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**Advanced Concepts for the Kinetic
Modeling of Fatty Acid Methyl Esters
Hydrogenation**

Maria Ines Cabrera*

Ricardo J. Grau†

*INTEC (UNL-CONICET), marines@santafe-conicet.gov.ar

†INTEC (UNL-CONICET), cqfina@santafe-conicet.gov.ar

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Advanced Concepts for the Kinetic Modeling of Fatty Acid Methyl Esters Hydrogenation*

Maria Ines Cabrera and Ricardo J. Grau

Abstract

Kinetic studies of the catalytic hydrogenation of vegetable oils and fatty acid methyl esters in liquid-phase are commonly performed in the framework of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism using the competitive and non-competitive adsorption models, which are certainly extreme. Based on the advanced concepts of multicentered adsorption and semi-competitive adsorption, mechanistic kinetic models including a distinction between occupied-sites and covered-sites by the large molecules of FAMEs were formulated without expressing an opinion a priori on whether the adsorption regime is competitive or non-competitive. The theoretical basis of the advanced kinetic modeling is described and successfully applied to three application examples of increasing complexity, including: (a) the hydrogenation of methyl oleate without cis-trans isomerization distinction, (b) the cis-trans isomerization and hydrogenation of the methyl oleate, and (c) the methyl linoleate hydrogenation including the cis-trans isomerization of the methyl oleate. The kinetic studies were carried out using a Ni/ α -Al₂O₃, at 398, 413, 428 and 443 K, under isobaric conditions at hydrogen pressures of 370, 510, and 650 kPa, in the absence of mass-transport limitation. After model discrimination based on statistical analysis and taking into account the physical meaning of the estimated parameters, semi-competitive adsorption models were found to be more realistic than the classical LHHW competitive and non-competitive ones, mainly because they give additional information indicating

*Corresponding author: Ricardo J. Grau, Professor at U.N.L. and Member of CONICET's Research Staff. María I. Cabrera, Professor at U.N.L. and Member of CONICET's Research Staff. Both authors are affiliated with Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), Universidad Nacional del Litoral (U.N.L.) and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). Güemes 3450, (3000) Santa Fe, Argentina; Fax: +54-342-4511547; e-mail: cqfina@santafe-conicet.gov.ar. The authors wish to express their gratitude to Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), and to Universidad Nacional del Litoral (UNL), from Argentina, for the financial support granted to this contribution.

that the adsorbed molecules of methyl linoleate and methyl oleate could cover up to 12 and 7 surface sites, respectively. These values are in adequate agreement with those expected from a rough computational simulation and seem to be the most interesting result, since they are factual and unattainable from the classical LHHW approaches.

KEYWORDS: hydrogenation, fatty acid methyl esters, kinetic modeling, semi-competitive adsorption

Introduction

In the early twentieth century, Wilhelm Normann was able to take advantage of Sabatier and Senderens's method for the heterogeneous catalytic hydrogenation of organic compounds in vapor-phase and successfully performed the catalytic hydrogenation of unsaturated fatty acids and glycerides in liquid-phase (Sabatier and Senderens (1897); Normann (1902, 1903)). Since then, the hydrogenation of vegetable oils (VOs) and fatty acid methyl esters (FAMES) has become one of the most important processes in edible oil and oleochemical industries (Deliy et al. (2005); Nohair et al. (2005)). The partial hydrogenation of polyunsaturated VOs has been selectively performed to improve their flavor stability and melting properties, and its use greatly increased in the 1950s (Coenen (1986); Veldinsk et al. (1997)). *Trans* fatty acids are products thereof and, consequently, they have been introduced into human foods. The adverse health implications of non-conjugated *trans* fatty acids (e.g., linoleic acid C18:2 *trans*-9 *cis*-12, and elaidic acid C18:1 *trans*-9) were overlooked during the early decades of their use. However, since the 1990s the harmful effects from *trans* have been a conspicuous topic in the biomedical and health literature (Mensink and Katan (1990); HMSO Report (2004)). Subsequently, the market for lower non-conjugated *trans*-isomer contents in partially hydrogenated VOs has increased. Over the last decades, there has been increasing interest in finding non-edible uses for these renewable sources due to their growing availability and environment compatibility. Polyunsaturated VOs used as environmentally friendly lubricants and fuel alternatives should be improved toward oxidation and NO_x emission by selective hydrogenation (Szybist et al. (2005); Izadifar and Zolghadri Jahromi (2007)). For these applications, a low content of both *trans*-isomers and saturated compounds is also mandatory for preserving the fluidity of the hydrogenated products (Ravasio et al. (2002)). Therefore, there is a renewed motivation to develop improved catalysts and to gain insight into the mechanistic aspects involved in the catalytic process (Bernas et al. (2002a, 2002b); Bernas et al. (2003a, 2003b); Choo et al. (2003); Ju and Jung (2003); Wright et al. (2003); Bernas et al. (2004); Boger et al. (2004); Bernas and Murzin (2005a); Fernández et al. (2005a, 2005b); Nohair et al. (2005); Schmidt and Schomächer (2007); Mäki-Arvela et al. (2008)).

As all novel practices, the hydrogenation process was mainly empirical in its early stages but as the field of heterogeneous catalysis grew, empiricism was increasingly left aside in favor of an analysis based on the kinetic modeling results. A quick review of the literature reveals that pioneering kinetic models describing VOs/FAMES hydrogenation processes were proposed by the mid 20th century (Grau et al. (1988)). Power-law models were used due to their simplicity, and reaction rates were found to be pseudo-first-order with respect to the VOs/FAMES (Bailey (1949); Swicklik et al. (1954); Boelhouwer et al. (1956);

Vandenheuvel (1956); Eldib and Albright (1957); Coenen (1960); Cousins and Feuge (1960); Nielsen et al. (1960); Wisniak (1960); Wisniak and Albright (1961); Scholfield et al. (1962); Albright (1965); Mounts and Dutton (1967); Stefanovic and Albright (1969); Albright (1970); Bern et al. (1975a, 1975b); Bern (1977); Marangozis (1977); Allen (1978); Snyder et al. (1978); Drozdowski and Zajac (1980); Allen (1981); Chen et al. (1981); Stenberg and Schöön (1985); Colen et al. (1988); Jovanović et al. (2002); Plourde et al. (2004)). However, this type of model does not allow representing any adsorption and surface reaction mechanism, or describing experimental data covering a wide range of conversion due to its limited applications to complex reaction networks. The use of more advanced kinetic models was forced to wait for the development of physical tools and computing science. Nowadays, hyperbolic models are recognized as standard to describe the hydrogenation kinetic behavior. Despite the fact that the assumption of uniformity of all catalytic sites can be a crude oversimplification, Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate equations have been widely adopted since the mid-to-late 1970s. Some examples of LHHW approaches are summarized in Table 1 (Hashimoto et al. (1971); Cordova and Harriot (1974); Marangozis et al. (1977); Susu et al. (1978); Tsuto et al. (1978); Gut et al. (1979); Susu and Ogunye (1981); Susu (1982); Liddefelt et al. (1983a, 1983b); Yermakova et al. (1985); Grau et al. (1986, 1987a); Magnusson (1987); Grau et al. (1988); Santacesaria et al. (1994); Jonker et al. (1997, 1998); Jonker (1999); Edvardsson et al. (2001); Fillion et al. (2002); Bernas and Murzin (2005b); Murzin and Simakova (2008)). The main reason for this choice is that hyperbolic models provide a better data fitting than power-law models, in both time and conversion domains. Major attention has been paid to elucidate whether the hydrogen (H) adsorption is dissociative or nondissociative and on discerning the competition mode between H and unsaturated VOs/FAMEs for adsorption on the catalytic sites. Moreover, rate-determining steps (RDS) have been scrutinized. Hence, the literature on the kinetic modeling of VOs/FAMEs hydrogenation is vast and growing, a wide spectrum of mathematical models of varying complexity and details being available. Despite the large amount of work done so far, an entire description of the intrinsic mechanism involving adsorption, hydrogenation and isomerization (geometrical and positional) of reacting species still cannot be obtained due to its complexity. Hence, several approximations are still being made today and, therefore, there is a need for research focused on the development and verification of mechanistic rate expressions (Veldinsk et al. (1997)).

In this regard, the validity of some usual assumptions underlying in LHHW rate equations describing the VOs/FAMEs hydrogenation is still debatable. First, it is ordinarily assumed that an adsorbed unsaturated molecule occupies one surface site, i.e., existing adsorption models do not properly consider steric

hindrance effects of adsorbed species. This is certainly an oversimplification since the large molecular size of VOs/FAMEs is overlooked. Second, the species adsorption is mainly described using the classical non-competitive model. The expectation of fully non-competitive adsorption would be somewhat forced from a physical point of view, since the real adsorption regime lies likely between the competitive and non-competitive extreme modes. Third, two types of adsorption sites are recurrently invoked to derive kinetic models based upon non-competitive adsorption between H and VOs/FAMEs. Although different conjectures concerning the nature of the active sites have been made (Heertje et al. (1974); Lidfelt et al. (1983a); Rodrigo et al. (1992)), the distinction of two types of sites would be not fully valid if the carbon-carbon double-bonds are mainly chemisorbed as σ -, π - and/or $\sigma\pi$ -complexes on the same metal surface sites for H adsorption. Concurrently, after arguing that hydrogen most likely adsorbs on sites between the large VOs/FAMEs molecules, it might be ambiguous to solve two uncoupled site balances at the surface, one for the adsorbed H and another for the adsorbed VOs/FAMEs. We think that these issues deserve special analysis because they could be rough simplifications in the kinetic modeling of the heterogeneous catalytic hydrogenation of these bulky organic molecules.

