Review

Kinetic modeling of hydrogenation reactions over metal-supported catalysts, recognizing the differences between the molecular size of hydrogen and organic species: A brief review

María I. Cabrera and Ricardo J. Grau*

INTEC (CONICET, U.N.L.) Güemes 3450, (3000) Santa Fe, Argentina

ABSTRACT

This brief review focuses on the evolving concepts related to the kinetic modeling of catalytic hydrogenation systems involving organic compounds of large molecular size. After a short paragraph introducing the scope of the article, different mathematical approaches are reviewed from a Chemical Reaction Engineering viewpoint. Their chronological development is described, going from the early simple LHHW model to recent advanced models based on the concept of multicentered and semicompetitive adsorption. First, the review presents and critically analyzes the simplest mathematical attempts to deal with the classical kinetic models based upon extreme adsorption regimes, i.e., competitive and non-competitive adsorption between hydrogen and organic molecules. Then, it discusses progressive attempts based on more rigorous frameworks for conciliating the understanding of finite differences in the molecular size of species, admitting a distinction between occupied-sites and covered-sites by the large molecules of organic species. Accordingly, the concepts of multicentered and semi-competitive adsorption are brought on the scene, and recent proposals are analyzed in detail to link the two seemingly separate kinetic models describing the extreme modes of competitive and non-competitive adsorption. The additional indication of the number of surface sites that would likely be covered by organic molecules appears to be the most fascinating result of these advanced approaches. Finally, the review highlights the need for examining the robustness of these recent approaches.

1. INTRODUCTION

As early as 1897, Sabatier and Senderens developed the heterogeneous catalytic hydrogenation of organic compounds in vapor phase including the conversion of nitrobenzene to aniline and oleic acid to stearic acid [1]. Fifteen years later, Wilhelm Normann showed that unsaturated fatty acids and glycerides could be catalytically hydrogenated in liquid phase [2-4]. In 1904, the use of higher hydrogen pressures by Ipatieff extended the sphere of possible hydrogenation reactions, which founded the basis of later technical developments in this field [5-9]. By 1913, no less than 183 hydrogenation patents had been recorded in various countries [10]. Since then, heterogeneous catalytic hydrogenation has been widely applied for the reduction of a variety of functional groups of great utility in both organic synthesis at laboratory scale and the industrial manufacture of fine chemicals [11, 12].

Hence, a wide spectrum of mathematical models of varying complexity and detail has been employed to describe the kinetic behavior of these

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*Corresponding author
cqfina@santafe-conicet.gov.ar

reacting systems. During the last decades, significant advances in physical tools and computing science have allowed capturing increasingly detailed levels of kinetic information leading to a better, more comprehensive understanding of reaction mechanisms, thus contributing to the development of more and more detailed kinetic models. Accordingly, the literature on the kinetic modeling of heterogeneous catalytic hydrogenation is vast and growing. For this reason, we have chosen to be selective rather than inclusive in this review, and to discuss kinetic modeling efforts performed in the prevalent mathematical framework of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) formalism. The review focuses especially on those approaches recognizing the differences between the molecular size of hydrogen and organic compounds. No attempt has been made here to review model discrimination and parameter estimation methods.

2. Background

2.1. Historical perspective

Like all young disciplines, heterogeneous catalytic hydrogenation was mainly empirical in its early stages. As the field of heterogeneous catalysis grew, empiricism was increasingly left aside in favor of a more deductive reasoning based on quantitative approaches. Therefore, scientists and engineers began to propose kinetic models to approximate experimental data. A quick perusal of the literature reveals that hydrogenation kinetic modeling slowly progressed until the last quarter of the 20th century. Indeed, its advance was forced to wait for the development of other disciplines, such as instrumental analytical chemistry, surface science, and computational sciences. However, despite significant advances in almost all required disciplines, an entire description of the true mechanism of many hydrogenation systems still cannot be obtained due to their complexity. Therefore, several approximations are still being made today.

Until four decades ago, power-law models were used on the basis of simplicity by most researchers and engineers to describe hydrogenation kinetics. It is beyond the scope of the present work to examine the numerous contributions made within
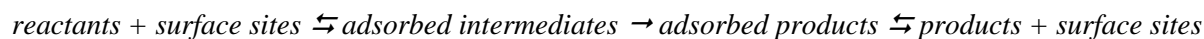
this framework. Only some general remarks will be made. The hydrogenation rate is expressed as

$$\Omega_A = k\, C_H^n\, C_A^m$$

where k is an overall rate constant accounting for both adsorption and surface reaction, and n and m are reaction orders with respect to the hydrogen (H) and substrate (A) concentrations, respectively.

The power-law model is simple and amenable for data fitting, but it does not allow representing any adsorption and surface reaction mechanism or describing experimental data over a wide range of the reactant conversion. Moreover, it is quite unsuitable for describing the hydrogenation of polyunsaturated compounds with intermediates being in strong competition for the vacant sites of the catalysts.

Nowadays, hyperbolic models are recognized as standard to describe surface mediated reactions as that shown in Scheme 1. The first influential approach to explain catalytic kinetic data of surface mediated reactions was made by Hinshelwood during the 1920s based on the Langmuir theory of ideal surfaces [13]. The succeeding Langmuir-Hinshelwood kinetics thus became an alternative to the power-law kinetics. However, the most meaningful contribution was made then by Hougen and Watson in 1943, whose proposal led to a systematic formulation of rate equations for surface-controlled catalytic reactions [14]. A few years later, the Hougen-Watson modeling was methodologically extended to explore rate-determining steps (RDS) [15]. These pioneering works have provided inspiration and criticism for further kinetic modeling, as recently reviewed by Weller [16]. Due to its usefulness and similarities, the Langmuir-Hinshelwood (L-H) and Hougen-Watson (H-W) approaches have been referred to as the Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach [17]. Even though the assumption of uniformity of all catalytic sites can be a crude oversimplification, LHHW rate equations have proven to be very practical in the kinetic modeling of hydrogenation reactions over metal-supported catalysts, and they have been widely adopted since the 1960s. There are several reasons for this choice, as pointed out by Murzin [18]. Many hydrogenation reactions

reactants + surface sites ⇆ adsorbed intermediates → adsorbed products ⇆ products + surface sites

Scheme 1. Successive steps in a surface mediated reaction, involving adsorption, surface reaction, and desorption.

take place under coverages and steady-state conditions leading to zero or first-order kinetics, which do not require treatment of the surface heterogeneity. Moreover, for a small degree of non-uniformity, the predictions based on uniform and non-uniform kinetic models are quite similar. Thus, for practical purposes in Chemical Reaction Engineering and Chemical Reactor Design, the classical LHHW kinetic equations provide simple and sufficiently descriptive models. However, there are some cases in which the classical approach is not enough to explain the kinetic behaviors.

