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Influence of the operating conditions and kinetic analysis of the selective hydrogenation of methyl oleate on Ru–Sn–B/Al₂O₃ catalysts

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Abstract The influence of the operating conditions and preparation methods of Ru–Sn–B/Al₂O₃ catalysts on the activity and selectivity for the hydrogenation of methyl oleate to oleyl alcohol was studied. It was found that catalysts prepared by incipient wetness (IW) are more active and selective than those prepared by co-impregnation. This better performance is possibly due to a lower level of residual chlorine. The experiences of hydrogenation of methyl oleate showed that activity increases as the reaction temperature increases while the selectivity to oleyl alcohol has a maximum value. This could be due to the higher activation energies for the hydrogenolysis of carboxymethyl groups than those found for C=C double bonds hydrogenation. The increase in operating pressure has a positive effect on the activity but it influences selectivity time patterns in a more complex way. Experiments carried out by varying methyl oleate/*n*-dodecane ratio show that the selectivity and conversion not depend on this parameter. A simple kinetic model is proposed.

Keyword Selective hydrogenation · Methyl oleate · Reaction kinetic · Ru–Sn–B/Al₂O₃

Introduction

Catalytic hydrogenation is widely used to chemically modify the properties of fats and oils or to obtain valuable chemical products. One of such product types are unsaturated fatty alcohols. Unsaturated fatty alcohols are used in detergents, in cosmetic ointments and creams, as plasticizers and defoamers and in textile and

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leather processing [1–4]. Oleyl alcohol is also used as an additive in petroleum and lubricating oils [5].

Fatty alcohols have been traditionally produced by the hydrogenation of the corresponding methyl or fatty esters using severe operating conditions (i.e. 250–300 atm, 250–300 °C). Copper chromite catalysts were used to obtain saturated alcohols [6] and zinc chromite catalysts, which are much less active for double bond hydrogenation, were used to obtain the unsaturated alcohols [7]. As a consequence of the growing importance of unsaturated fatty alcohols as components of many chemical formulations, there has been an increasing concern to develop new catalytic formulations with better activity and selectivity for the hydrogenation of unsaturated fatty acid and esters with preservation of its original ethylenic double bonds. Some attempts were made to produce fatty alcohols under milder operating conditions using noble metal based catalysts [8–10]. Such catalysts have much more hydrogenating activity at lower temperature, but in their “pure” formulations (i.e. without metallic function modifiers) they have very poor selectivity towards unsaturated alcohols. The main goal of these studies is hydrogenate/hydrocrack the COOH or COOR groups of fatty acids or esters without the simultaneous hydrogenation of C=C bounds in the main carbon chain. As it is well known, ethylenic bonds are easily hydrogenated so the improvement of catalyst selectivity towards the formation of unsaturated alcohols is not an easy task.

Novel catalyst formulations proposed until now to meet these requirements mostly include some metals of VIII group (Pt, Rh, Ru, etc.) with some modifiers or promoters [8, 11]. It must be recalled here that such catalyst should be more environmentally benign than those containing Cr. One of the most promising catalysts seemed to be those based on Ru–Sn. These catalysts were very selective to hydrogenate ethyl acetate to produce ethanol, but did not exhibit good selectivity to obtain unsaturated fatty alcohols from fatty acids or esters [12]. The incorporation of B as modifier significantly improves such selectivity as it was previously reported [11, 13–15]. The catalysts preparation method used also has a noticeable influence on selectivity, as the metallic Ru–Sn interaction strongly depends on this procedure (i.e. metal deposition, reduction and activation methods). It was found that catalysts with a strong Ru–Sn interaction had better selectivity towards oleyl alcohol formation [14]. Piccirilli et al. [16] have found that some transesterification between methyl oleate and formed oleyl alcohol to produce heavy esters are significant. Another side reaction of some importance was found to be the *cis*–*trans* double bond isomerization in the main hydrocarbon chain as reported by Costa et al. [17].

