalysts for isobutane dehydrogenation. J Catal 1994;148:771–8.
[28] Verbeek H, Sachtler WMH. The study of the alloy of platinum and tin by chemisorption. J Catal 1976;42:257–67.
[29] Imai T, Hung CW. US Patent 4430,517.
[30] Cortright RD, Dumesic JA. Effects of potassium on silica-supported Pt and Pt/Sn catalyst for isobutane dehydrogenation. J Catal 1995;157:576–83.
[31] Do PTM, Shen M, Jentoft R, Resasco D. Deoxygenation of methyl esters on supported Pt catalysts: effect of Sn and K (in preparation).
[32] Brown JC, Gulari E. Hydrogen production from methanol decomposition over Pt/Al_2O_3 and ceria promoted Pt/Al_2O_3 catalysts. Catal Commun 2004;5:431–6.
[33] Haitao L, Wenlei X. Tranesterification of soybean oil to biodiesel with Zn/I2 catalyst. Catal Lett 2006;107:25–30.
[34] Wenlei X, Hong P, Ligong C. Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. Appl Catal A Gen 2006;300:67–74.
[35] Wenlei X, Xiaoming H, Haitao L. Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst. Bioresour Technol 2007;98:936–9.
[36] Bezard JA. The component triglycerides of palm kernel oil. Lipids 1971;6:630–4.
[37] Bezard JA, Bugaut M, Clement G. Triglyceride composition of coconut oil. J Am Oil Chem Soc 1971;48:134–9.