Recognizing that large organic molecules could cover more surface sites than hydrogen, and that the real adsorption regime lies likely between both extreme adsorption modes, new approaches based on the concepts of multicentered and semi-competitive adsorption have recently been proposed in an effort to develop more realistic kinetic models.

2.2. Concepts and underlying assumptions

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 most cases, the first approach has been preferred over the second one. This preference is due to the fact that kinetic models based on the QSSA would involve more adjustable parameters, increasing 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.

Much attention has been paid to address RDS in the reaction sequences and to elucidate whether the hydrogen adsorption is dissociative or nondissociative, as well as on discerning the competition mode between the hydrogen and organic compounds for adsorption on the vacant surface sites. A survey of the literature regarding adsorption modes reveals that much work has been performed on the basis of the classical competitive and non-competitive models, which are certainly extremes. Some examples are summarized in Table 1 (ref. [19]-[80]). Upon examination, a general rule for selecting one or another adsorption model cannot be picked out promptly. Occasionally, the same or similar systems have been modeled using dissimilar adsorption models. Nevertheless, a criterion appears to be prevailing. It is often argued that the adsorption is competitive in nature when the reacting organic species have small molecular size. Otherwise, the non-competitive adsorption model is usually preferred. Kinetic modeling based upon these extreme adsorption regimes is then reviewed in Section 3.

In the LHHW classical approach, it is ordinarily assumed that the organic molecule adsorbs on one surface site. This is an oversimplification, since the molecular size of the reacting organic compound is overlooked. Moreover, the expectation of fully competitive and non-competitive adsorption would be somewhat forced from a physical point of view, since the real adsorption regime lies likely between both adsorption modes. These features inspired the concepts of multicentered adsorption recognizing that the organic molecule covers several surface sites and the semi-competitive adsorption noticing that there is always a fraction of the surface sites between the larger organic molecules remaining available for the non-competitive adsorption of hydrogen [54, 81, 82]. Recent examples are summarized in Table 2 (ref. [83]-[88]). Details and distinctive features of both novel approaches are specially highlighted in Section 4.

Finally, the most simple hydrogenation system encountered in practice will be used for

Table 1. Some hydrogenation studies using kinetic models based upon extreme adsorption regimes.

Compounds	Catalysts	Models	References
Citral	Ni/Al$_2$O$_3$	Competitive	Salmi *et al.*, 2007 [19]
Furfuryl alcohol	Ru/TiO$_2$	Competitive	Tike and Mahajani, 2007 [20]
D-actose	Ru/C	Non-competitive	Kuusisto *et al.*, 2007 [21]
Cinnamaldehyde	Cu/SiO$_2$	Competitive	Marchi *et al.*, 2007 [22]
Toluene	Pt/Al$_2$O$_3$	Non-competitive	Castaño *et al.*, 2007 [23]
Propyne	Pd/cluster	Non-competitive	Brandão *et al.*, 2007 [24]
1-5-Cyclooctadiene	Pd/Al$_2$O$_3$	Competitive	Schmidt and Schomäcker, 2007 [25]
Benzene	Ni/ Al$_2$O$_3$	Non-competitive	Metaxas and Papayannakos, 2006 [26]
Sterols	Pd/C	Non-competitive	Wärnå *et al.*, 2006 [27]
D-lactose	Ni/sponge	Non-competitive	Kuusisto *et al.*, 2006 [28]
Citral	Pt/SiO$_2$	Competitive	Mukherjee and Vannice, 2006 [29]
Acetophenone	Pt/Al$_2$O$_3$	Competitive	Gao *et al.*, 2006 [30]
Sterols	Pd/polym	Competitive	Helminen *et al.*, 2006 [31]
Red. Alk. aniline	Pd/Al$_2$O$_3$	Competitive	Roy *et al.*, 2005 [32]
2-Butyne-1,4-diol	Pd/C	Non-competitive	Kiwi-Minsker *et al.*, 2005 [33]
Cinnamaldehyde	Ru-Sn	Non-competitive	Hájek *et al.*, 2004 [34]
Isooctenes	Pt/Al$_2$O$_3$	Non-competitive	Lylykangas *et al.*, 2004 [35]
Propylene	Pd/clusters	Competitive	Brandão *et al.*, 2004 [36]
n-Butenes	Pd/Al$_2$O$_3$	Competitive	Bressa *et al.*, 2003 [37]
Tetralin/naphthalene	Ni/Al$_2$O$_3$	Competitive	Lylykangas *et al.*, 2002 [38]
Naphthalene	Ni/Al$_2$O$_3$	Non-competitive	Rautanen *et al.*, 2002 [39]
α-Methylstyrene	Pd/Al$_2$O$_3$	Non-competitive	Meille *et al.*, 2002 [40]
Soybean oil	Ni/Al$_2$O$_3$	Non-competitive	Fillon *et al.*, 2002 [41]
Citral	Pt/TiO$_2$	Competitive	Singh and Vannice, 2000 [42]
Citral	Pt/SiO$_2$	Competitive	Singh and Vannice, 2000 [43]
Toluene	Ni/Al$_2$O$_3$	Non-competitive	Rautanen *et al.*, 2000 [44]
2,2-Dimethylol-1butanal	Ni/SiO$_2$	Competitive	Rantakylä *et al.*, 2000 [45]
o-Nitrophenol	Pd/C	Non-competitive	Choudhary and Sane, 1999 [46]
BTX	Ni/SiO$_2$	Non-competitive	Keane and Patterson, 1999 [47]
2,4-Dinitrotoluene	Ni/zeol.	Competitive	Malyala and Chaudhari, 1999 [48]
Ethyl pyruvate	Pt/Al$_2$O$_3$	Competitive	Blaser *et al.*, 1998 [49]
Unsaturated edible oils	Pd/C	Non-competitive	Jonker *et al.*, 1988 [50]
Isobutene	Pd/Sn	Competitive	Cortright *et al.*, 1998 [51]
BTX	Ni/Al$_2$O$_3$	Non-competitive	Toppinen *et al.*, 1997 [52]
Benzaldehyde	Pt/TiO$_2$	Competitive	Vannice and Poondi, 1997 [53]
Ethyl pyruvate	Pt/Al$_2$O$_3$	Non-competitive	Murzin, 1997 [54]
Cinnamaldehyde	Ru/Al$_2$O$_3$	Non-competitive	Neri *et al.*, 1997 [55]
Methyl oleate	Ni/Al$_2$O$_3$	Non-competitive	Jonker *et al.*, 1997 [56]
Nitrotoluene derivatives	Pd/C	Competitive	Neri *et al.*, 1997 [57]
2,4-Dinitrotoluene	Pd/Al$_2$O$_3$	Competitive	Rajashekharam *et al.*, 1997 [58]
Alkylbenzenes	Ni/Al$_2$O$_3$	Competitive	Toppinen *et al.*, 1996a-b [59, 60]
1,5,9-Cyclododecatriene	Pd/Al$_2$O$_3$	Non-competitive	Benaissa *et al.*, 1996 [61]
Buta-1,3-diene	Pd/Al$_2$O$_3$	Non-competitive	Goetz *et al.*, 1996 [62]