Catalyst selectivity also depends on the residual chlorine content after the usual preparation procedures. Tahara et al. [18] found that the presence of chlorine in the catalysts favors the reduction of Sn down to its lower valence state which has been associated to a better alcohol production. On the other hand, Ishii et al. [19] and Echeverri et al. [20] reported a negative effect of chlorine on Ru–Sn catalysts for methyl oleate hydrogenation. Chlorine washing with pure or alkaline water would therefore improve both catalysts activity and selectivity.

In this work, the influence of both reaction conditions (stirring speed, temperature, pressure, reactant concentration) and the catalyst preparation method is studied. A simple kinetic model is also proposed, which could be useful to

rationally explore such influences which somewhat unexpectedly have a good fitting of experimental results.

Experimental

Catalysts preparation procedures

γ -Al₂O₃ (Cyanamid Ketjen CK-300, pore volume = 0.5 cm³ g⁻¹, Sg (BET) = 180 m² g⁻¹, mean pore radius = 50 Å, particle size 35–80 mesh) was used as support. This material was previously calcined at 500 °C (4 h under flowing air, heating rate 10 °C min⁻¹) in order to eliminate any adsorbed contaminants.

Co-impregnation (CI) method

The procedures were those described by Narasimhan et al. [8]. The support is first immersed in an excess of aqueous solution of metal precursors salts (RuCl₃·xH₂O and SnCl₂·2H₂O). This system was left to stand during 12 h in order to assure a homogeneous distribution of these salts into the particles of support. The precursor salts were then reduced with an aqueous solution of sodium borohydride. Impregnated solids were filtered, water washed and dried under flowing N₂ at 120 °C. A reduction step with flowing H₂ (300 °C, 2 h) was then performed, and the catalysts were let to cool down to ambient temperature and H₂ was then swept with N₂. This catalyst was labeled Ru–Sn–B(CI).

Incipient wetness (IW) method

This procedure was that described by Shoenmaker-Stolk et al. [21] The support was wetted with exactly the pore volume of aqueous solution of metal precursor salts in the required amounts to achieve the desired metal content. Wetted samples were left to stand for 12 h. A step of reduction with excess sodium borohydride aqueous solution was then performed. After this, the solids were filtered, rinsed with water until acid neutrality and dried during 4 h at 120 °C under flowing N₂. The last preparation step included reduction with H₂ at 300 °C, cooling, and hydrogen purging with N₂ as described before. This catalyst was labeled Ru–Sn–B (IW).

Determination of Ru, Sn and Cl in the catalyst samples

The Ru and Sn contents of catalysts were determined by ICP (Perkin Elmer, Optima 2100 DV) after acid digestion. Chlorine contents of samples after activation were determined by a modified Volhard-Charpentier method [22].

Methyl oleate hydrogenation tests

A stainless steel stirred autoclave (240 cm³ effective volume) was used for these reaction tests. Operating conditions were varied one at once, left the remaining ones

unchanged. Standard reaction conditions chosen were: temperature: 290 °C; hydrogen pressure: 50 atm; mass of catalyst (IW): 1 g; reactant volume: 4 mL; solvent (*n*-dodecane) volume: 60 mL and stirring speed: 800 rpm. Reactant and solvent (methyl oleate and *n*-dodecane) were Sigma-Aldrich 99 % grade.

Reaction products were analyzed by GC (Varian 3400 CV) using a Chevron ZB-FFAP capillary column (length: 30 m, inner diameter: 0.25 mm ID). Analysis conditions were: injector temperature: 220 °C, column temperature: 200 °C for 1 min, 2 °C min⁻¹ ramp up to until 260 °C and then isothermal. Detector (FID) temperature: 265 °C, carrier gas: N₂. Identification of reaction products was previously done by GC–MS (Shimadzu QP-5000), using the same capillary column. Only oleyl alcohol, methyl stearate, stearyl alcohol and methyl oleate were only detected as significantly compounds in the reactor samples.

