Liquid phase hydrogenation of citral and intermediaries over Ir/TiO$_2$/SiO$_2$ catalysts: Kinetic study

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Abstract

Kinetics of the hydrogenation of citral and its intermediaries over Ir/TiO$_2$/SiO$_2$ catalysts has been studied. The effect of various parameters such as the initial concentration, H$_2$ pressure partial, temperature and weight of catalyst were examined. A high selectivity towards unsaturated alcohols using this catalyst was demonstrated. The initial rates increased linearly with the catalyst weight. The reaction rate obeys a kinetics represented by the Langmuir–Hinshelwood model. A single site model suggesting the surface reaction as the rate determining step provided the best fit of the experimental data for the hydrogenation of citral and alcohols (geraniol, nerol and citronellol), while a dual site represent the best kinetics for the hydrogenation of citronellal.
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1. Introduction

The kinetic studies reveal the relative adsorption strength between reactant and different products. The usual reaction kinetic model, such as Langmuir–Hinshelwood (L–H) is used for these studies, but it is evident that if the reaction is structure sensitive (activity and selectivity dependent of the particle sizes or surface-active) can change the reaction mechanism [1]. Not only activity, but also selectivity depends on the reaction parameters, for instance the product selectivity can vary with different initial reactant concentrations. The reactant structure and the nature of the support can affect the reaction order with respect to the reactant. Thus, the strong metal support interaction (SMSI) effect has a large impact on the reaction kinetics hydrogenation [2].

Hydrogenation reactions of α,β-unsaturated aldehydes to their corresponding unsaturated alcohol are a class of reactions that posses a high value in the fine chemistry. The main difficulty is to hydrogenate selectively the carbonyl group, keeping intact the C=C double bond, which is easily hydrogenated over most conventional catalysts to give saturated aldehydes as the primary products [3,4]. It is well known that supports able to produce the effect SMSI generate an important enhancement in the activity for the hydrogenation of C=O group, when are submitted at high temperature reduction (HTR: 773 K). Reyes et al. [5,6] found a marked shift in activity for the hydrogenation of C=O group of citral over Ir/TiO$_2$ and Ir/TiO$_2$/SiO$_2$ HTR catalysts. The reduction at high temperature leads to a surface decoration of the iridium metal crystallites by TiO$_x$ species, contributing to the polarization of the carbonyl group, C=O, and they make easier the hydrogenation of citral to produce corresponding unsaturated alcohols: geraniol and nerol.

It has been showed that often, reaction order with respect to the substrate is zero for the unsaturated molecules; in agreement to Langmuir–Hinshelwood kinetic law [7]. Singh and Vannice [2] in the hydrogenation of citral over Pt/TiO$_2$–HTR catalysts have found a negative first-order and near zero-kinetic order for the initial rate of citral hydrogenation catalysts with respect to citral concentration and hydrogen pressure, respectively. Conversely, the kinetics of liquid phase hydrogenation of citral showed for Reyes et al; displayed a negative near second-order dependence on citral concentration and near first-order depen-

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dence on hydrogen pressure; the reaction kinetics was described by a conventional Langmuir–Hinshelwood treatment [5]. Tianen et al. [8] formulate the kinetic of citral hydrogenation on a Ni/Al$_2$O$_3$ catalyst, under the conditions studied; being citronellol the primary reaction product, but the extent of formation of this unsaturated alcohol was lower. A model involving competitive and fast adsorption steps as well as rate-determining hydrogenation steps was proposed. Yilmaz et al. [9] have studied the kinetics of citral hydrogenation over Pd supported on clinoptilolite rich natural zeolite. This support did not favor the production of the unsaturated alcohol, being citronellal the principal product, close to 90% at complete conversion of citral.

The experimental reaction order with respect to hydrogen pressure gives information for proposing a kinetic model. The reaction order with respect to hydrogen in hydrogenation reaction is often close to one for citral [7], cinnamaldehyde [10] and acetophenone [11] hydrogenation, which indicates weakly bonded hydrogen on the metal surface. Zero-order dependence on the initial reactant concentration was observed for cinnamaldehyde hydrogenation over Pt/SiO$_2$ catalyst in ethanol at 50 °C and 2.9 MPa hydrogen [12]. Slightly negative order close to zero was observed in citral hydrogenation in hexane over several monometallic Pt catalysts supported on SiO$_2$ or TiO$_2$ [1], whereas the reaction order over Pt/TiO$_2$ catalyst with respect to citral was 0.9, it is consistent with a kinetic equation including the CO surface coverage [7]. Carbon monoxide originated from the decarbonylation reaction, inhibits the hydrogenation reaction. It has been reported that the selectivity to unsaturated alcohols change with the initial concentration of the reactant. Thus, in cinnamaldehyde hydrogenation over Pt/SiO$_2$ in ethanol at 50 °C and 2.9 MPa of hydrogen [10] and over Pt/C monolith in toluene at 30 °C and 5 MPa, where selectivity to cinnamyl alcohol increases in parallel to an increase in the initial concentration of cinnamaldehyde. This effect might be explained by different adsorption mode of cinnamaldehyde at higher initial reactant concentrations namely the self-assembling of the aromatic ring preferring the end-on adsorption.