Table 1 continued..

Compounds	Catalysts	Models	References
2,4-Dinitrotoluene	Pd/C	Non-competitive	Neri *et al.*, 1995 [63]
3-Methyl-crotonaldehyde	Pt	Competitive	Birchem *et al.*, 1994 [64]
p-Chloronitrobenzene	PtM/Al$_2$O$_3$	Competitive	Coq *et al.*, 1992 [65]
p-Chloronitrobenzene	RuSn/RuPb/RuGe	Competitive	Tijani *et al.*, 1991 [66]
Ethylene	Pt	Competitive	Cortright *et al.*, 1991 [67]
2,4-Dinitrotoluene	Pd/C	Non-competitive	Hanssen *et al.*, 1990 [68]
Cinnamaldehyde	Pt-Sn/Nylon	Non-competitive	Tronconi *et al.*, 1990 [69]
2-Ethylhexenal	Pd/SiO$_2$	Competitive	Niklasson, 1988 [70]
2-Tert-butylphenol	Ni/Co/Ru	Non-competitive	Kut *et al.*, 1988 [71]
Acetone	Pt/TiO$_2$/Al$_2$O$_3$/SiO$_2$/Au	Competitive	Sen and Vannice, 1988 [72]
Methyl linolenate	Ni/Al$_2$O$_3$	Non-competitive	Grau *et al.*, 1988 [73]
Methyl linoleate	Ni/Al$_2$O$_3$	Non-competitive	Grau *et al.*, 1987 [74]
Methyl ester of fatty acids	Cu and Ni/Al$_2$O$_3$	Competitive	Magnusson, 1987 [75]
Methyl oleate	Ni/Al$_2$O$_3$	Non-competitive	Grau *et al.*, 1986 [76]
Sunflower oil	Pd/Al$_2$O$_3$	Non-competitive	Gut *et al.*, 1979 [77]
Methyl linoleate	Pd/C	Non-competitive	Tsuto et al., 1978 [78]
Acetone	Ni	Competitive	Lemcoff, 1977 [79]
Styrene	Pd/Al$_2$O$_3$	Competitive	Mochizuki and Matsui, 1976 [80]

Table 2. Some hydrogenation studies using kinetic models based upon intermediate adsorption regimes.

Compounds	Catalysts	Models	References
Methyl linoleate	Ni/Al$_2$O$_3$	Semi-competitive	Cabrera and Grau, 2007 [83]
Methyl oleate	Ni/Al$_2$O$_3$	Semi-competitive	Cabrera and Grau, 2006 [84]
o-Xilene	Pd/Al$_2$O$_3$	Semi-competitive	Backman *et al.*, 2005 [85]
Alkylbenzenes	Ni Raney	Semi-competitive	Salmi *et al.*, 2004 [86]
Xylose	Ni Raney	Semi-competitive	Salmi *et al.*, 2004 [86]
1-Phenil1-1,2-propadiene	Pd/Al$_2$O$_3$	Multicentered	Toukoniity *et al.*, 2003 [87]
Xylose	Ni Raney	Semi-competitive	Mikkola *et al.*, 2000 [88]

illustration purposes, and it is represented by the following overall reaction

$$A + H_2 \rightarrow S$$

where the organic compound undergoing hydrogenation and the product thereof are denoted by A and S, respectively. Although there are diverse hydrogenation mechanisms, which depend on many factors, such as functional group to be hydrogenated, nature of the catalyst and operating conditions, a reaction mechanism must be adopted for illustration purposes. We take the classical one featuring sequential addition of adsorbed H-atoms to the reacting organic compounds [89].

It must be stressed that these adoptions (reaction scheme and mechanism) are only made for the sake of simplicity, and they are not a mandatory requirement to account for the distinctive features characterizing the different approaches to be reviewed.

3. Kinetic models describing extreme adsorption regimes

3.1. Kinetic models based upon competitive adsorption

For competitive adsorption, the hydrogenation mechanism can be written as shown in Table 3. It should be noted that all species adsorb on the same type of active sites, named $\otimes$ sites, x being the number of sites interacting with the adsorbed organic molecule equal to 1 (π-adsorption) or 2 (2σ-adsorption). This is a common simplification, which neglects the molecular size of the reacting organic compound.

Assuming the QSSA for the adsorption rate of species, the surface coverages of adsorbed species are given by

$$\Theta_A = K_A C_A (\Theta_\otimes)^x \qquad (1)$$

$$\Theta_S = K_S C_S (\Theta_\otimes)^x \qquad (2)$$

$$\Theta_{H_{2/n}} = (K_H C_H)^{1/n} \Theta_\otimes \qquad (3)$$

where the coverage of $\otimes$ vacant sites is subjected to the following site balance equation for competitive adsorption

$$\Theta_\otimes + \Theta_{H_{2/n}} + x[\Theta_A + \Theta_S] = 1 \qquad (4)$$

which has negligible surface coverage of the half-hydrogenated intermediate as an underlying assumption.