Based on the advanced concepts of multicentered adsorption (Murzin et al. (1997); Salmi et al. (2004); Murzin and Salmi (2005)) and semi-competitive adsorption (Mikkola et al. (2002); Toukoniitty et al. (2003); Salmi et al. (2004); Backman et al. (2005)), we recently reported the kinetic modeling of the methyl oleate hydrogenation recognizing that large molecules of FAMEs could occupy several surface sites close to that (or those) interacting with the double-bond being adsorbed, and that the true adsorption regime is likely between the above mentioned extreme adsorption modes (Cabrera and Grau (2006)). Stimulating results prompted us to examine the robustness of such approach to analyze more complex reacting systems. In the present contribution, the kinetic modeling of the methyl linoleate hydrogenation including *cis/trans* methyl oleate isomerization is presented. Results and distinctive features characterizing this novel approach are highlighted.

Table 1. Some hydrogenation studies using classical LHHW kinetic models based upon extreme adsorption modes

| VOs/FAMEs | Catalyst | Phase | Adsorption model | Reference |
|------------------------|---|--------|------------------|----------------------------|
| Cottonseed oil | Ni/SiO ₂ | Liquid | Non-competitive | Hashimoto et al. (1971) |
| Methyl linoleate | Pd/C | Liquid | Non-competitive | Cordova et al. (1974) |
| Cottonseed oil | Ni/SiO ₂ | Liquid | Competitive | Marangozis et al. (1977) |
| Palm oil | Ni/Al ₂ O ₃ | Liquid | Non-competitive | Susu et al. (1978) |
| Methyl linoleate | Pd/C | Liquid | Non-competitive | Tsuto et al. (1978) |
| Sunflower seed oil | Ni/Al ₂ O ₃ | Liquid | Non-competitive | Gut et al. (1979) |
| Soybean oil | Ni/Al ₂ O ₃ | Liquid | Non-competitive | Susu and Ogunye (1981) |
| Groundnut oil | Ni/Al ₂ O ₃ | Liquid | Non-competitive | Susu et al. (1982) |
| Methyl oleate | Ni/Al ₂ O ₃ | Vapor | Non-competitive | Lidefelt et al (1983a) |
| Methyl linoleate | Ni/Al ₂ O ₃ | Vapor | Non-competitive | Lidefelt et al (1983b) |
| Methyl linoleate | Ni-Al | Liquid | Non-competitive | Yermakova et al. (1985) |
| Methyl oleate | Ni/Al ₂ O ₃ | Liquid | Non-competitive | Grau et al. (1986) |
| Methyl linoleate | Ni/Al ₂ O ₃ | Liquid | Non-competitive | Grau et al. (1987) |
| Methyl linolenate | Cu/Al ₂ O ₃ ; Ni/Al ₂ O ₃ | Vapor | Competitive | Magnusson (1987a) |
| Methyl linolenate | Ni/Al ₂ O ₃ | Liquid | Non-competitive | Grau et al. (1988) |
| Rapeseed oil | Pd/C | Liquid | Non-competitive | Santacesaria et al. (1994) |
| Methyl oleate | Ni/ SiO ₂ | Liquid | Non-competitive | Jonker et al. (1997) |
| Vos and FAMEs | Ni/SiO ₂ | Liquid | Non-competitive | Jonker et al. (1998) |
| FAMEs | Ni/SiO ₂ | Liquid | Non-competitive | Jonker (1999) |
| Linoleic acid | Pd/MgO | Liquid | Non-competitive | Edvardsson et al. (2001) |
| Soybean oil | Ni/Al ₂ O ₃ | Liquid | Non-competitive | Fillion et al. (2002) |
| FAMEs of sunflower oil | Pd/Al ₂ O ₃ ; Pd/Al ₂ O ₃ | Liquid | Non-competitive | Bernas and Murzin (2005b) |
| Linoleic acid | Ru/Al ₂ O ₃ | Liquid | Non-competitive | Murzin and Simakova (2008) |

Materials and Methods

Materials

A 25 wt% Ni/ α -Al₂O₃ catalyst (specific surface area 185 m²/g, mean particle diameter 2.5 μ m, mean pore diameter 8 nm) was used in all kinetic experiments. The catalyst was preactivated *in-situ* according to a previously reported procedure (Grau et al. (1987b)). Mixtures of methyl oleate/methyl stearate (*cis*-methyl oleate 61.76 wt %; *trans*-methyl oleate 26.18 wt%; 12.06 methyl stearate wt%) and of methyl linoleate/methyl oleate (*cis*-9,*cis*-12-linoleate 62.51 wt%; *cis*-oleate 36.69 wt %; *trans*-oleate 0.80 wt%) were used in the hydrogenation experiments. Nitrogen gas (AgaGas, 99.999% pure) and hydrogen gas (AgaGas, 99.999% pure) were flowed through a Deoxo unit and a drying column before use. Methyl heptadecanoate (Aldrich, 99%) was used as internal standard in GC analyses.

Apparatus and operating conditions

All hydrogenation reactions were performed in a 300 mL steel Parr reactor (Parr Instruments Co. Model 4842). A combined system of electrical heating and coolant circulation allowed us to achieve a fast dynamic control of the reaction temperature, which was kept within ± 0.5 K. The pressure was measured with a strain-gauge pressure transducer (Ashcroft, Model K2) and maintained within ± 5 kPa with a pressure controller (Cole Parmer, Model 68502-10). Hydrogen flow was monitored with a mass flow meter (Matheson 8110) and recorded with a data recorder (Cole Parmer, 250-mm Flatbed). Details of the experimental setup can be found elsewhere (Grau et al. (1986, 1987a, 1988)).

The ranges of the operating conditions were chosen to cover those typically used in industrial processing. The kinetic experiments were performed isothermally at 398, 413, 428 and 443 K, under isobaric conditions at hydrogen pressures of 370, 510, and 645 kPa. The initial catalyst loading was 0.2 wt% with respect to the FAME mixture. The stirring rate was settled at 1000 rpm to ensure negligible mass-transfer effects on the intrinsic reaction rate. A cup-and-cap (CAC) device allowed a facile and safety *in-situ* conditioning of the catalyst and reaction mixture before starting the hydrogenation reaction, as reported in our previous studies of the liquid-phase hydrogenation of FAMEs (Grau et al. (1986, 1987a, 1987b, 1988)). No induction times were observed. The reproducibility of the experimental data was $\pm 1\%$.

Kinetic experiments

A typical procedure was as follows: A precise amount of catalyst (8×10^{-2} g) was placed into the cup mounted on the upper part of the CAC device. The mixture of FAMES to be hydrogenated (40 g) was loaded into the reaction vessel. After assemblage, the reaction vessel was degassed by high vacuum, purged three times with nitrogen, flushed with oxygen-free hydrogen while stirring at room temperature and pressurized at the reaction pressure. Then, the reaction system was heated up to the desired reaction temperature. After stabilization during 120 min at the reaction conditions, the liquid phase became saturated with hydrogen gas and the Ni catalyst preactivated. Finally, the reaction was allowed to start by suddenly imbedding the cup (containing the catalyst) into the reaction mixture, as described elsewhere (Grau et al. (1987b)). Zero time was taken just at that moment. The sampling was performed at different time intervals, with on-line removing of the catalyst using a sinter metal filter. The liquid samples were analyzed by gas chromatography with *cis-trans* methyl oleate resolution. The progress of the hydrogenation was followed until the conversion of the studied FAME was close to completion.

Quantitative GC analysis

The GC analysis was performed on a gas chromatograph (Shimadzu GC-17AATF) equipped with a capillary column (SP-2330, 30 m \times 0.25 mm ID). Nitrogen was used as carrier gas (at 0.6 mL/min) using a split ratio of 100:1. The column temperature was kept constant at 463 K. The flame ionization detector (FID) and injector temperatures were 513 K and 523 K, respectively. Methyl heptadecanoate was used as internal standard for quantification of methyl linoleate, *cis*-methyl oleate, *trans*-methyl oleate and methyl stearate concentrations in the reaction samples.

Results and Discussion

Effects of mass transport phenomena

The effects of mass transport phenomena were experimentally evaluated according to the technique previously reported from our group (Cabrera and Grau (2006)). Table 2 shows the experimental data and parameters used for estimation of the mass transfer effects on the reaction kinetics. The initial hydrogenation rate was found to be nearly first-order for the hydrogen and almost zero-order for the methyl linoleate. By varying the catalyst loading, the gas-liquid mass-transfer resistance was found to be less than 3.7×10^{-2} s. Thus, the resulting ratio between

the highest initial hydrogenation rate and the maximum interfacial transport rate of hydrogen was below 2.4×10^{-2} , suggesting practically negligible gas-liquid mass-transfer limitations.

The values of the corresponding Weisz and Prater modules were found to be $\Phi_H < 1.2 \times 10^{-3}$ and $\Phi_{cc-L} < 5.3 \times 10^{-2}$, which indicated the absence of intraparticle diffusion limitations. Therefore, extraparticle mass transport effects were also expected to be negligible. The resulting values of the liquid-solid mass-transfer resistances were found to be within the $5.8\text{-}8.1 \times 10^{-2}$ s and $2.9\text{-}4.0 \times 10^{-1}$ s ranges for hydrogen and methyl linoleate, respectively. The corresponding values of the ratio between the highest initial hydrogenation rate and the maximum extraparticle mass-transfer rate were lower than 1.8×10^{-3} and 3.9×10^{-3} , respectively, which revealed negligible extraparticle mass-transfer limitations for both reactants. Therefore, under the operating conditions used in this study, the kinetic data are practically unaffected by the mass-transfer phenomena. Temperature gradients are also unlikely to occur because the reaction is moderately exothermic (Veldinsk et al. (1997)).