Results and discussion

Chemical analysis of catalysts

The metals and chlorine contents of catalysts prepared using the CI and IW methods are shown in Table 1. Ru and Sn contents achieved with both methods are virtually the same. The catalyst prepared by CI, on the other hand, had a higher level of Cl, B and Na than that prepared by incipient wetness.

The washing step in catalyst preparation had the purpose of removing residual chlorine as its presence is considered detrimental for the selective hydrogenation of methyl oleate to oleyl alcohol [19, 20]. Chlorine was more easily removed from the catalyst prepared by the IW technique and also a higher B removal was noted for this catalyst by washing. Ru and Sn contents were not significantly changed upon washing for both catalysts.

Influence of operating conditions

Stirring speed

Some exploratory reaction runs were first made to reveal the possible existence of external diffusional limitations. Those experiences were done at 290 °C and 50 atm, and the reactor was initially charged with 1 g of catalyst, 4 mL of methyl oleate and 60 mL of dodecane (solvent). Three agitation levels were used: 546, 800 and

Table 1 The metal percentage of catalysts determined by ICP and chlorine percentage obtained by Volhard–Charpentier method

Catalyst	Ru	Sn	B	Na	Cl
Ru–Sn–B (CI)	1.16	1.56	0.64	4.03	0.42
Ru–Sn–B (IW)	0.95	1.56	0.45	0.54	0.12

1,096 rpm. The results showed that in this range the agitation speed does not have any significant influence on conversion values. Product distribution patterns were neither significantly modified as the agitation level varied (results not shown). A stirring speed of 800 rpm was chosen therefore as standard for all kinetics experiments.

Reaction temperature

Several kinetic runs were done within the 250–310 °C temperature range. Conversion values increase, as expected, when temperature level rises (Fig. 1). The formation of light hydrocarbons was not observed because it is expected at temperatures higher than 300 °C. [23]. The selectivity for oleyl alcohol was defined as its molar percentage within the reaction products (oleyl alcohol, methyl stearate and stearyl alcohol). This variable goes through a maximum at some intermediate run time as can be seen in Fig. 2. At higher reaction times, the oleyl alcohol formed by the selective hydrogenation of methyl oleate is fully hydrogenated to the corresponding saturated fatty alcohol (stearyl alcohol). Higher selectivities are achieved at 290 °C. At higher temperatures (310 °C), the hydrogenation rate noticeably increases so the intermediate oleyl alcohol is rapidly transformed in stearyl alcohol, which is a final product. Maxima in selectivities are shifted to longer reaction times at lower reaction temperatures, as expected.

Product selectivities at the point where oleyl alcohol selectivity is the maximum for each reaction temperature level are shown in Table 2. These results could be explained taking into account that activation energies associated with hydrogenolytic-type reactions are usually higher than for simple $-C=C-$ bonds hydrogenations. When the reaction temperature increases, the rates of transformation of methyl esters to fatty alcohols are favored over the simple double bond hydrogenation ones. However, at higher temperature, the double bond $C=C$ is also

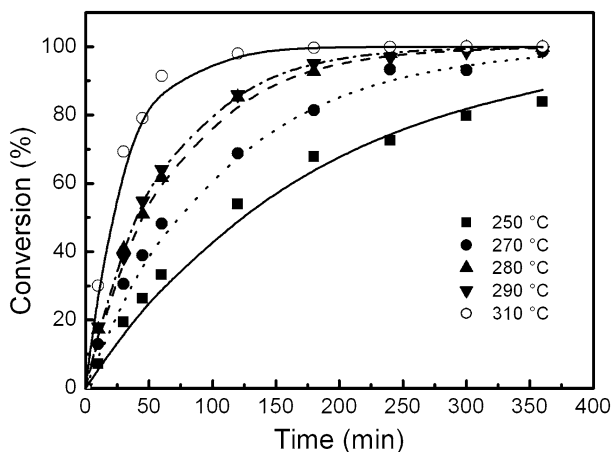


Fig. 1 Methyl oleate conversion as a function of time at several reaction temperatures