Substituting Eqs. (1)-(3) into Eq. (4), the site balance equation can finally be written as

$$[1 + (K_H C_H)^{1/n}]\Theta_\otimes + x[K_A C_A + K_S C_S](\Theta_\otimes)^x = 1 \qquad (5)$$

which describes the full competition of all the species for the $\otimes$ vacant sites.

Depending on which reaction step is assumed to be RDS, different hydrogenation rate equations result in terms of the coverages of the reacting species:

- For 1st H-addition as RDS (step C3)

$$\Omega_A = k_{SH}\, \Theta_{H_{2/n}}\, \Theta_A \qquad (6)$$

- For 2nd H-addition as RDS (step C4)

$$\Omega_A = k_1 K_{SH}\, (\Theta_{H_{2/n}})^2 \Theta_A \qquad (7)$$

The above set of equations has to be implicitly solved for $\Theta_\otimes$ unless $x = 1$ (π-adsorption). For this latter case, the replacement of the surface coverages results in the final rate equations:

- For 1st H-addition as RDS

$$\Omega_A = \frac{k_{SH}\, (K_H C_H)^{1/n} K_A C_A}{[1 + (K_H C_H)^{1/n} + K_A C_A + K_S C_S]^2} \qquad (8)$$

- For 2nd H-addition as RDS

$$\Omega_A = \frac{k_1\, K_{SH}\, (K_H C_{H_2})^{2/n} K_A C_A}{[1 + (K_H C_H)^{1/n} + K_A C_A + K_S C_S]^3} \qquad (9)$$

Eqs. (8) and (9) are usually referred to as the LHHW-type model with competitive adsorption between the hydrogen and organic molecules. In the above equations, the terms in the denominator account for the full competition between species for the $\otimes$ vacant sites. This type of rate equations has been commonly used to represent kinetic data in a large number of catalytic hydrogenation systems (see Table 1), but usually a good data fitting in both time and conversion domains can be only achieved when the organic compounds have small molecular size.

Table 3. Reaction mechanism for competitive adsorption.

$n \otimes + H_2$	$\leftrightarrows$	$n \otimes\text{-}H_{2/n}$	$K_H, (k_H \text{ and } k_{-H})$	(C1)
$x \otimes + A$	$\leftrightarrows$	$(x\otimes)\text{-}A$	$K_O, (k_O \text{ and } k_{-O})$	(C2)
$(x\otimes)\text{-}A + \otimes\text{-}H_{2/n}$	$\leftrightarrows$	$(x\otimes)\text{-}SH + (2-n)\otimes\text{-}H + (n-1)\otimes$	$K_{SH}, (k_{SH} \text{ and } k_{-SH})$	(C3)
$(x\otimes)\text{-}SH + \otimes\text{-}H$	$\rightarrow$	$(x\otimes)\text{-}S + \otimes$	k_1	(C4)
$(x\otimes)\text{-}S$	$\leftrightarrows$	$S + x\otimes$	$K_S, (k_S \text{ and } k_{-S})$	(C5)

where $\otimes$ denotes adsorption site for both hydrogen and organic molecules; n is either 1 for non-dissociative adsorption of hydrogen or 2 for dissociative adsorption of hydrogen; and x is either 1 for π-adsorption or 2 for 2σ-adsorption.

3.2. Kinetic models based upon non-competitive adsorption

For non-competitive adsorption, the reaction mechanism can be summarized as shown in Table 4. It should be remarked that two types of adsorption sites, $\otimes$ and $\oplus$, are used to account for the independent adsorption of hydrogen and organic molecules, respectively.

Accordingly, after assuming the QSSA for the adsorption rates, the coverages of adsorbed species are given by

$$\Theta_A = K_A C_A (\Theta_\oplus)^x \tag{10}$$

$$\Theta_S = K_S C_S (\Theta_\oplus)^x \tag{11}$$

$$\Theta_{H_{2/n}} = (K_H C_H)^{1/n} \Theta_\otimes \tag{12}$$

where the coverages of organic compounds are assumed to be dependent on $\Theta_\oplus$, and that of hydrogen is expressed as proportional to $\Theta_\otimes$.

Then, the availability of $\otimes$ and $\oplus$ sites is usually described by two uncoupled site balance equations as follows

$$\Theta_\oplus + x[\Theta_A + \Theta_S] = 1 \tag{13}$$

$$\Theta_\otimes + \Theta_{H_{2/n}} = 1 \tag{14}$$

which after substitution of the coverages become

$$\Theta_\oplus + x(K_A C_A + K_S C_S)(\Theta_\oplus)^x = 1 \tag{15}$$

$$[1+(K_H C_H)^{1/n}]\Theta_\otimes = 1 \tag{16}$$

Eqs. (15) and (16) describe the competition between the organic compounds for the $\oplus$ vacant sites and the independent adsorption of hydrogen on the $\otimes$ sites, respectively. Eqs (6) and (7)

describing the hydrogenation rate for 1st and 2nd H-addition as RDS, respectively, complete the kinetic model. Once again, the resulting set of equations has to be solved iteratively for $\Theta_\otimes$ unless $x = 1$ (π-adsorption). In this case, after substitution of surface coverages, the resulting hydrogenation rate equations are:

- For 1st H-addition as RDS (step N3)

$$\Omega_A = \frac{k_{SH}(K_H C_H)^{1/n} K_A C_A}{[1+(K_H C_H)^{1/n}][1+K_A C_A + K_S C_S]} \tag{17}$$

- For 2nd H-addition as RDS (step N4)

$$\Omega_A = \frac{k_1 K_{SH}(K_H C_H)^{2/n} K_A C_A}{[1+(K_H C_H)^{1/n}]^2 [1+K_A C_A + K_S C_S]} \tag{18}$$

Eqs. (17) and (18) are referred to as the LHHW-type model with non-competitive adsorption, which is characterized by two independent adsorption terms in the denominator. This type of equations has been successfully used to describe the kinetic data of numerous catalytic hydrogenation systems (see Table 2). Generally, when the molecular sizes of organic compounds undergoing reaction are much larger than that of the hydrogen molecule, these functional forms provide a better data fitting than those of the competitive model.