Kinetic modeling

Figure 1 illustrates an artist's view of *cis*-9-methyl oleate and *cis*-9,*cis*-12-methyl linoleate π -adsorbed on Ni(111). Two features are noticeable. First, these large molecules cover additionally several surface sites adjacent to that (or those) interacting with the double-bond being adsorbed. Second, the blocking of access to surface sites by nearby FAMEs determines a competition between them for a fraction of the vacant-sites only, while the H molecules can access all vacant-sites without any impediment. From this understanding, and by admitting a distinction between occupied-sites and covered-sites by large organic molecules being adsorbed, we have recently put forward a rigorous approach to link the classical LHHW kinetic models describing the competitive and non-competitive adsorption, without having to draw the common distinction between two types of surface sites. The resulting general model, named semi-competitive, also provides additional information suggesting quantitative values for the two issues above mentioned (Cabrera and Grau (2006)).

Table 2. Experimental data and parameters used for estimation of the mass transfer effects on the methyl linoleate hydrogenation rate.^a

| | Units | Operating conditions | |
|--|------------------------------------|----------------------|-----------------|
| | | 398 K / 370 KPa | 443 K / 645 KPa |
| $\Omega_H^{max} \times 10^6$ | $\text{mol cm}^{-3} \text{s}^{-1}$ | 5.2 | 17.5 |
| $[k_b a_b]^{-1} \times 10^2$ | s | 3.7 | 3.5 |
| $[k_c a_c]^{-1} \times 10^1$ | s | 4.0 | 2.9 |
| $\frac{\Omega_H^{max}}{k_b a_b C_H^*} \times 10^2$ | — | 1.14 | 2.4 |
| $\frac{\Omega_{CC-L}^{max}}{k_c a_c C_{CC-L}} \times 10^2$ | — | 0.7 | 1.5 |
| $D_L^{eff} \times 10^6$ | $\text{cm}^2 \text{s}^{-1}$ | 1.2 | 1.8 |
| $D_H^{eff} \times 10^6$ | $\text{cm}^2 \text{s}^{-1}$ | 5.5 | 7.4 |
| $\Phi_{CC-L} \times 10^2$ | — | 1.3 | 5.3 |
| $\Phi_H \times 10^3$ | — | 0.5 | 1.2 |

^a Experimental data for catalyst loading of 0.2 wt% and stirring rate of 1000 rpm. k_b and k_c gas-liquid and liquid-solid mass-transfer coefficients; a_c , interfacial area per unit volume; C_{CC-L} , initial concentration of cc-L in bulk liquid phase; C_H^* , concentration of dissolved hydrogen in bulk liquid phase; Ω_{CC-L}^{max} and Ω_H^{max} , cc-L and H₂ maximum reaction rates, respectively; D_L^{eff} and D_H^{eff} , cc-L and H₂ effective intraparticle diffusion coefficients, respectively; Φ_{cc-L} and Φ_H , cc-L and H₂ Weisz and Prater modules, respectively.

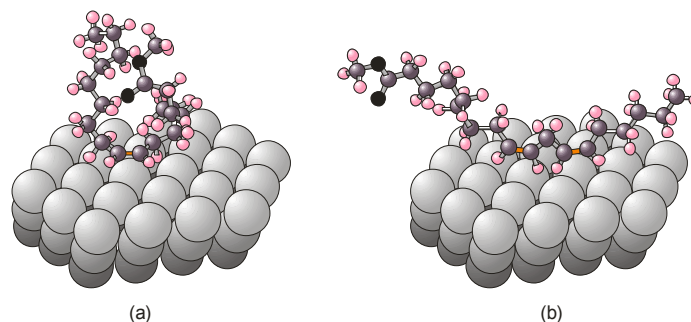
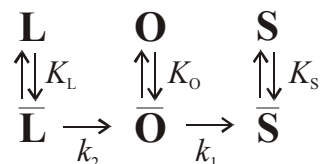


Figure 1. Artist's view of cis-9-methyl oleate (a) and cis-9,cis-12-methyl linoleate (b) π -adsorbed on Ni(111). Molecular structures optimized by using AM1 method.

Before advancing to the specific kinetic modeling of FAMEs hydrogenation, central concepts concerning that approach will be illustrated using the most simple sequential catalytic hydrogenation network encountered in practice, which is represented in Scheme 1.



Scheme 1. Sequential hydrogenation reaction scheme. L, O, and S represent di-unsaturated, mono-unsaturated, and saturated compounds, respectively.

(a) Semi-competitive adsorption model

H and VO/FAME molecules are assumed to be competing for the same type of surface sites, named \otimes -sites. The i -VO/FAME ($i = L, O, \text{ and } S$) molecule is considered to be interacting with x_i \otimes -sites on which its carbon-carbon double-bond is justly adsorbed. In addition, s_i \otimes -sites (closely adjacent to those x_i \otimes -sites) are expected to be additionally covered by a molecule since the VO/FAME molecular size is much larger than the distance between neighbouring \otimes -sites. The s_i \otimes -sites are supposed to be inaccessible for the adsorption of another molecule of VO/FAME, but they are available for adsorption of H molecules by virtue of their small size. Very succinctly stated, the i -FAME molecule effectively covers $(x_i + s_i)$ \otimes -sites, s_i being only accessible for H adsorption. The concept is schematically illustrated in Fig. 2.

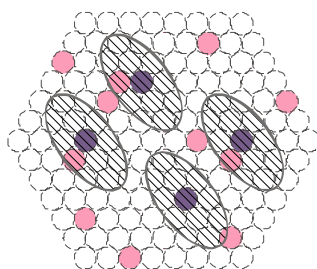


Figure 2. Schematic top view representation of occupied-sites (shaded regions) and covered-sites by adsorbed molecules of hydrogen and large organic compounds (dashed regions), with uncovered sites between them.

Within this understanding framework, there are two forms of expressing the surface site balance equation

$$x_L \Theta_L + x_O \Theta_O + x_S \Theta_S + \Theta_{H_2/n} + \Theta_{\otimes} = 1 \quad (1)$$

$$(x_L + s_L) \Theta_L + (x_O + s_O) \Theta_O + (x_S + s_S) \Theta_S + \Theta_{H_2/n}^U + \Theta_{\otimes}^U = 1 \quad (2)$$

where Eq. (1) establishes the relationship to be fulfilled for the species surface coverages at the catalyst surface level, and Eq. (2) accounts for the coverage inventory as observed from a top view such as depicted in Fig. 2. Superscript U denotes uncovered by VO/FAME molecules. Thus, Θ_{\otimes} and Θ_{\otimes}^U are the \otimes -vacant-site coverages for H and VO/FAMEs adsorption, respectively. It should be noticed that x_i is either 2 for adsorption involving a 2σ -complex or 1 for adsorption forming a π -complex, and n is either 1 for non-dissociative adsorption or 2 for dissociative adsorption.

Assuming the quasi-equilibrium approximation for the adsorption of the species

$$\Theta_{H_2/n} = (K_H C_{H_2})^{1/n} \Theta_{\otimes} \quad (K_H = k_H / k_{-H}) \quad (3)$$

$$\Theta_L = K_L C_L (\Theta_{\otimes}^U)^{x_L} \quad (K_L = k_L / k_{-L}) \quad (4)$$

$$\Theta_O = K_O C_O (\Theta_{\otimes}^U)^{x_O} \quad (K_O = k_O / k_{-O}) \quad (5)$$

$$\Theta_S = K_S C_S (\Theta_{\otimes}^U)^{x_S} \quad (K_S = k_S / k_{-S}) \quad (6)$$

and defining f as the ratio between the \otimes -occupied-sites and \otimes -covered-sites by VO/FAMEs

$$f = \frac{\sum x_i \Theta_i}{\sum (x_i + s_i) \Theta_i} \quad (7)$$

where the summation extends over the all adsorbed VO/FAMEs, the site balance equation can be rewritten as

$$x_L K_L C_L (\Theta_{\otimes}^U)^{x_L} + x_O K_O C_O (\Theta_{\otimes}^U)^{x_O} + x_S K_S C_S (\Theta_{\otimes}^U)^{x_S} + f [1 + (K_H C_H)^{1/n}] \Theta_{\otimes}^U = f \quad (8)$$

which governs the coverage of \otimes -sites effectively available for the adsorption of VO/FAMES and establishes that the maximum coverage by these is only the fraction f of the \otimes -vacant-sites.

The adsorption model is completed by the following relationship arising from Eqs. (1), (2) and (7), which establishes the connection between the uncovered and total \otimes -vacant-site coverages.

$$\Theta_{\otimes} = \frac{1-f \{1 - [1 + (K_H C_H)^{1/n}] \Theta_{\otimes}^U\}}{1 + (K_H C_H)^{1/n}} \quad (9)$$

From Eq. (7), it should be noticed that f should have values within the $0 < f \leq 1$ range. The special case of f equal to unity ($s_i = 0$) describes a one-to-one correspondence between \otimes -occupied-sites and \otimes -covered-sites, as expected for small molecules. The special case of f approaching zero ($s_i \gg x_i$) suggests that the \otimes -covered-sites are much more than those \otimes -occupied-sites, as expected for very large molecules. For VO/FAMES, f values are expected a priori to be intermediates between both extremes. Eqs. (8) and (9) have been found to be advantageous for kinetic modeling because besides describing the semi-competitive adsorption model, the classical LHHW equations for competitive and non-competitive adsorption arise as asymptotic cases. This feature is clearly noticeable for $x_L = x_O = x_S = 1$ (π -adsorption) because explicit equation rates are feasible of being obtained for this case only, as illustrated in what follows.