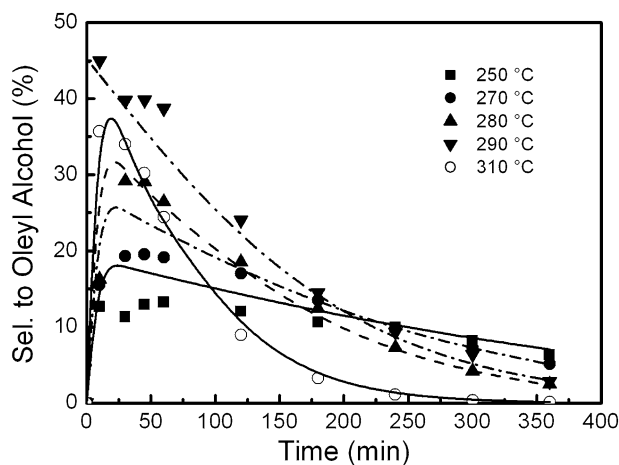


Fig. 2 Selectivity to oleyl alcohol as a function of time at several reaction temperatures

Table 2 Selectivity to the different products of reaction at different temperatures of operation and different reaction times where the selectivity to oleyl alcohol is maximum

Reaction Temperature °C	Reaction Time, min	Selectivity, %		
		Oleyl alcohol	Methyl stearate	Stearyl alcohol
250	60	13.3	86.7	0.0
270	30	19.3	63.7	17.0
280	30	29.2	54.6	16.2
290	10	44.9	44.4	10.7
310	10	35.7	49.1	15.2

hydrogenated producing methyl stearate. On the other hand, methyl stearate is an intermediate so their amounts never reach high values.

Influence of hydrogen pressure

The effect of hydrogen pressure was explored at three levels: 20.5, 50 and 61.5 atm. The temperature was kept at 290 °C and charge characteristics and stirring speed were set at the same values as for the preceding paragraph. Fig. 3 shows that methyl oleate conversion noticeably increases as hydrogen pressure rises from 20.5 up to 50 atm, which is reasonably expected as for most organic hydrogenations. A further increase in the pressure (61.5 atm) did not have nevertheless a significant effect on conversion. The hydrogen pressure also has a marked effect on oleyl alcohol selectivity values and time patterns (Fig. 4). At low pressures (i.e. 20.5 atm), the selectivity to oleyl alcohol monotonically increases all over the reaction time span. At higher pressures (50 and 61.5 atm), a definite maximum in this variable is reached at the beginning of runs. Selectivity is higher at an intermediate pressure

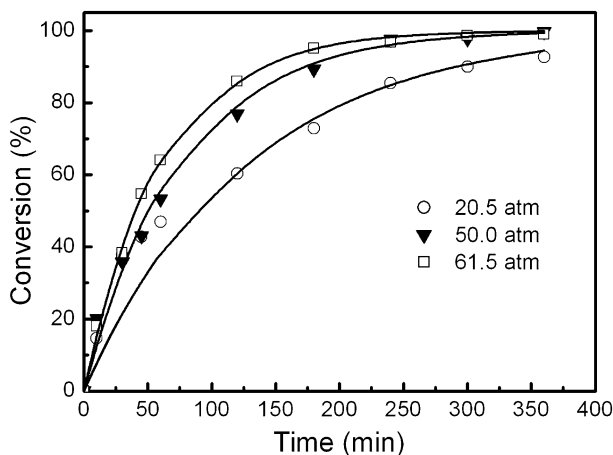


Fig. 3 Methyl oleate conversion as a function of time at different operating pressures