As above stated, two types of adsorption sites have recurrently been invoked to derive non-competitive models. Although there are different conjectures concerning the nature of the active sites, this distinction would be rather not fully valid if the hydrogen and organic molecules were certainly chemisorbed on active sites of the same type, as is usual in unsaturated hydrocarbon

Table 4. Reaction mechanism for non-competitive adsorption.

$n \otimes + H_2$	$\leftrightarrows$	$n \otimes \text{-}H_{2/n}$	K_H, (k_H and k_{-H})	(N1)
$x \oplus + A$	$\leftrightarrows$	$(x\oplus)\text{-}A$	K_O, (k_O and k_{-O})	(N2)
$(x\oplus)\text{-}A + \otimes\text{-}H_{2/n}$	$\leftrightarrows$	$(x\oplus)\text{-}SH + (2-n)\otimes\text{-}H + (n-1)\oplus$	K_{SH}, (k_{SH} and k_{-SH})	(N3)
$(x\oplus)\text{-}SH + \otimes\text{-}H$	$\rightarrow$	$(x\oplus)\text{-}S + \otimes$	k_1	(N4)
$(x\oplus)\text{-}S$	$\leftrightarrows$	$S + x \oplus$	K_S, (k_S and k_{-S})	(N5)

where $\otimes$ and $\oplus$ denote adsorption sites for the hydrogen and organic molecules, respectively; n is either 1 for non-dissociative adsorption of hydrogen or 2 for dissociative adsorption of hydrogen; and x is either 1 for π-adsorption or 2 for 2σ-adsorption.

hydrogenation. Concurrently, it might be ambiguous to solve two uncoupled balances of sites at the surface, one for the adsorbed organic compounds and another for the adsorbed hydrogen, as described by Eqs. (13) and (14). However, this issue has not received much criticism in the literature. We think that it deserves special analysis because it could be a rough simplification, if not a flaw, in most cases. What is important is to conciliate the description of the physical occurrence with a mathematical formulation expressing it correctly. In this way, successive attempts have recently been made towards more general formulations. Their most distinctive features are presented in the following Section.

4. Kinetic models describing multicentered and semi-competitive adsorption

Figure 1 illustrates an artist's view of a small molecule as ethylene and a larger one as *cis*-methyl oleate adsorbed on Ni(111). It can be seen that the short hydrocarbon molecule covers only the surface sites on which it is adsorbed, but the larger molecule additionally covers several adjacent surface sites. Besides, the non-competitive adsorption of hydrogen can take place on the interstitial surface sites remaining inaccessible for the larger molecules due to steric hindrance. From this understanding, new concepts, such as multicentered and semi-competitive adsorption, emerged as central ideas for developing more advanced kinetic models. The main features of these novel approaches are analyzed below.

4.1. Kinetic models based upon multicentered adsorption

The multicentered adsorption model describes the fact that the adsorbed organic molecule could occupy several surface sites close to that or those interacting with the double bond being adsorbed. In addition, the adsorption mode can shift toward the configuration that requires less space when several species are being adsorbed [81, 82]. This concept has been experimentally verified for the toluene and methylcyclohexane adsorption on Ni catalysts [90], and it has also been used to explain the product distribution in enantio- and regioselective hydrogenation processes [86].

After assuming that x_A and x_S are the number of sites required for the adsorption of organic compounds A and S, respectively, the use of the QSSA for the adsorption rates yields the following expressions for the surface coverages

$$\Theta_A = K_A C_A (\Theta_\otimes)^{x_A} \tag{19}$$

$$\Theta_S = K_S C_S (\Theta_\otimes)^{x_S} \tag{20}$$

$$\Theta_{H_{2/n}} = (K_H C_H)^{1/n} \Theta_\otimes \tag{21}$$

where, for competitive adsorption, the coverage of $\otimes$ vacant sites is subject to the site balance equation

$$\Theta_\otimes + \Theta_{H_{2/n}} + x_A \Theta_A + x_S \Theta_S = 1 \tag{22}$$

which, as stated above, has negligible surface coverage of the half-hydrogenated intermediate.

Substitution of Eqs. (19)-(21) into Eq. (22) finally gives the nonlinear equation
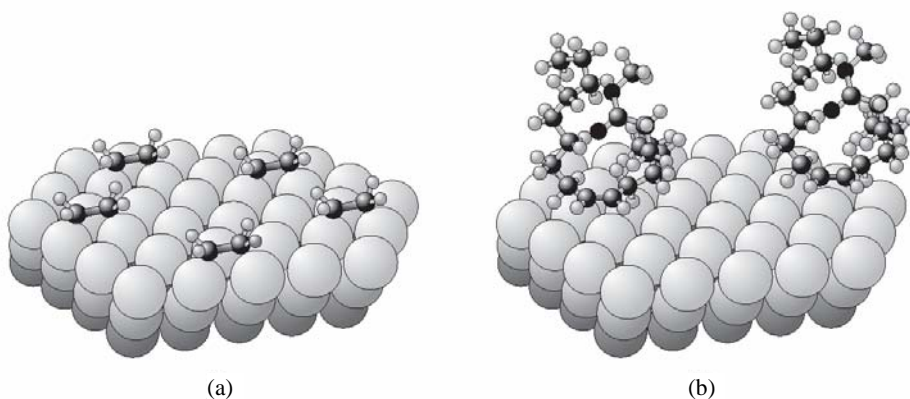

(a)   (b)

Figure 1. Artist's view of adsorption of small and large molecules on Ni(111): (a) ethylene; (b) *cis*-methyl oleate.

$$[1+(K_H C_H)^{1/n}]\Theta_\otimes + x_A K_A C_A (\Theta_\otimes)^{x_A}$$
$$+ x_S K_S C_S (\Theta_\otimes)^{x_S} = 1 \qquad (23)$$

which describes a full competition of all the species for the $\otimes$ vacant sites, and it has to be implicitly solved for $\Theta_\otimes$ since the values of x_A and x_S have to be estimated by data fitting. It should be recognized that unlike the classical competitive adsorption model in which x represents the number of surface sites interacting with the double bond being adsorbed (e.g., 1 for π-adsorption or 2 for 2σ-adsorption), here x_A and x_S stand for the number of $\otimes$ sites effectively occupied by the adsorbed organic molecules.