(b) Competitive adsorption model

Solving Eqs. (8) and (9) for $f = 1$, it yields

$$\Theta_{\otimes}^U = \Theta_{\otimes} = \frac{1}{[1 + (K_H C_H)^{1/n} + K_L C_L + K_O C_O + K_S C_S]} \quad (10)$$

and, therefore, Eqs. (3-6) become

$$\Theta_{H_2/n} = \frac{(K_H C_{H_2})^{1/n}}{[1 + (K_H C_H)^{1/n} + K_L C_L + K_O C_O + K_S C_S]} \quad (11)$$

$$\Theta_L = \frac{K_L C_L}{[1 + (K_H C_H)^{1/n} + K_L C_L + K_O C_O + K_S C_S]} \quad (12)$$

$$\Theta_O = \frac{K_O C_O}{[1 + (K_H C_H)^{1/n} + K_L C_L + K_O C_O + K_S C_S]} \quad (13)$$

$$\Theta_S = \frac{K_S C_S}{[1 + (K_H C_H)^{1/n} + K_L C_L + K_O C_O + K_S C_S]} \quad (14)$$

which are the typical expressions describing the H and VO/FAMEs surface coverages into the framework of the classical LHHW competitive adsorption model.

c) Non-competitive adsorption model

Solving Eqs. (8) and (9) for $f \rightarrow 0$, it yields

$$\Theta_{\otimes}^U = \frac{f}{1 + K_L C_L + K_O C_O + K_S C_S} \quad (15)$$

$$\Theta_{\otimes} = \frac{1}{1 + (K_H C_H)^{1/n}} \quad (16)$$

and, therefore, Eqs. (3-6) become

$$\Theta_{H_2/n} = \frac{(K_H C_{H_2})^{1/n}}{[1 + (K_H C_H)^{1/n}]} \quad (17)$$

$$\Theta_L = \frac{f K_L C_L}{[K_L C_L + K_O C_O + K_S C_S]} \quad (18)$$

$$\Theta_O = \frac{f K_O C_O}{[K_L C_L + K_O C_O + K_S C_S]} \quad (19)$$

$$\Theta_S = \frac{f K_S C_S}{[K_L C_L + K_O C_O + K_S C_S]} \quad (20)$$

which are expressions similar to those describing the H and VO/FAMEs surface coverages into the framework of the classical LHHW non-competitive adsorption model.

Therefore, indubitably, the cases of competitive and non-competitive adsorption can be matched in a continuous form by varying f from unity to a small but non-zero value, respectively. Accordingly, the model for intermediate values of f is understood as describing a semi-competitive adsorption regime. Since it is readily recognized that FAMEs are preferred to VOs for the study of the intrinsic kinetics (Tsuto et al. (1978); Coenen (1986); Grau et al. (1986, 1987a, 1988); Jonker et al. (1997); Jonker (1999); Deliy et al. (2005); Fernández et al. (2005b)), the usefulness of this approach will be illustrated for the kinetic modeling of the liquid-phase hydrogenation of methyl oleate and methyl linoleate over a Ni/ α -Al₂O₃ catalyst.

Application examples

Three application examples of increasing complexity are considered hereafter, including: (a) the hydrogenation of methyl oleate without *cis-trans* isomerization distinction, (b) the *cis-trans* isomerization and hydrogenation of the methyl oleate, and (c) the methyl linoleate hydrogenation including the *cis-trans* isomerization of the methyl oleate.

Common model assumptions are as follows: 1) There is a unique type of \otimes -sites for the adsorption of H and FAMEs. 2) The H adsorption can be either non-dissociative or dissociative. 3) The *i*-FAME molecule can adsorb as a 2σ complex interacting with two neighboring nickel atoms ($x_i = 2$) or as a π complex involving a single nickel atom ($x_i = 1$). 4) No distinction is made for carbon-carbon double-bond migration products, i.e., for any reaction mechanism the double-bond migration was not analyzed. 5) The hydrogenation of the double bond is explained on the basis of the Horiuti-Polanyi mechanism (Horiuti and Polanyi (1934)). 6) The fractional surface coverages by intermediate adsorbed species are negligible as compared to those of bulk species, unless otherwise indicated. 7) The fractional surface coverage by the methyl stearate is not neglected a priori. 8) The value of f does not depend on temperature.

Two approaches have been used for the practical application of the LHHW formalism. The first one is based on the fact that the adsorbed species are in fast equilibrium before the RDS. Thus, the hydrogenation rate is proportional to the surface coverage of species reacting in the RDS, and the resulting expressions have reaction terms in the numerator and pure adsorption terms in the denominator. The second approach is based on applying the quasi steady-state approximation (QSSA) to solve the intermediate species concentrations. In the present study, the first approach is preferred over the second one, unless otherwise

indicated. This preference is due to the fact that kinetic models based on the QSSA would involve more adjustable parameters, increasing both the complexity of the rate expressions and the probability of better data fitting due to a mere increase in the number of parameters and not because of an intrinsically superior model.

Nonlinear regression analysis of experimental data was performed for the resulting kinetic models. The residual sum of squares between experimental data and theoretical predictions was minimized by a modified Levenberg-Marquardt algorithm combined with a procedure for solving nonlinear least squares problems (Marquardt (1963)). The numerical integration of the hydrogenation rate equations was performed using a Runge-Kutta (2,3) pair method (Brankin et al. (1991)). The optimization of the kinetic parameters was achieved by fitting the experimental data for all three pressures at the reference temperature of 413 K, followed by the estimation of the activation energies and adsorption heats according to the Arrhenius and Van't Hoff laws in the 398-443 K range. Concerning the significance of the estimated parameters, the individual 95% confidence intervals have been calculated. The analysis of the significance of the overall regression and the goodness-of-fit were appraised based upon Fisher's test (Froment and Hosten (1981)). The regression was considered to be meaningful when the F_{calc} value was greater than the corresponding tabulated F -value. The highest F_{calc} value was taken as indicative of the best kinetic model. The adequacy of the fitting was also checked by physical interpretation of the estimates. Methodological details can be found in a previous contribution (Cabrera and Grau (2006)).

(a) Hydrogenation of the methyl oleate

The most simple reaction scheme describing the methyl oleate hydrogenation is used to introduce the new approach. The reaction pathway is shown in Scheme 2. The following equilibria and elementary reactions are considered: adsorption of methyl oleate (O) on \otimes -sites; reversible first H-addition to adsorbed O affording a half-hydrogenated surface intermediate SH, followed by an irreversible second H-addition yielding methyl stearate (S) and a further fast desorption to give bulky S.



Scheme 2. Reaction pathway of the methyl oleate hydrogenation to methyl stearate according to the Horiuti-Polanyi mechanism.

Under the aforementioned common assumptions and reaction scheme, the methyl oleate hydrogenation rate can be described by the following overall-rate equations:

- For first H-addition as RDS

$$\frac{d}{dt}C_O = -k_{O/SH} (K_H C_{H_2})^{1/n} \Theta_{\otimes}^U K_O C_O (\Theta_{\otimes}^U)^{x_O} \quad (21)$$

- For second H-addition as RDS

$$\frac{d}{dt}C_O = -k_1 K_H C_{H_2} (\Theta_{\otimes}^U)^n K_O C_O (\Theta_{\otimes}^U)^{x_O} \quad (22)$$

where k_1 is a lumped parameter.

In Eqs. (21) and (22), as follows from Eq. (8), Θ_{\otimes}^U is governed by the following expression

$$x_O K_O C_O (\Theta_{\otimes}^U)^{x_O} + x_S K_S C_S (\Theta_{\otimes}^U)^{x_S} + f [1 + (K_H C_H)^{1/n}] \Theta_{\otimes}^U = f \quad (23)$$

which has to be solved numerically for Θ_{\otimes}^U because it is impossible to obtain an explicit expression for Θ_{\otimes}^U , unless $x_O = x_S = 1$ (π -adsorption). Besides Θ_{\otimes}^U is coupled to Θ_{\otimes}^U by Eq. (9). Here, f is derived from Eq. (7)

$$f = \frac{x_O K_O C_O + x_S K_S C_S}{(x_O + s_O) K_O C_O + (x_S + s_S) K_S C_S} \quad (24)$$

Depending on different combinations of intrinsic adsorption modes and elementary RDS, eight rival kinetic models were formulated and subsequently evaluated. The optimization of the parameters started with the estimation of k_1 or \hat{k}_1 , K_H , K_O , and K_S in the f domain, at 413 K, by fitting methyl oleate concentration vs. time data from 93 observations. The value of K_S was found to be at least 100-folds lower than that of K_O for all the kinetic models. This is in agreement with the observed preferential adsorption of the unsaturated compounds over the saturated ones (Tsuto et al. (1978); Liddefelt et al. (1983a, 1983b); Coenen (1986); Grau et al. (1986, 1987a); Magnusson (1987); Grau et al.

(1988); Edvardsson et al. (2001)), and the fast desorption rate of the methyl stearate (Marangozis et al. (1977); Tsuto et al. (1978); Fillion et al. (2002)). In order to reduce the number of the parameter to be estimated, K_S was ruled out. Thus, f became time independent and, consequently, it could be considered like any other parameter to be estimated. A first parameter optimization was performed at the reference temperature of 413 K; a further optimization was then made for estimating activation energies and adsorption heats by fitting the data at all temperatures according to the Arrhenius and Van't Hoff laws.

After careful model discrimination on statistical basis provided by the SSQ and F_{calc} values, the model explaining the hydrogenation kinetics via dissociative adsorption of hydrogen ($n = 2$), with the methyl oleate molecule interacting with a single surface site ($x_0 = 1$) and second H-addition being RDS, proved to be the best candidate for describing the data satisfactorily and with physically reasonable parameters. Figure 3 shows the experimental and predicted composition profiles in the time domain. The fitted parameter values are summarized in Table 3.

Even though estimates were statistically indistinguishable for the competitive and semi-competitive adsorption modes, the latest model appears to be as more realistic due to the following two features. First, it exhibits physically reasonable values for the estimated parameters, as analyzed elsewhere (Cabrera and Grau (2006)). Second, and more distinctively, it gives additional insight into the amount of surface sites that could be covered by the adsorbed molecule of methyl oleate. Indeed, the optimized value of f suggests that the methyl oleate molecule could cover up to 7 surface sites. This value is in close agreement with that roughly estimated from molecular optimization using the AM1 method, as can be inferred from the artist's illustration depicted in Fig. 4.