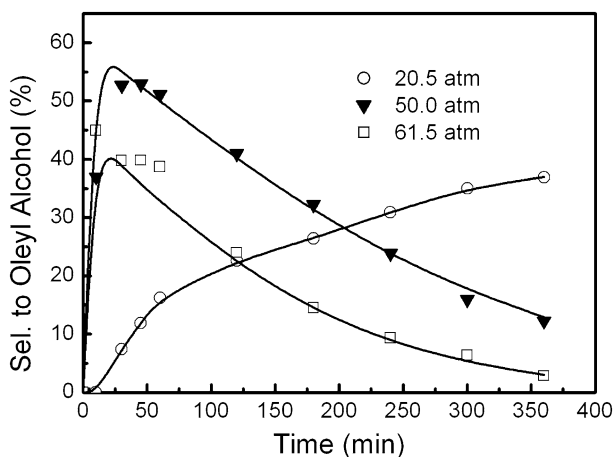


Fig. 4 Selectivity to oleyl alcohol as a function of time at different operating pressures

level which reflects a compromise between the formation of the unsaturated alcohol and the hydrogenation of its C=C double bond at higher pressures.

Influence of methyl oleate/solvent ratio

In order to complete the studies on the effect of main operating parameters, a series of runs were done to study the influence of reactant concentration I_e on the activity and selectivity to oleyl alcohol. Three levels of methyl oleate initial concentration were fixed using 2, 4 and 8 mL of methyl oleate and the same volume of dodecane (60 mL).

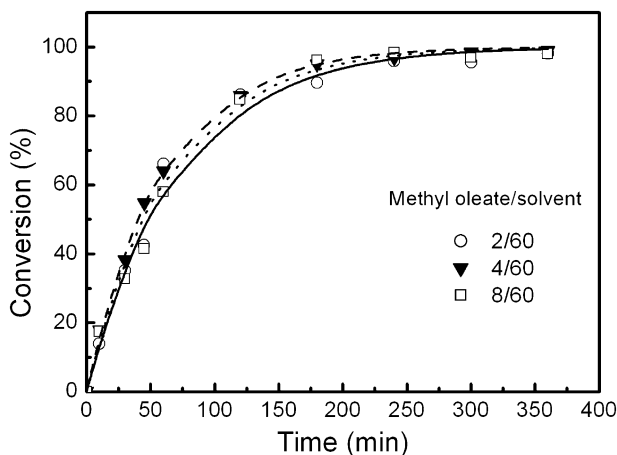


Fig. 5 Methyl oleate conversion as a function of time for different methyl oleate/solvent ratios

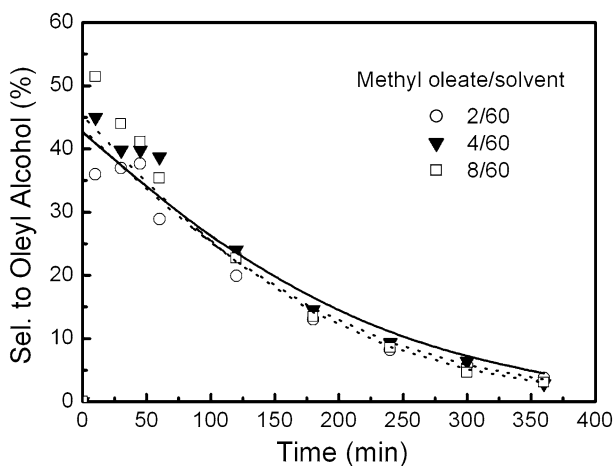


Fig. 6 Selectivity to oleyl alcohol as a function of time for different methyl oleate/solvent ratios

It can be seen in Fig. 5 that the conversion does not depend on the reactant concentration in a definite way. The selectivity to oleyl alcohol (Fig. 6) shows similar reaction time patterns for the three methyl oleate/solvent ratio used. It seems that higher reactant concentration favors higher selectivity values at the beginning of the reaction, but at higher reaction times, such differences almost disappear.