This approach proved to be useful to explain kinetic regularities in asymmetric hydrogenation over modified metal catalysts. Indeed, it has been successfully applied in deriving advanced kinetic models explaining enantio- and regio-selective effects in the hydrogenation of 1-phenyl-1,2-propanedione over the cinchonidine-modified Pt/Al$_2$O$_3$ catalyst [87], the multicentered adsorption concept being also applied to the larger modifier molecule of cinchonidine. It is remarkable that classical LHHW models were found to be unable to provide a good description of the changes in the regio- and enantioselectivity produced by varying the modifier concentration.

4.2. Kinetic models based upon semi-competitive adsorption

Keeping in mind that in the presence of large organic molecules there is always a fraction of the total surface sites being accessible for non-competitive adsorption of hydrogen molecules, the concept of semi-competitive adsorption has been proposed by Salmi and Murzin [85-88]. Thus, the semi-competitive adsorption model accounts for the fact that the true competition regime probably lies between the competitive and non-competitive extremes. Some attempts of hydrogenation kinetic modeling based on this concept are summarized in Table 2. Two similar approaches have been put forward to derive the hydrogenation rate equations in this framework. Both approaches are reviewed below.

4.2.a. Approach I

The pioneering approach proposing semi-competitive adsorption is based on the inference that complex organic molecules can only occupy a fraction α of the total surface sites. The concept is illustrated in Fig. 2. The site balances comprising all of the adsorbed species can been written as [85]

$$\Theta_\oplus + (K_H C_H)^{1/n}\Theta_\oplus + x[\Theta_A + \Theta_S] = \alpha \qquad (24)$$

$$\Theta_\otimes = \Theta_\oplus + x[\Theta_A + \Theta_S](1-\alpha) \qquad (25)$$

$$\Theta_\otimes + (K_H C_H)^{1/n}\Theta_\otimes + x[\Theta_A + \Theta_S] = 1 \qquad (26)$$

where $\oplus$ and $\otimes$ denote the vacant sites for the adsorption of organic compounds and hydrogen, respectively. The characteristic feature is parameter α, which is equal to 1 for the classical competitive adsorption model, and less than 1 for the semi-competitive adsorption model.

Explicit equations describing coverages of $\oplus$ and $\otimes$ vacant sites can only be obtained for $x = 1$. Calculations for this case give

$$\Theta_\otimes = \frac{1+(1-\alpha)(K_A C_A + K_S C_S)}{D} \qquad (27)$$

$$\Theta_\oplus = \frac{1}{D} \qquad (28)$$

where

$$D = [1+(K_H C_H)^{1/n}][1+(1-\alpha)(K_A C_A + K_S C_S)]$$
$$+ K_A C_A + K_S C_S \qquad (29)$$

It should be stressed that α is an additional adjustable parameter having a value between 1 and 0 if semi-competitive adsorption takes place.
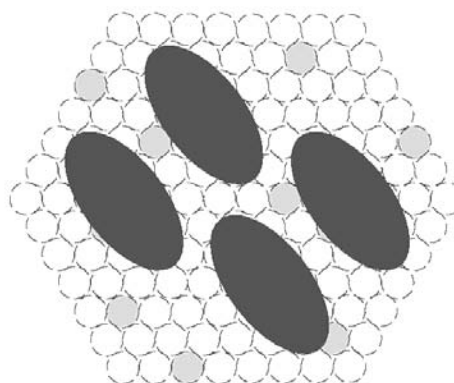

Figure 2. Schematic representation of the surface sites occupied by hydrogen adsorption on interstitial sites remaining between large organic molecules adsorbed on Ni(111).

Two asymptotic cases can be examined for α approaching the extreme values of 1 and 0.

- For $\alpha = 1$, Eqs. (27)-(29) reduce to the following relationship

$$\Theta_\otimes = \Theta_\oplus = \frac{1}{1 + K_A C_A + K_S C_S + (K_H C_H)^{1/n}} \qquad (30)$$

which is exactly the equation governing the full competition between hydrogen and organic compounds. In this approach, the classical LHHW competitive model is then just an asymptotic case of the semi-competitive model.

- For $\alpha \to 0$, it would be expectable that the resulting equations approach those characterizing the LHHW non-competitive model. However, the resulting asymptotic expressions describing the hydrogenation rate do not exactly match those of the classical model, such as Eqs. (17) and (18).

This approach has been successfully applied to derive kinetic models describing the hydrogenation of aldehydes over Raney nickel, more precisely, the reduction of the carbonyl group of xylose to obtain xylitol [86]. It has also been applied to the kinetic modeling of the *o*-xylene hydrogenation over Pd/Al$_2$O$_3$ [85]. Besides explaining the main kinetic regularities, one remarkable finding is the additional indication that the adsorbed molecule of *o*-xylene could cover up to seven surface sites, in agreement with calculations from molecular modeling, and also with our rough representation shown in Fig. 3.

4.2.b. Approach II

Admitting a distinction between occupied-sites and covered-sites by large molecules of organic compounds to be hydrogenated, a rigorous proposal has recently been made to link the classical LHHW kinetic models describing the extreme modes of competitive and non-competitive adsorption, without having to draw the common distinction between two types of surface sites [84]. A semi-competitive model has arisen naturally. It has been assumed that the large organic molecule can additionally cover $s \otimes$ sites closely adjacent to the $x \otimes$ sites on which it is justly adsorbed. Concisely, it has been proposed that an organic molecule covers $(x + s) \otimes$ sites. The $s \otimes$ sites are inaccessible for the adsorption of another organic molecule due to steric hindrance, but they are available for hydrogen adsorption. The concept is illustrated in Fig. 4.