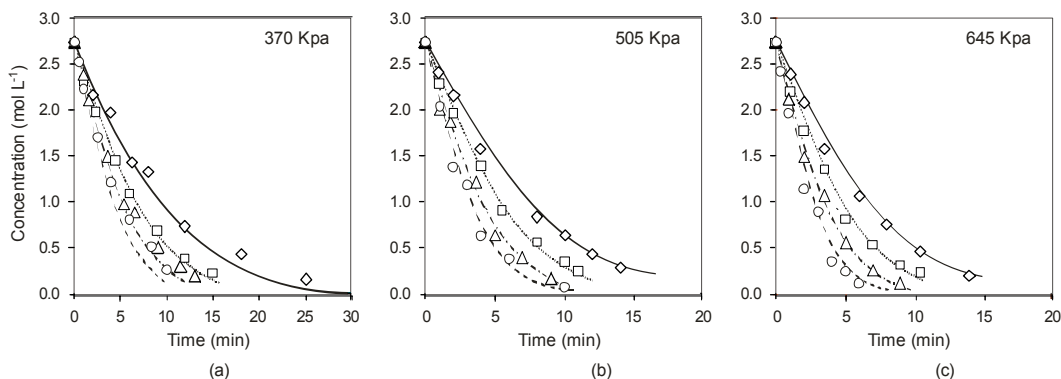


Figure 3. Experimental and predicted profiles of the methyl oleate in the conversion domain, at 370, 505 and 645 Kpa. (\diamond) 398 K; (\square) 313 K; (\bullet) 428 K; and (\circ) 443 K.

Table 3. Fitted parameter values for the semi-competitive kinetic model describing the hydrogenation of methyl oleate, in the range of $398 \leq T \leq 443$ K and $370 \leq P_{H_2} \leq 645$ Kpa.

| Parameters | Units | Values ^a |
|--------------------------------------|-----------------------------------|-------------------------------|
| f | — | 0.16 ± 0.01 |
| covered \otimes -sites | — | 6.27 ± 0.39 |
| $\hat{k}_1 \times 10^4$ ^b | $\text{mol L}^{-1} \text{s}^{-1}$ | 5.98 ± 0.04 ^b |
| K_O ^b | $\text{mol}^{-1} \text{L}$ | 49.44 ± 0.43 ^b |
| K_H ^b | $\text{mol}^{-1} \text{L}$ | 19.17 ± 0.31 ^b |
| E | kJ mol^{-1} | 75.17 ± 0.73 |
| $-\Delta H_O$ | kJ mol^{-1} | 10.13 ± 0.64 |
| $-\Delta H_H$ | kJ mol^{-1} | 77.70 ± 0.73 |

^a Values correspond to 95.5 % confidence limits.

^b Value at the reference temperature of 413 K.

The semi-competitive adsorption model revealed a fractional surface coverage of the chemisorbed hydrogen ranging from 0.30 to 0.40, and an apparent fractional coverage of themethyl oleate as large as 0.42. However, the fractional coverage just at the catalyst surface level was nearly 0.06 because the adsorbed molecule could cover up to almost seven surface sites. This finding suggests that, under the studied operating conditions, more than half of surface sites remain vacant during the hydrogenation process.

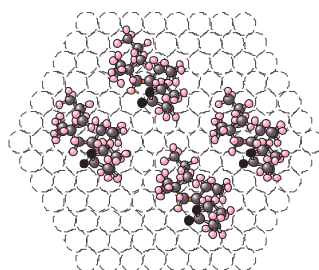


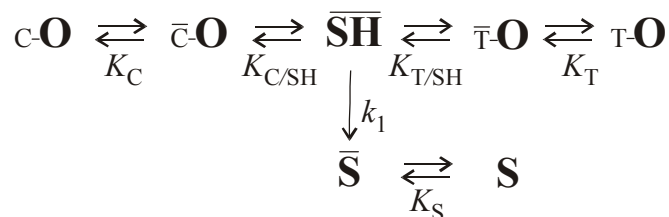
Figure 4. Artist's view of cis-methyl oleate adsorbed on Ni(111). The C9,10 double bond has been arbitrarily placed on-top of Ni atoms.

(b) *Cis-trans* isomerization and hydrogenation of the methyl oleate

Although it is still a subject of debate whether the *cis-trans* isomerization proceeds via a σ -alkyl complex as a half-hydrogenated intermediate or via a H-abstraction-addition mechanism involving a π -complex as intermediate

(Fernández et al. (2005b)), the classical Horiuti-Polanyi mechanism is here used to describe the elementary reaction steps. The well-known reaction pathway depicted in Scheme 3 is thus adopted. It involves adsorption of *cis*-methyl oleate (C-O) and *trans*-methyl oleate (T-O) followed by a reversible first H-addition yielding a half-hydrogenated intermediate (SH) having a single bond which can freely rotate allowing geometrical isomerization; a further irreversible second H-addition to SH affords methyl stearate (S), which is fast desorbed.

From results of the application example (a), it can be adduced that: (i) H adsorption is dissociative ($n = 2$); (ii) the adsorption of S is negligible as compared to that of mono-unsaturated compounds; (iii) the adsorption of C-O and T-O takes place on a single \otimes -site involving π -adsorption ($x_{T-O} = x_{C-O} = 1$); and (iv) the molecule of methyl oleate covers nearly 6.25 \otimes -sites, whichever the geometric isomer. Besides, based on our experimental data, any adequate kinetic model should be able to account for the kinetic behavior: v) a slow approaching to *trans/cis* equilibrium during the course of the hydrogenation with an equilibrium concentration ratio nearly 3.5, which is attained earlier at increased temperature; and, vi) C-O and T-O hydrogenation rates practically equal as suggested by the equilibrium concentration constant ratio after achieving high conversion levels (stearate formed > 85 %).



Scheme 3. Reaction pathway of *cis-trans* isomerization and hydrogenation of methyl oleate to methyl stearate according to the Horiuti-Polanyi mechanism. C and T denote *cis* and *trans* lumped mono-unsaturated compounds without distinction of positional isomers, respectively.

Under the aforementioned model assumptions, and taking into account the described behavior, the derived overall-rate equations are as follows

$$\begin{aligned}
 \frac{d}{dt} C_{\text{C-O}} = & -k_{\bar{\text{C/T}}} \sqrt{K_{\text{H}} C_{\text{H}_2}} \Theta_{\otimes} \Theta_{\bar{\text{C-O}}} + \frac{k_{\bar{\text{C/T}}}}{K_{\bar{\text{C/T}}}} \sqrt{K_{\text{H}} C_{\text{H}_2}} \Theta_{\otimes} \Theta_{\bar{\text{T-O}}} \\
 & - k_1 K_{\text{H}} C_{\text{H}_2} (\Theta_{\otimes})^2 \Theta_{\bar{\text{C-O}}} \quad (25)
 \end{aligned}$$

$$\begin{aligned} \frac{d}{dt} C_{T-O} = & k_{\bar{C}/\bar{T}} \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{\bar{C}-O} - \frac{k_{\bar{C}/\bar{T}}}{K_{\bar{C}/\bar{T}}} \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{\bar{T}-O} \\ & - k_1 K_H C_{H_2} (\Theta_{\otimes})^2 \Theta_{\bar{T}-O} \end{aligned} \quad (26)$$

where

$$\Theta_{\bar{C}-O} = K_C C_{C-O} \Theta_{\otimes}^U \quad (27)$$

$$\Theta_{\bar{T}-O} = K_T C_{T-O} \Theta_{\otimes}^U \quad (28)$$

$$K_{\bar{C}/\bar{T}} = k_{\bar{C}/\bar{T}} / k_{-\bar{C}/\bar{T}} \quad (29)$$

In obtaining equations (25)-(29), we have assumed $k_{C/SH} = k_{T/SH}$, i.e., the values of the forward-reaction rate constants for the first H-addition to c-O and T-O were considered to be equal. It seems that there is no physically invalidating reason for this adoption, which is a mandatory condition to achieve equal hydrogenation rates of both isomers. Here Θ_{\otimes}^U is governed by the following site balance equation

$$K_C C_{C-O} \Theta_{\otimes}^U + K_T C_{T-O} \Theta_{\otimes}^U + f [1 + (K_H C_{H_2})^{1/n}] \Theta_{\otimes}^U = f \quad (30)$$

with Θ_{\otimes}^U being coupled to Θ_{\otimes} as described by Eq. (9). Note that Θ_{\otimes}^U can be explicitly obtained from Eq. (30) due to c-O and T-O are π -adsorbed.

After assuming that K_C and K_T equilibrium constants are equal (Gut et al. (1979); Grau et al. (1986); Santacesaria et al. (1994); Jonker et al. (1997); Fillion et al. (2002)), the values of K_C , K_T , K_H , \hat{k}_1 , and f were taken from the application example (a). The isomerization equilibrium constant $K_{C/T}$ was assumed to be 3.45 at 413 K ($-\Delta H_{C/T} = 2.52 \text{ kJ mol}^{-1}$) as accurately estimated in our previous contribution (Grau et al. (1986)). Consequently, the forward-reaction rate constant $k_{C/T}$ and the corresponding activation energy $E_{C/T}$ remain the only two unknown parameters to be determined from data fitting. Both parameters were estimated by fitting 186 data from *cis*- and *trans*-methyl oleate concentration profiles. The data fitting results are given in Fig. 5 and the calculated parameter values are summarized in Table 4. A comparison of the theoretical and experimental profiles shows an excellent overall description. Profiles clearly assert the rule stating to minimize temperature and maximize pressure when seeking low *trans* content.

Activation energy E_{CT} was found to be quite larger than values generally reported in the available literature, but it is in relatively good agreement with the value of $71.65 \pm 9.16 \text{ kJ mol}^{-1}$ reported in the modeling of the soybean oil kinetics, including gas-liquid mass transfer effects, to determine the intrinsic kinetics (Fillion et al. (2002)).