Influence of the catalyst preparation method

In previous works, we have found that the preparation method has marked influence on the electronic structure of the Ru and its interaction with Sn [14]. Thus, the metal activity is strongly affected by this procedure. The catalysts prepared by CI using

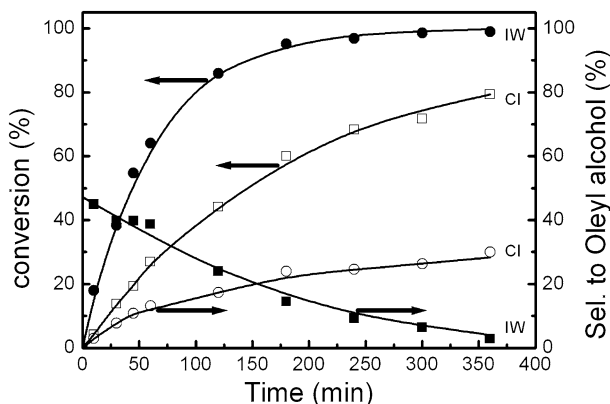


Fig. 7 Conversion and selectivity time patterns for CI and IW catalysts

sodium borohydride had high selectivity to oleyl alcohol, while the Ru–Sn catalysts prepared by CI without the incorporation of B were not selective to oleyl alcohol formation whatever their activation mode (calcination or reduction) [14]. This behavior was attributed to the different degree of interaction between Ru and Sn. Catalysts with strong Ru–Sn interaction are selective to oleyl alcohol, but if the Ru–Sn interaction is weak, the selectivity is very poor. Moreover, it has been indicated that the presence of Cl negatively affects the selectivity [19, 20]. Therefore, the behavior of two catalysts was also studied: one prepared by CI and one prepared by the IW technique, using sodium borohydride in both cases as a reducing agent. The experiments to compare the two catalysts were done at the standard conditions previously mentioned. It can be seen in Fig. 7 that higher conversion is obtained with the catalyst prepared by incipient wetness, while the selectivity to oleyl alcohol for the catalyst prepared by CI always increases with the reaction time. The IW catalyst has a maximum of selectivity to oleyl alcohol with reaction time as it has been shown previously, being greater than the obtained with the catalyst prepared by CI. Fig. 8 shows the yield to oleyl alcohol as a function of reaction time, it can be seen that the yield passes through a maximum for the catalyst prepared by IW while the yield to oleyl alcohol continuously increases for the catalyst prepared by CI. The results reported in Table 1 show that the catalyst prepared by IW possesses 0.12 % of Cl while the prepared by CI is 0.42 % of Cl. Therefore, greater selectivity of the WI catalyst is possibly due to its lower content of Cl and that probably has more Ru–Sn interaction. The latter was explored using XPS (X-ray photoelectron spectroscopy) and infrared spectroscopy with Fourier transform of CO (FTIR-CO) [14].

Simplified kinetic model

In order to give a more rational basis to the analysis of the obtained kinetic data, a simple reaction model was formulated, which was based on the reaction scheme proposed by Pouilloux et al. [24] which is reproduced in Scheme 1. On the other

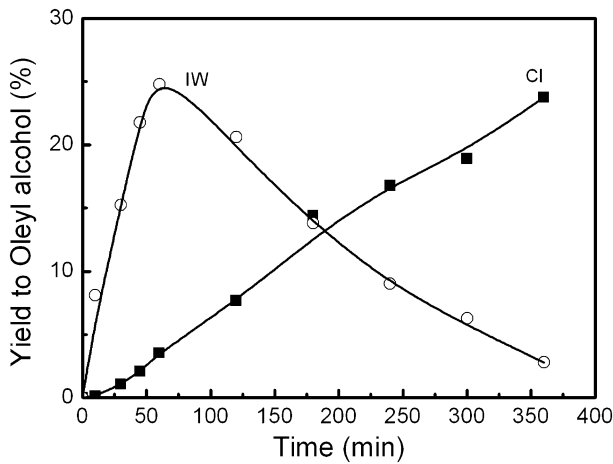
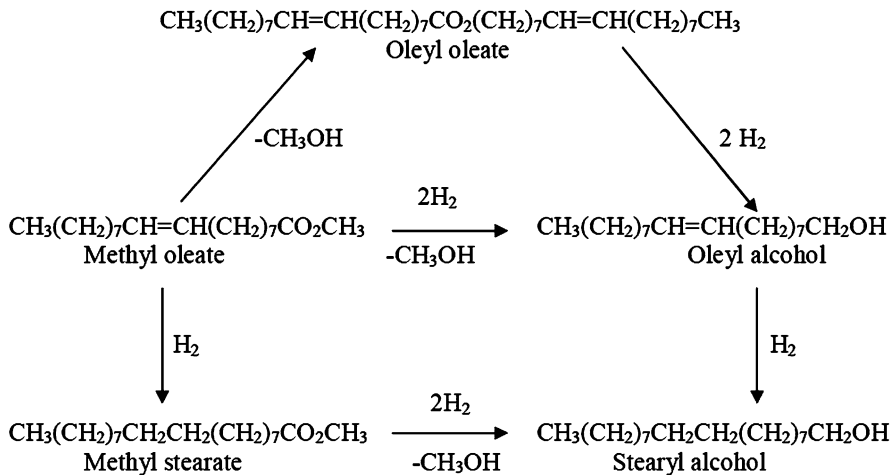