Thus, the coverages of the adsorbed species can be expressed as

$$\Theta_A = K_A C_A (\Theta_\otimes^U)^x \qquad (31)$$

$$\Theta_S = K_S C_S (\Theta_\otimes^U)^x \qquad (32)$$

$$\Theta_{H_{2/n}} = (K_H C_H)^{1/n} \Theta_\otimes \qquad (33)$$

where superscript U denotes uncovered by the organic molecules. It should be noted that the existence of a unique type of active sites has been assumed, indicated as $\otimes$ site, $\Theta_\otimes$ being the surface
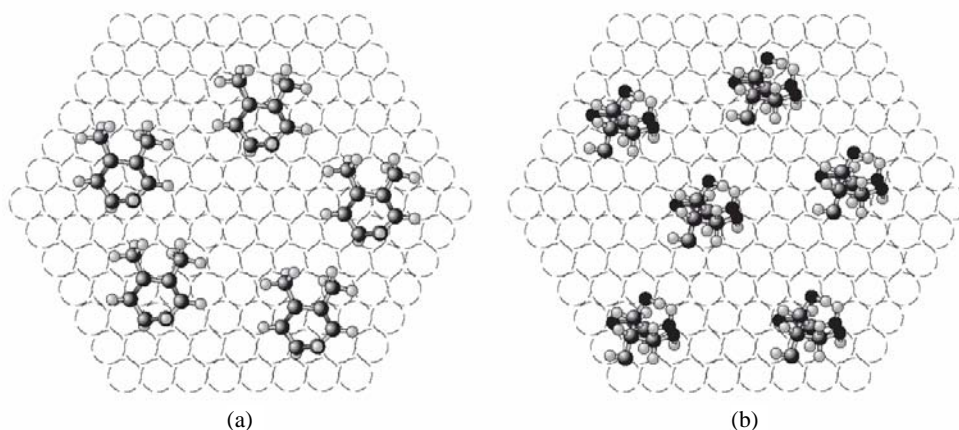

Figure 3. Rough representation of adsorbed organic molecules on Ni(111). The centers of the double bonds have been arbitrarily placed on the top of Ni atoms: (a) *o*-xylene; (b) xylose.
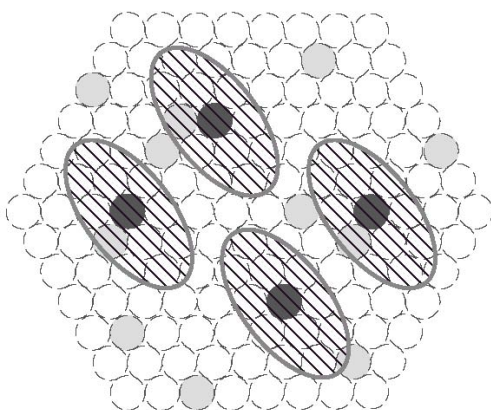
Figure 4. Schematic representation of occupied-sites (shaded regions) and covered-sites (dashed regions) by adsorbed hydrogen and larger organic molecules. Note that hydrogen could also adsorbs on surface sites available under the large organic molecules.

coverage of $\otimes$ vacant sites and $\Theta_\otimes^U$ the fraction remaining uncovered between the adsorbed organic molecules. Then, there are two forms of expressing the site balance equation

$$\Theta_\otimes + \Theta_{H_{2/n}} + x[\Theta_A + \Theta_S] = 1 \tag{34}$$

$$\Theta_\otimes^U + \Theta_{H_{2/n}}^U + (x+s)[\Theta_A + \Theta_S] = 1 \tag{35}$$

where Eq. (34) establishes the relationship to be fulfilled at the catalyst surface, and Eq. (35) accounts for the site inventory as observed from a top view as depicted in Fig. 4.

Defining a parameter f as the ratio between the occupied-sites and covered-sites,

$$f = \frac{x}{(x+s)} \tag{36}$$

and after some algebra, the site balance equation can be finally written as

$$x[K_A C_A + K_S C_S](\Theta_\otimes^U)^x + f[1+(K_H C_H)^{1/n}]\Theta_\otimes^U = f \tag{37}$$

which establishes that the maximum surface coverage of adsorbed organic compounds can only be the fraction f of the total $\otimes$ vacant sites. This equation also governs the coverage of $\otimes$ sites effectively available for the adsorption of the organic molecules. The mathematical model has been completed by the following equation

$$\Theta_\otimes = \frac{1 - f\{1 - [1+(K_H C_H)^{1/n}]\Theta_\otimes^U\}}{1+(K_H C_H)^{1/n}} \tag{38}$$

which establishes the relationship between the uncovered surface coverage of $\otimes$ sites and the overall surface coverage of $\otimes$ vacant sites.

Eqs. (37) and (38) have been found suitable to describe the surface site balance because the classical equations for competitive and non-competitive adsorption can be directly derived as asymptotic cases for f equal to 1 and nearly 0, respectively. This feature is clearly observable for $x = 1$ since explicit equation rates are feasible of being obtained for this case, as described below.

- For $f = 1$ ($s = 0$), there is a one-to-one correspondence between occupied-sites and covered-sites by the adsorbed species, as expected for small molecules. Solving Eqs. (37) and (38) for this case, it yields

$$\begin{aligned}\Theta_\otimes^U &= \Theta_\otimes \\ &= \frac{1}{[1+(K_H C_H)^{1/n} + K_A C_A + K_S C_S]}\end{aligned} \tag{39}$$

and, using this result, the hydrogenation rate equations become as follows

- For 1st H-addition as RDS (step C3)

$$\Omega_A = \frac{k_{SH}(K_H C_H)^{1/n} K_A C_A}{[1+(K_H C_H)^{1/n} + K_A C_A + K_S C_S]^2} \tag{40}$$

- For 2nd H-addition as RDS (step C4)

$$\Omega_A = \frac{k_1 K_{SH}(K_H C_H)^{2/n} K_A C_A}{[1+(K_H C_H)^{1/n} + K_A C_A + K_S C_S]^3} \tag{41}$$

which are those describing the classical LHHW competitive model, as compared to Eqs. (8) and (9).