Taking in account that the supported oxides TiO$_2$/SiO$_2$ has been used as catalysts and supports for different reactions [6,13] because this system are very promising for metal catalyst preparations and investigation of various aspects of SMSI effect, because at low concentration Ti ions may be considered as isolated and immobilized in the SiO$_2$ matrix [14]. One method for dispersing titania on oxide supports is via grafting, that involve the reaction of hydroxyl groups on a silica surface with metal precursors such as titanium alkoxide [6,15,16]. However, in supported metals on these oxides, the SMSI effect only has been observed with high titanium content and a well-defined anatase crystalline phase [16]. This behavior also was found for Ir/TiO$_2$/SiO$_2$ catalysts [6] with the advantage of the high surface area titania, which is desirable to disperse the metal and increase their activity. The aim of this work is to describe the kinetics for these catalysts in hydrogenation reactions of citral, geraniol, nerol, citronellal and citronellol using the Langmuir–Hinshelwood treatment. The effect of citral concentration was studied in the concentration range from 0.025 to 0.1 M; hydrogen partial pressure in the range from 0.20 to

0.62 MPa; reaction temperature between 323 and 363 K; and the catalyst weight, ranged from 0.1 to 0.3 g.

2. Experimental

2.1. Synthesis and characterization of Ir/TiO$_2$/SiO$_2$ (Ir/G)

Titanium isopropoxide (Aldrich, reagent grade) was dispersed in toluene (150 mL) and added on aerosil silica (Syloid-266-Grace Davidson) which was activated at 423 K under vacuum. The resultant mixture was stirred for 16 h under inert atmosphere at solvent reflux temperature. Then, the modified silica was filtered, washed with toluene, ethyl ether and deionized water. The resulting solid was dried for 5 h under vacuum at 423 K. The same procedure was repeated with the obtained sample to produce a Ti enrichment. Thus, after three cycles a TiO$_2$ loading of 24 wt.% was achieved. This solid was impregnated with an aqueous solution of H$_2$IrCl$_6$ to give an Ir loading of 1 wt.%. The impregnated solids were dried at 343 K for 6 h, calcined in air at 673 K during 4 h and reduced at 773 K (HTR) for 2 h, to get Ir/TiO$_2$/SiO$_2$ HTR catalysts.

2.2. Characterization

Nitrogen adorption at 77 K and hydrogen chemisorption at 298 K were carried out in a Micromeritic ASAP 2010 apparatus. Particles size was determined by TEM micrographs obtained in JEOL Model JEM-1200 EXII.

2.3. Activity measurements

The citral used in the present study was provided by Merck (>98%, mixture of *E*- and *Z*-isomers having a molar ratio 65:35). Reactions were conducted in a batch reactor at a constant stirring rate (1000 rpm) batch. To carry out the kinetic study over the catalysts (Ir/TiO$_2$/SiO$_2$ HTR) only one variable was modified in each experiment, keeping constant all the others variables. The effect of citral concentration was studied in the concentration range from 0.025 to 0.1 M in heptanes (Fluka >99%); hydrogen partial pressure in the range from 0.20 to 0.62 MPa; reaction temperature between 323 and 363 K; the catalyst weight, ranged from 0.1 to 0.3 g. In all the reactions, internal diffusion limitations were also shown to be absent by applying the Weisz–Prater parameter, which gave a maximum value of 0.18 [17]. Therefore, all these results indicate the absence of any transport limitations from the kinetic data included in this paper. The absence of oxygen was assured by flowing He through the solution, as well as when the reactor was loaded with the catalyst and reactants at atmospheric pressure during 30 min. Prior the experiment, all catalysts were reduced *in situ* under hydrogen flow of 20 cm^3 min^{-1} at atmospheric pressure and temperature of 363 K. Blank experiments showed no catalytic activity due to the supports under these conditions. Reaction products were analyzed in a GC-Varian 3400 furnished with an HP Wax column of 30 m and 0.53 mm I.D. The GC analysis was performed using a flame ionization detector, using He as carrier, and the column was kept at a constant temperature, 393 K. Under these analytical condi-

Table 1
Characterization results of Ir/TiO$_2$/SiO$_2$ catalyst

% de TiO$_2$	24
S_{BET} (m^2 g^{-1})	253
d_{TEM} (nm)	1.3
H/Ir$_{Quim}$	0.017

tions, the retention time of the reported reactants and products were: citronellal, 15 min; citral (*E*), 21.2 min; citral (*Z*), 23.7; nerol, 31.2 min; geraniol, 36.5 min; citronellol, 33.5 min.

3. Results and discussion

3.1. Characterization

Table 1 summarizes the characteristics of the catalyst studied. The TEM micrographs showed a narrow metal particle size distribution being the average crystal size of 1.3 nm. On the other hand, H$_2$ chemisorption revealed a H/Ir ratio of 0.017 indicative of a substantial coverage of the metallic particles by partially reduced species of the support, due to the SMSI effect as has been reported previously [6].