The E_{CT} value was found to be only 1.2 times larger than that of the hydrogenation reactions. Other literature values are nearly 1.5 times (Jonker et al. (1997); Fillion et al. (2002)). It should be noticed that although the isomerization reaction is slightly exothermic, an increase in reaction temperature increases the *trans* content since both the *cis/trans* equilibrium is only achieved after surpassing 85% conversion of methyl oleate and the isomerization rate constant k_{CT} has an activation energy greater than that of the hydrogenation constant \hat{k}_1 .

It should be pointed out that the well-known kinetic mechanism was tested using this new approach recognizing the differences in the molecular size of hydrogen and FAMEs. The semi-competitive model was able to describe the main kinetic peculiarities of *cis*- and *trans*- methyl oleate formation in the course of methyl oleate hydrogenation in liquid-phase. Physically reasonable values for the estimated parameters were obtained and the results undoubtedly display that the semi-competitive adsorption concept is workable for this classic reaction network.

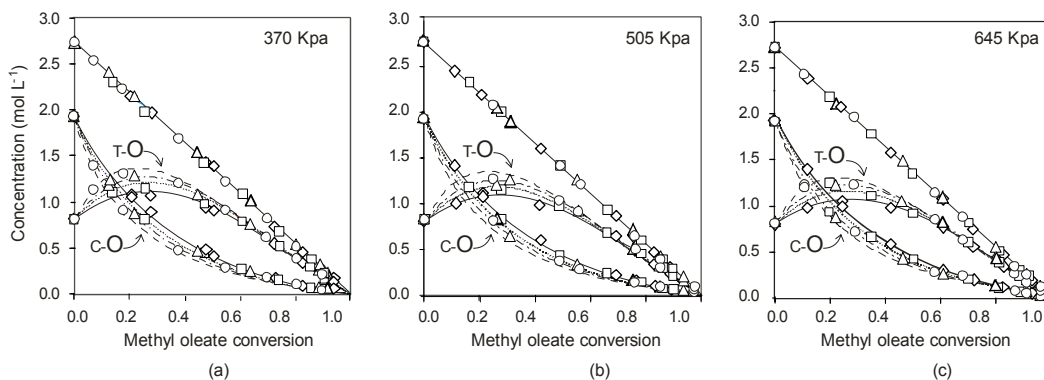


Figure 5. Experimental and predicted profiles of the *cis*- and *trans*-methyl oleate in the conversion domain, at 370, 505 and 645 Kpa. (◊) 398 K; (◻) 313 K; (•) 428 K; and (◊) 443 K.

Table 4. Fitted parameter values for the semi-competitive kinetic model describing the *cis-trans* isomerization and hydrogenation of methyl oleate, in the range of $398 \leq T \leq 443$ K and $370 \leq P_{H_2} \leq 645$ KPa.

| Parameters | Units | Values ^a |
|-----------------------------|-----------------------------------|-------------------------------|
| f | — | 0.16 ± 0.01 |
| covered \otimes -sites | — | 6.27 ± 0.69 |
| $\hat{k}_1 \times 10^4$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 5.98 ± 0.04 ^b |
| $k_{C/T} \times 10^4$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 4.83 ± 0.07 ^b |
| $K_{C/T}$ | — | 3.45 ± 0.01 ^d |
| $K_C = K_T$ | $\text{mol}^{-1} \text{L}$ | 49.44 ± 0.43 ^b |
| K_H | $\text{mol}^{-1} \text{L}$ | 19.17 ± 0.31 ^b |
| E_1 | kJ mol^{-1} | 75.17 ± 0.73 |
| E_{isom} | kJ mol^{-1} | 83.98 ± 1.09 |
| $-\Delta H_C = -\Delta H_T$ | kJ mol^{-1} | 10.13 ± 0.64 |
| $-\Delta H_H$ | kJ mol^{-1} | 77.70 ± 0.73 |
| $-\Delta H_{\text{isom}}$ | kJ mol^{-1} | 2.52 ± 0.12 ^d |

^a Values correspond to 95.5 % confidence limits.

^b Value at the reference temperature of 413 K.

^c Optimized value from the application example (a).

^d Value from the reference (Grau et al. (1986)).

(c) Hydrogenation of the methyl linoleate including the *cis-trans* isomerization of the methyl oleate

Kinetic models describing the methyl linoleate hydrogenation have been formulated on the basis of reaction networks including the *cis/trans* methyl oleate isomerization (Albright (1965); Hashimoto et al. (1971); Gut (1979); Susu and Ogunye (1981); Grau et al. (1987a, 1988); Fillion et al. (2002)). However, the mechanistic meaning of the reaction pathway from the *cis-cis* methyl linoleate (CC-L) to the *trans*-methyl oleate (T-O) was left open. The *cis-cis/cis-trans* isomerization of methyl linoleate must be included in the reaction network as a way to explain the most direct reaction pathway from CC-L to T-O. Intermediate formation of CT-L *trans*-adsorbed and further desorption to free CT-L, followed by (re)adsorption as CT-L *cis*-adsorbed, are sequential steps suggested for supporting that reaction pathway (Jonker (1999)). However, the conjecture of di-unsaturated compounds adsorbed through a single double-bond only, like mono-unsaturated ones, is here left aside for several reasons. The most important one is that the mono-unsaturated and di-unsaturated molecular structures exhibit meaningful

differences, as illustrated in Fig. 6. An inspection of cc -L and ct -L structures reveals that their two double-bonds are very close to being on the same plane, providing a small steric impediment toward the simultaneous adsorption of the two double-bonds. This fact suggests that both isomers are promising candidates to be also adsorbed through two double-bonds. A more accurate estimation using surface science tools is mandatory to confirm this expectation but its corroboration is beyond the scope of this work.

Understanding that adsorption of two double-bonds is also feasible, the suggested reaction network is shown in Scheme 4. The following equilibria and elementary reaction steps are suggested: cc -L is first π -adsorbed through only one double-bond interacting with a single surface site yielding $c\bar{c}L$, which can undergo either hydrogenation to free c -O via a σ -bonded half-hydrogenated intermediate or adsorption of its second double-bond affording $\bar{c}\bar{c}L$ 2π -adsorbed. The $\bar{c}\bar{c}L$ can, in turn, undergo H-addition and rearrangement to form a π - σ bonded half-hydrogenated complex which gives either $\bar{c}TL$ 2π -adsorbed by σ -bond rotation and H-subtraction or $\bar{c}O$ π -adsorbed by a second H-addition. The two double-bond adsorbed $\bar{c}TL$ remain strongly adsorbed and by H-addition and rearrangement they yield a π - σ bonded half-hydrogenated intermediate, which by a second H-addition gives $\bar{t}O$ π -adsorbed. The remaining reaction steps are those previously described in the application example (b). The suggested reaction mechanism is basically in agreement with that proposed in a recent study of the *cis/trans* methyl oleate formation during hydrogenation of methyl oleate over Pd/MgO (Deliy et al. (2005)). In that study, unfortunately, kinetic models were not put forward to disclose their data fitting capability.

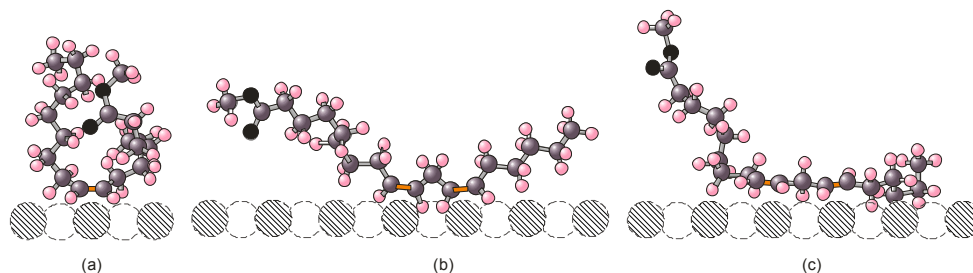
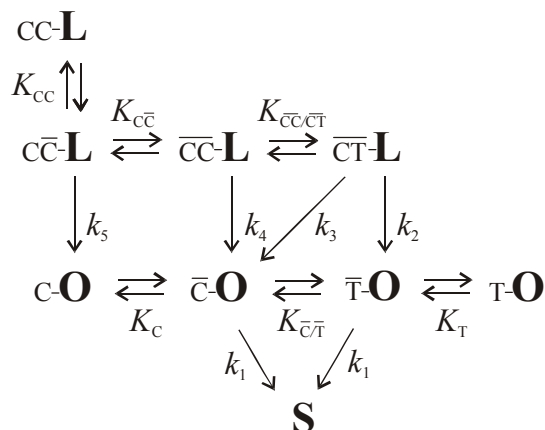


Figure 6. Molecular structures of *cis*-methyl oleate (π -adsorbed), and *cis-cis* methyl linoleate and *cis-trans* methyl linoleate (2π -adsorbed).



Scheme 4. Overall-reaction pathway of the *cis-cis* methyl linoleate hydrogenation accounting the *cis-trans* isomerization and hydrogenation of the methyl oleate to methyl stearate. Here cc-L and ct-L denote *cis-cis* and *cis-trans* lumped di-unsaturated compounds without distinction of positional isomers, respectively. Likewise, c-O and t-O denote *cis* and *trans* lumped mono-unsaturated compounds without distinction of positional isomers, respectively.