- For $f \to 0$ ($s \gg x$), the covered-sites are much more than those occupied-sites by the organic, as expected for molecules much larger than hydrogen. Solving Eqs. (37) and (38) for this case, it yields

$$\Theta_\otimes^U = \frac{f}{K_A C_A + K_S C_S} \tag{42}$$

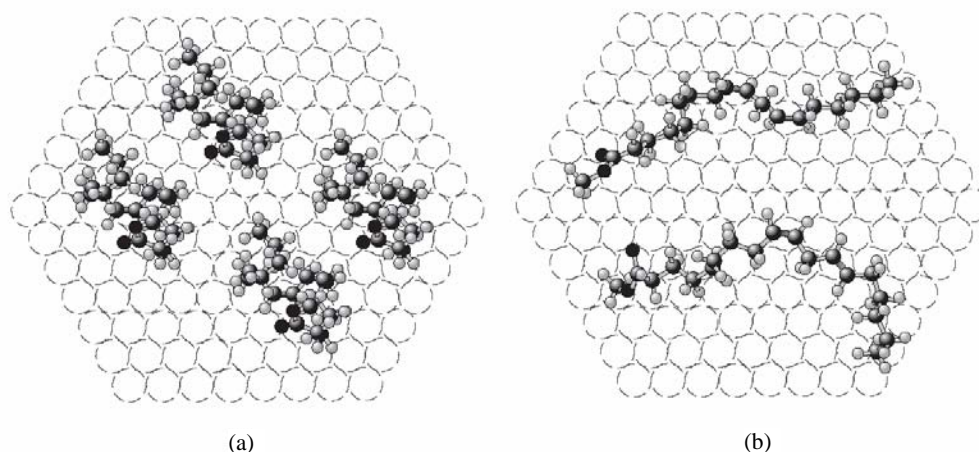$$\Theta_\otimes = \frac{1}{1+(K_H C_H)^{1/n}} \tag{43}$$

Figure 5. Artist's view of adsorption of fatty acid methyl esters on Ni(111). The centers of the double bonds have been arbitrarily placed on the top of Ni atoms: (a) single bounded *cis*-methyl oleate; (b) double bonded *cis*, *cis*- and, *cis*, *trans*- methyl linoleate.

and, therefore, the hydrogenation rate equations become as follows

- For 1st H-addition as RDS (step C3)

$$\Omega_A = \frac{k_{SH}(K_H C_H)^{1/n} f\, K_A C_A}{[1+(K_H C_H)^{1/n}][K_A C_A + K_S C_S]} \qquad (44)$$

- For 2nd H-addition as RDS (step C4)

$$\Omega_A = \frac{k_1 K_{SH}(K_H C_H)^{2/n} f\, K_A C_A}{[1+(K_H C_H)^{1/n}]^2 [K_A C_A + K_S C_S]} \qquad (45)$$

which are in agreement with the non-competitive LHHW model. As a distinctive feature, the denominator term describing the competition between the organic compounds differs from that of classical Eqs. (17) and (18). The absence of summand 1 in this term appears to be reasonable because the competition between the organic compounds is only for fraction *f* of the ⊗ vacant sites, which for this asymptotic case approaches value 0.

Therefore, by varying parameter *f*, this approach allowed matching in a continuous form the extreme competitive and non-competitive models. The usefulness of this approach has been illustrated for the kinetic modeling of the liquid-phase hydrogenation of the methyl oleate and methyl linoleate over a Ni/Al$_2$O$_3$ catalyst [84, 85]. From these studies, the model considering semi-competitive adsorption gave additional indication

of the fact that the adsorbed molecule of methyl oleate could cover up to seven surface sites, while that of methyl linoleate, up to twelve surface sites. These values are in agreement with those estimates using the AM1 method. This is schematically depicted in Fig. 5. Although the competitive and semi-competitive models were found to be statistically indistinguishable, these findings consequently indicate that the semi-competitive model seems to be more realistic that the classic LHHW models.

5. CONCLUDING REMARKS

Without any doubts, there is a growing tendency to use catalytic methods for the synthesis and production of multifunctional fine chemical products involving large molecular size. Heterogeneous catalytic hydrogenation is the historically leading method and, it is not surprising that much attention has been focused on a better mechanistic understanding and a more reliable kinetic modeling for reactor design. Accordingly, the methods for obtaining kinetic information about catalytic hydrogenation processes are becoming highly sophisticated. A review of all related issues appears to be a very pretentious task; therefore, the focus of this brief review was only restricted to some aspects of the mathematical kinetic modeling in the framework provided by the LHHW formalism.

Despite the vast information regarding some limitations of a Langmuir approach in treating surface mediated catalytic reactions, LHHW kinetic models have been usually preferred and successfully used for purposes of kinetic and reactor modeling because they generally provide good data fitting. This contribution looked at this issue from the viewpoint of analyzing limitations and abilities of both classical and advanced approaches for kinetic modeling recognizing the differences between the molecular sizes of hydrogen and organic compounds.

The classical LHHW kinetics featuring competitive adsorption between hydrogen and organic molecules neglect molecular sizes, i.e., the likely multicentered nature of the adsorbed organic molecules has been deliberately ignored. On the other hand, the classical LHHW kinetics based on non-competitive adsorption has been formalized assuming the existence of two types of surface sites for explaining the independent adsorption of small hydrogen and larger organic molecules. As expected, the first approach proved to be appropriate for the modeling of hydrogenation systems involving organic compounds of small molecular size, while the second one for larger organic molecules. Nevertheless, in most practical cases, the second approach would be an ambiguous formulation reflecting a fundamental incompleteness which emerges from the use of two uncoupled balances of sites, one for the adsorbed organic compounds and another for the adsorbed hydrogen. The multicentered adsorption model based on the premise that the adsorbed organic molecule could occupy several surface sites adjacent to that (or those) interacting with the double bond being adsorbed has been a primary improved approach to avoid the above mentioned weakness of the classical LHHW kinetic models. However, it is unable to account for the fact that between the large organic molecules there is always a fraction of the total surface sites being accessible for the non-competitive adsorption of hydrogen. This feature has more recently been explained by more advanced kinetic models featuring semi-competitive adsorption, which also describe the extreme adsorption models as asymptotic cases. 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, by factual. These stimulating results would encourage further studies, especially on the examination of the robustness of these recent approaches for analyzing different heterogeneous catalytic hydrogenation systems for organic synthesis in vapor and liquid phases.

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