Fig. 8 Oleyl alcohol yields as a function of time for CI and IW catalysts



Scheme 1 Reaction scheme for the hydrogenation of methyl oleate [25]

hand, despite the numerous kinetic models developed for fats and oils double bond hydrogenation and the existence of reasonable proposals for reaction pathways for selective hydrogenation of carboxymethyl groups, no such studies are found in the literature.

To obtain a useful kinetic model, the absence of significant mass transfer limitations must be granted. The virtual independence of results on stirring speed (see Sect. “[Stirring speed](#)”) indicates negligible external mass transfer effects on reaction rates.

Internal diffusive effects can be assessed using the classical Weisz-Prater criterion [25]:

$$\phi = \frac{r_{\text{obs}} \cdot \rho_p \cdot d_p^2}{36 \cdot C_s \cdot D_{\text{eff}}} \leq 0.3$$

Rates of methyl oleate consumption were estimated from the slope of conversion versus time plots (Fig. 1). The highest value was found at 310 °C, extrapolated to zero conversion and it amounts $4.6 \times 10^{-6} \text{ mol s}^{-1} \text{ g}^{-1}$. From the support porosity and a value of 3.65 g cm^{-3} for the density of solid $\gamma\text{-Al}_2\text{O}_3$, the catalyst particle density (ρ_p) was computed as 1.29 g cm^{-3} . The mean catalysts particle size (d_p) corresponding to the used sieving range is 0.034 cm. The higher observed rate was an initial (i.e. zero time) rate, so the oleate concentration at catalyst surface (C_s), calculated from the oleate/solvent ratio in the mixture charged to the reactor results to be $1.84 \times 10^{-4} \text{ mol cm}^{-3}$. Using a value of $1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the molecular diffusivity of methyl oleate [26] and the values of particle density and porosity, the effective diffusivity is $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. A value of $\Phi = 0.08$ was finally obtained, so the absence of significant internal diffusive effects is ascertained.

No heavy esters were found in our studies, so our kinetic model proposal results in a very simple one with only four components (methyl oleate, oleyl alcohol, methyl stearate and stearyl alcohol). The kinetics for each model step are supposed to be first order and irreversible, and the effect of hydrogen is not taken into account explicitly and is assumed to be somehow included into rate constants. Another reasonable simplification would come from the chemical similarity of methyl oleate/methyl stearate and oleyl alcohol/stearyl alcohol molecules. Regarding selective hydrogenation of methyl esters to its corresponding alcohols, the presence or absence of a lonely double bound far from the terminal carboxymethyl group to be hydrogenated should not influence this reaction rate significantly. The rate constants for C=C double bound hydrogenation should also not depend much on the presence of a remote carboxymethyl or hydroxyl group. The proposed model has therefore only two rate constants: one for selective hydrogenation of carboxymethyl groups ($k_{\text{C=O}}$) and the other for C=C double bounds hydrogenation ($k_{\text{C=C}}$).