From the results of application example (b), it can be quoted that: *i*) H adsorption is dissociative ($n = 2$); *ii*) the adsorption of S is negligible as compared to that of mono-unsaturated compounds; *iii*) the adsorption of c-O and t-O takes place on a single \otimes -site involving π -adsorption ($x_{\text{t-O}} = x_{\text{c-O}} = 1$); *iv*) the molecule of methyl oleate (*cis*- and *trans*) covers up to 7 \otimes -sites, whichever the geometric isomer; *v*) the *trans/cis* methyl oleate equilibrium is slowly approached and attained earlier at increased temperature; *vi*) the second-H-addition is RDS in the methyl oleate hydrogenation process; and, *vii*) the hydrogenation rates of both isomers are equal. In addition, after analyzing our experimental data, any adequate kinetic model must be able to account for the following kinetic behavior: *viii*) an almost zero-order kinetics with respect to the methyl linoleate concentration until reaching a conversion of 60%; *ix*) a virtually linear dependence of the *trans/cis* methyl oleate ratio until reaching a methyl linoleate conversion of about 85%, whichever the reaction temperature and hydrogen pressure; *x*) a drastic *cis/trans* isomerization after surpassing that mentioned conversion; *xi*) a linear relationship between the methyl stearate formation and the methyl linoleate conversion during the early stages of the hydrogenation process; and, *xii*) a nearly first-order kinetics with respect to the dissolved hydrogen concentration, as previously discussed in effects of mass transport phenomena.

Under the aforementioned common assumptions and reaction scheme, the overall-rate equations can be described by the following:

- For first H-addition as RDS in the methyl linoleate hydrogenation and second H-addition as RDS in the methyl oleate hydrogenation

$$\begin{aligned} \frac{d}{dt} C_{CC-L} = & -k_5 \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{CC-T}^- - k_4 \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{CC-L}^- \\ & - (k_3 + k_2) \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{CT-L}^- \end{aligned} \quad (31)$$

$$\begin{aligned} \frac{d}{dt} C_{C-O} = & k_5 \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{CC-T}^- + k_4 \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{CC-L}^- + k_3 \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{CT-L}^- \\ & - k_1 K_H C_{H_2} \Theta_{\otimes} \Theta_{C-O}^- - k_{C/T}^- \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{C-O}^- + \frac{k_{C/T}^-}{K_{C/T}^-} \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{T-O}^- \end{aligned} \quad (32)$$

$$\begin{aligned} \frac{d}{dt} C_{T-O} = & k_2 \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{CT-L}^- - k_1 K_H C_{H_2} \Theta_{\otimes} \Theta_{T-O}^- \\ & + k_{C/T}^- \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{C-O}^- - \frac{k_{C/T}^-}{K_{C/T}^-} \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{T-O}^- \end{aligned} \quad (33)$$

- For second H-addition as RDS in the methyl linoleate hydrogenation and second H-addition as RDS in the methyl oleate hydrogenation

$$\begin{aligned} \frac{d}{dt} C_{CC-L} = & -k_5 K_H C_{H_2} \Theta_{\otimes} \Theta_{CC-T}^- - k_4 K_H C_{H_2} \Theta_{\otimes} \Theta_{CC-L}^- \\ & - (k_3 + k_2) K_H C_{H_2} \Theta_{\otimes} \Theta_{CT-L}^- \end{aligned} \quad (34)$$

$$\begin{aligned} \frac{d}{dt} C_{C-O} = & k_5 K_H C_{H_2} \Theta_{\otimes} \Theta_{CC-T}^- + k_4 K_H C_{H_2} \Theta_{\otimes} \Theta_{CC-L}^- + k_3 K_H C_{H_2} \Theta_{\otimes} \Theta_{CT-L}^- \\ & - k_1 K_H C_{H_2} \Theta_{\otimes} \Theta_{C-O}^- - k_{C/T}^- \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{C-O}^- + \frac{k_{C/T}^-}{K_{C/T}^-} \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{T-O}^- \end{aligned} \quad (35)$$

$$\begin{aligned} \frac{d}{dt} C_{T-O} = & k_2 K_H C_{H_2} \Theta_{\otimes} \Theta_{CT-L}^- - k_1 K_H C_{H_2} \Theta_{\otimes} \Theta_{T-O}^- \\ & + k_{C/T}^- \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{C-O}^- - \frac{k_{C/T}^-}{K_{C/T}^-} \sqrt{K_H C_{H_2}} \Theta_{\otimes} \Theta_{T-O}^- \end{aligned} \quad (36)$$

In Eqs. (31)-(33) and (34)-(36) the surface coverages are given by the following quasi-equilibrium equations

$$\Theta_{\text{CC-L}} = K_{\text{CC}} C_{\text{CC-L}} \Theta_{\otimes}^{\text{U}} \quad (37)$$

$$\Theta_{\overline{\text{CC-L}}} = K_{\overline{\text{CC}}} \Theta_{\overline{\text{CC-L}}} \Theta_{\otimes} \quad (38)$$

$$\Theta_{\text{C-O}} = K_{\text{C}} C_{\text{C-O}} \Theta_{\otimes}^{\text{U}} \quad (39)$$

$$\Theta_{\overline{\text{T-O}}} = K_{\overline{\text{T}}} C_{\overline{\text{T-O}}} \Theta_{\otimes}^{\text{U}} \quad (40)$$

and with $\Theta_{\overline{\text{CT-L}}}$ governed by the following relationships:

- for first H-addition as RDS in the methyl linoleate hydrogenation:

$$\Theta_{\overline{\text{CT-L}}} = \frac{k_{\overline{\text{CC/CT}}}}{(k_2 + k_3) \sqrt{K_{\text{H}} C_{\text{H}_2}} + \frac{k_{\overline{\text{CC/CT}}}}{K_{\overline{\text{CC/CT}}}}} \Theta_{\overline{\text{CC-L}}} \quad (41)$$

- for second H-addition as RDS in the methyl linoleate hydrogenation:

$$\Theta_{\overline{\text{CT-L}}} = \frac{k_{\overline{\text{CC/CT}}} \sqrt{K_{\text{H}} C_{\text{H}_2}}}{(k_2 + k_3) K_{\text{H}} C_{\text{H}_2} + \frac{k_{\overline{\text{CC/CT}}}}{K_{\overline{\text{CC/CT}}} \sqrt{K_{\text{H}} C_{\text{H}_2}}} \Theta_{\overline{\text{CC-L}}} \quad (42)$$

As distinctive feature, it should be remarked that the adsorption rate of CC-L to $\overline{\text{CCL}}$ π -adsorbed was assumed to be proportional to $\Theta_{\otimes}^{\text{U}}$, while the adsorption rate of $\overline{\text{CCL}}$ to $\overline{\text{CCL}}$ 2π -adsorbed was supposed as proportional to Θ_{\otimes} because we believe the second carbon-carbon double-bond is in competition with H for the nearby \otimes -sites on which the first carbon-carbon double bond is justly adsorbed. In the above equations k_1 , k_2 , k_3 , k_4 , k_5 , $k_{\overline{\text{CC/CT}}}$, $K_{\overline{\text{CC/CT}}}$, $k_{\overline{\text{C/T}}}$, and $K_{\overline{\text{C/T}}}$ are lumped kinetic parameters. Moreover, in Eqs. (37)-(40), $\Theta_{\otimes}^{\text{U}}$ is governed by the following site balance equation

$$\Theta_{\otimes}^U = \frac{1}{[2K_{\overline{CC}} \Theta_{\otimes} + 1]K_{CC} C_{CC-L} + K_O [C_{C-O} + C_{T-O}] + f [1 + \sqrt{K_H C_H}]} \quad (43)$$

where Θ_{\otimes} is coupled to Θ_{\otimes}^U by Eq. (9). Here, f can be derived from Eq. (7) as

$$f = \frac{[2K_{\overline{CC}} \Theta_{\otimes} + 1]K_{CC} C_{CC-L} + K_O [C_{C-O} + C_{T-O}]}{[(2 + s_{\overline{CC}})K_{\overline{CC}} \Theta_{\otimes} + (1 + s_{\overline{CC}})]K_{CC} C_{CC-L} + (1 + s_O)K_O [C_{C-O} + C_{T-O}]} \quad (44)$$

Although f is now dependent on time, the unknown $s_{\overline{CC}}$ and $s_{\overline{CC}}$ are constant parameters. Because no changes in the number of \otimes -sites additionally covered by $\overline{CC-L}$ and $\overline{CC-L}$ are envisaged from the optimized molecular structure of $\overline{CC-L}$, after assuming $s_{\overline{CC}} = s_{\overline{CC}} = s_{CC}$, the value of s_{CC} was the parameter to be estimated, instead of f . The values of K_C , K_T , K_H , $K_{\overline{C}/\overline{T}}$, $k_{\overline{C}/\overline{T}}$, k_1 , and s_O , and the corresponding activation energies, adsorption heats and isomerization enthalpy were taken from the application example (b). Therefore, K_{CC} , $K_{\overline{CC}}$, $K_{\overline{CC}/\overline{CT}}$, $k_{\overline{CC}/\overline{CT}}$, k_2 , k_3 , k_4 , k_5 , and s_{CC} remain as unknown parameters to be determined from data fitting.

Depending on different combinations of elementary reaction steps and RDS, six rival kinetic models were formulated and subsequently evaluated. The optimization of the parameters started with the estimation of the parameters at 413 K, by fitting methyl linoleate, *cis*-methyl oleate and *trans*-methyl oleate concentration vs. time data from 288 observations. A further optimization was then made for estimating activation energies and adsorption heats by fitting the data at all temperatures according to the Arrhenius and Van't Hoff laws.

After model discrimination on the statistical basis of the resulting SSQ and F_{calc} values, the kinetic model explaining the *cis-cis/cis-trans* methyl linoleate isomerization via two successive adsorption steps interacting with a single surface site, i.e., π -adsorption followed by 2 π -adsorption; and second H-addition being RDS in the hydrogenation sequence, proved to be the best candidate for describing the data satisfactorily and with physically reasonable parameters. The data fitting results are given in Fig. 7 and the calculated parameter values are summarized in Table 5.

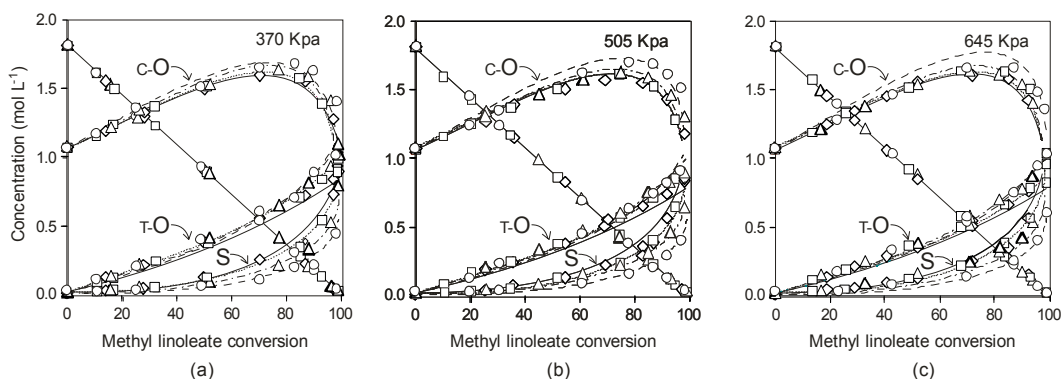


Figure 7. Experimental and predicted profiles of the *cis*-methyl oleate, *trans*-methyl oleate and methyl stearate in the conversion domain, at 370, 505 and 645 Kpa. (\diamond) 398 K; (\square) 313 K; (\bullet) 428 K; and (\circ) 443 K.

It is noticeable that the theoretical and experimental profiles are in good agreement. Once again, even though estimates were statistically indistinguishable for the competitive and semi-competitive adsorption modes, the latest model appears to be as more realistic due to the following two features. It exhibits physically reasonable values for the estimated parameters. First, the rate constants values and activation energies are in good agreement with those reported in the literature (Veldinsk et al. (1997)). Second, the values of the double bond adsorption constants for the successive π - and 2π -adsorption of methyl linoleate were found to be nearly 15.37 and 28.67 mol⁻¹ L, respectively, suggesting less hindrance for adsorption of the second double bond, as expected. Moreover, despite the fact that there are no reported values for each adsorption constant, the value of the lumped adsorption constant $K_L = K_{CC/C\bar{C}} K_{C\bar{C}/C\bar{C}}$ is nearly 440 mol⁻¹ L, which is almost one order of magnitude greater than that obtained in an uncoupled form for the methyl oleate adsorption constant (see Table 5). This relative value is in good agreement with those reported in the literature (Veldinsk et al. (1997)). Third, and more meaningful, the amount of surface sites being covered by the adsorbed molecule of methyl linoleate has been estimated to be nearly 11.5. This value is in very close agreement with that roughly estimated from molecular optimization using the AM1 method, as can be seen from the artist's illustration depicted in Fig. 8.

Table 5. Fitted parameter values for the semi-competitive kinetic model describing the methyl linoleate hydrogenation including *cis-trans* isomerization of the methyl oleate, in the range of $398 \leq T \leq 443$ K and $370 \leq P_{H_2} \leq 645$ Kpa.

| Parameters | Units | Values ^a |
|-------------------------------------|-----------------------------------|---------------------------------|
| covered \otimes -sites by CC-L | sites | 11.50 ± 4.50 |
| covered \otimes -sites by C-O/T-O | sites | 6.27 ± 0.89 ^c |
| K_{CC} | $\text{mol}^{-1} \text{L}$ | 15.37 ± 2.03 ^b |
| $K_{C\bar{C}}$ | $\text{mol}^{-1} \text{L}$ | 28.67 ± 3.76 ^b |
| $K_{\bar{C}\bar{C}/\bar{C}\bar{T}}$ | — | 2.16 ± 0.75 ^b |
| $k_{\bar{C}\bar{C}/\bar{C}\bar{T}}$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 0.48 ± 0.10 ^b |
| $\hat{k}_1 \times 10^4$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 5.98 ± 0.04 ^{b,c} |
| $\hat{k}_2 \times 10^2$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 6.61 ± 0.83 ^b |
| $\hat{k}_3 \times 10^1$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 1.21 ± 0.46 ^b |
| $\hat{k}_4 \times 10^2$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 9.92 ± 1.05 ^b |
| $\hat{k}_5 \times 10^4$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 1.49 ± 0.46 ^b |
| $k_{C/T} \times 10^4$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 4.83 ± 0.07 ^b |
| $K_{C/T}$ | — | 3.45 ± 0.01 ^{b,c} |
| $k_{CC/TT}$ | $\text{mol L}^{-1} \text{s}^{-1}$ | 0.48 ± 0.12 ^{b,c} |
| $K_{CC/TT}$ | — | 2.16 ± 0.72 ^d |
| $K_C = K_T$ | $\text{mol}^{-1} \text{L}$ | 49.44 ± 0.43 ^{b,c} |
| K_H | $\text{mol}^{-1} \text{L}$ | 19.17 ± 0.31 ^{b,c} |
| E_1 | kJ mol^{-1} | 75.17 ± 0.73 ^c |
| E_2 | kJ mol^{-1} | 108.61 ± 3.94 |
| E_3 | kJ mol^{-1} | 85.93 ± 3.05 |
| E_4 | kJ mol^{-1} | 83.46 ± 2.45 |
| E_5 | kJ mol^{-1} | 102.04 ± 3.87 |
| $E_{C/T}$ | kJ mol^{-1} | 83.98 ± 1.09 ^c |
| $E_{CC/TT}$ | kJ mol^{-1} | 77.68 ± 1.79 |
| $-\Delta H_C = -\Delta H_T$ | kJ mol^{-1} | 10.13 ± 0.64 ^c |
| $-\Delta H_H$ | kJ mol^{-1} | 77.70 ± 0.73 ^c |
| $-\Delta H_{C/T}$ | kJ mol^{-1} | 2.52 ± 0.12 ^d |
| $-\Delta H_{CC/TT}$ | kJ mol^{-1} | 5.50 ± 0.47 |

^a Values correspond to 95.5 % confidence limits. ^b Value at the reference temperature of 413 K. ^c Optimized value from the application example (a).

^d Value from reference (Grau et al. (1986)).

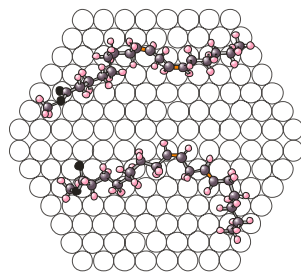


Figure 8. Artist's view of cis-cis and cis-trans methyl linoleate adsorbed on Ni(111). The C9,10 and C12,13 double bonds have been arbitrarily placed on-top of Ni atoms.

The semi-competitive adsorption model revealed a fractional surface coverage of the chemisorbed hydrogen ranging from 0.30 to 0.40, and apparent fractional coverages of the methyl linoleate and methyl oleate varying from 0.60 to close zero and 0.05 to 0.40, respectively. However, the real fractional coverages at the catalyst surface level were in the 0.05-0.01 and 0.01-0.06, respectively, because the adsorbed molecule of methyl linoleate and methyl oleate could cover up to almost twelve and seven surface sites, respectively. This finding suggests that surface sites remain vacant in great extent during the hydrogenation process due to steric hindrance arising from the large molecular size of FAMES.

Conclusions

The kinetic modeling of the liquid-phase hydrogenation of methyl linoleate and oleate over Ni/ α -Al₂O₃ was performed on the basis of elementary step mechanisms involving different regimes of competition between hydrogen and FAMES for adsorption on the same type of surface sites. Admitting the distinction between occupied-sites and covered-sites by the large molecules of FAMES, general rate equations able to provide a workable way to survey the semi-competitive adsorption as intermediate regime were formulated, and the classical LHHW competitive and non-competitive rate equations linked as extreme cases. The theoretical basis of the advanced kinetic modeling was described and successfully applied to three application examples of increasing complexity, including: (a) the hydrogenation of methyl oleate without *cis-trans* isomerization distinction, (b) the *cis-trans* isomerization and hydrogenation of the methyl oleate, and (c) the methyl linoleate hydrogenation including the *cis-trans* isomerization of the methyl oleate. Kinetic experiments in the absence of mass-transport limitation were carried out at $398 \leq T \leq 443$ K and $370 \leq P_{H_2} \leq 645$ Kpa, using a catalyst loading of 0.2 wt% and a stirring rate of 1000 rpm.

A statistical analysis of regression using our experimental data shows the adequacy of the mechanistic kinetic models featuring: dissociative adsorption of hydrogen, the two double-bonds of the methyl linoleate molecule adsorbed through two consecutive steps involving π -adsorption and 2π -adsorption, the single double-bond of the methyl oleate molecule adsorbed via single π -adsorption, second insertion of hydrogen as RDS in the hydrogenation sequence, and non equilibrium *cis-trans* isomerization. Statistical results do not allow a well-defined discrimination between rival models with competitive and semi-competitive adsorption. However, the kinetic models considering semi-competitive adsorption appear to be more realistic than the competitive ones because they give additional insight into the amount of surface sites that can be covered by the adsorbed molecule of FAMEs. Indeed, results from the semi-competitive model indicate that the adsorbed molecules of methyl linoleate and methyl oleate could cover up to 12 and 7 surface sites, respectively. These values are in adequate agreement with those expected from a rough computational simulation and seem to be the most fascinating result, since they are factual and unattainable from the classical approaches.

Even though the few contributions published so far show that the semi-competitive model cannot provide a definite statistical discrimination with some of the extreme regimes of adsorption, a rough prediction of the number of surface sites covered by the organic molecules seems to be the most fascinating result, given its factual character. These stimulating results would encourage further studies, especially on the examination of the robustness of this recent approach for analyzing different heterogeneous catalytic hydrogenation systems for organic synthesis.

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