$$\begin{aligned} \frac{dn_A}{dt} &= -(k_{\text{C=O}} + k_{\text{C=C}}) n_A \\ \frac{dn_B}{dt} &= -k_{\text{C=O}} n_B + k_{\text{C=C}} n_A \\ \frac{dn_C}{dt} &= -k_{\text{C=C}} n_C + k_{\text{C=O}} n_A \end{aligned}$$

where $k_{\text{C=O}}$ is the rate constant for $-\text{COOMe}$ group hydrogenation, $k_{\text{C=C}}$ is the rate constant for $\text{C} = \text{C}$ group hydrogenation where n_A , n_B and n_C are the amounts of substance for methyl oleate, oleyl alcohol and methyl stearate, in order. This differential equations system is readily solved to get:

$$\begin{aligned} \ln(Y_C + Y_A) &= -k_{\text{C=C}} t \\ \ln(Y_A) &= -(k_{\text{C=O}} + k_{\text{C=C}}) t \end{aligned}$$

where, Y_A is the molar fraction of methyl oleate within the reaction products, Y_B is the molar fraction of oleyl alcohol within the reaction products, t = reaction time (s)

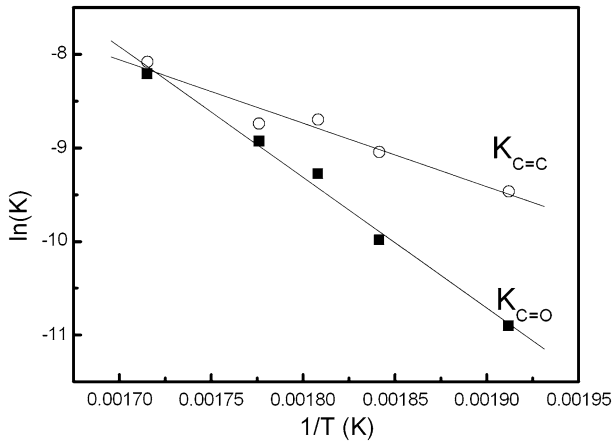


Fig. 9 Arrhenius plots of estimated rate constants

Table 3 Values of rate constant as a function of the operating pressure

Pressure (atm)	$K_{C=C} \text{ (s}^{-1}\text{)}$	$K_{C=O} \text{ (s}^{-1}\text{)}$
20.5	7.10×10^{-5}	6.28×10^{-5}
50.0	1.40×10^{-4}	9.27×10^{-5}
61.5	1.47×10^{-4}	9.84×10^{-5}

Values of rate constants obtained from the regression analysis of experimental data are presented in Fig. 9 and the corresponding activation energies for both reaction types can also be determined, being its values $E_{C=O} = 116 \text{ kJ mol}^{-1}$ and $E_{C=C} = 56 \text{ kJ mol}^{-1}$. These values are close to 103 kJ mol^{-1} reported by Coenen et al. [23] for the formation of unsaturated fatty alcohols.

Table 3 shows the values of the rate constants of reaction at the three explored pressure levels. It shows that the rate constants increases with pressure of H_2 indicating that the reaction depends on the amount of H_2 dissolved in the reactant medium. These rate “constants” should include some hydrogen pressure term which arises from the absence of a hydrogen concentration term in the kinetic expressions used in the simple model. A positive effect of pressure on the constants values is expected in this sense.

Conclusions

The experiments of methyl oleate hydrogenation showed that an increase in reaction temperature leads to an increase in activity while the selectivity to oleyl alcohol goes through a maximum. This is because the reactions of hydrogenation of $C=C$ double bond have lower activation energies than hydrogenolytic reactions.

The increase in operating pressure favors the hydrogenation reactions but once past a certain threshold its influence on conversion is marginal.

The experiments carried out by varying the ratio of methyl oleate/*n*-dodecane show that the selectivity and conversion mostly does not depend on this parameter.

The catalyst prepared by the IW method is more active and selective than that prepared by CI method. His greatest selectivity is attributed to a better elimination of chlorine as the amount of active material (Ru) is almost the same.

A very simple first order kinetic model, which can be useful to compare catalyst performance more rationally is proposed and reasonably represents the obtained results.

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