Catalytic studies were performed in a batch reactor using under standard condition at 363 K and 0.2 g of catalysts meanwhile either the concentration of substrate or the hydrogen pressure were varied.

3.2. Effect of the initial concentration of citral and intermediaries

The effect of concentration citral on the rate was examined by using four different concentrations of citral (0.025, 0.050, 0.075 and 0.1 M). Fig. 1 displays typical concentration–time plot of citral hydrogenation over the catalyst studied at constant hydrogen pressure (0.62 MPa), temperature (363 K) and weight of catalyst (0.2 g). It can be seen that the main products in citral hydrogenation over Ir/TiO$_2$/SiO$_2$ catalysts were geraniol and nerol which corresponding to the hydrogenation products of the carbonyl function, and in minor extension, citronellal and citronellol. For citral hydrogenation, the selectivity to any product does not change with the reaction time. The catalyst keeps the
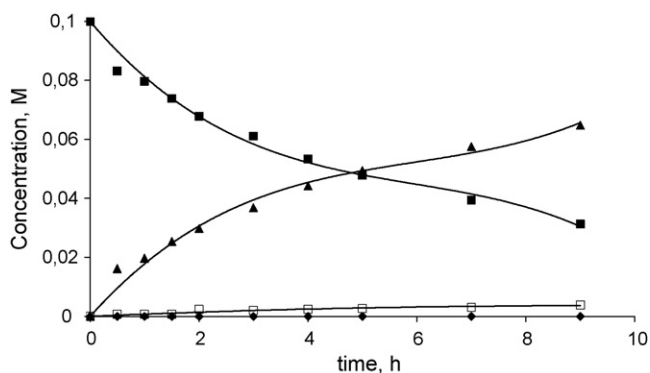

Fig. 1. Citral conversion as a function of time over Ir/TiO$_2$/SiO$_2$ catalysts: (■) citral; (▲) geraniol + nerol; (◆) citronellal; (□) citronellol.
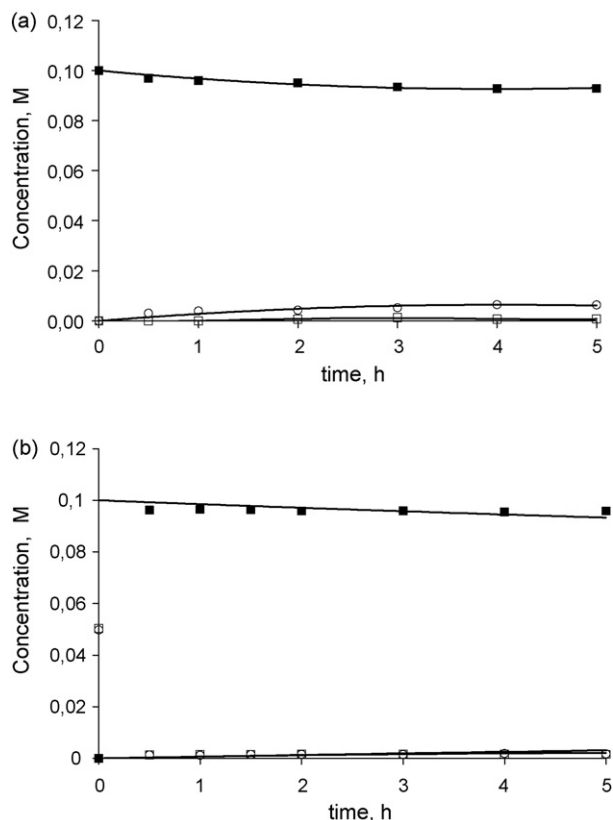

Fig. 2. Unsaturated alcohol conversion as a function of time over Ir/TiO$_2$/SiO$_2$ catalysts: (■) (a) geraniol and (b) nerol; (○) citronellol; (□) others (*cis*-3,7-dimethyl-2-octenol + 3,7 dimethyl-octane).

high selectivity towards the unsaturated alcohol. This is facilitated by the enhanced reaction rate to the formation of geraniol over Ir/TiO$_2$/SiO$_2$ (HT) that inhibits secondary reactions leading to citronellol and citronellal which may be a consequence of an alteration in competitive adsorption which prevents the re-adsorption of these molecules.

The hydrogenation of unsaturated alcohols of citral hydrogenation also was studied over the same range of concentrations of 0.025 to 0.01 M. The results of hydrogenation for geraniol (Fig. 2a) demonstrated that the reaction produced only citronellol which is rapidly transformed to 3,7-dimethyl-octanol, especially when the concentration feed of geraniol, is lower; being the selectivity affected by this factor, intrinsically related with adsorption mode of the molecule. For nerol hydrogenation (Fig. 2b) the main products were citronellol and others products such as *cis*-3,7-dimethyl-2-octenol and 3,7 dimethyl-octane, however, these compound traces are produced mainly with the increases in the substrate concentration, indicating that it is possible to hydrogenate the double bond at the position C2 or C7. The formation of citronellal via isomerization of nerol was not observed. This is consistent with the results reported by Singh et al. [18], who observed negligible isomerization of nerol to citronellal.

With regard to the citronellal hydrogenation the main products were isopulegol and citronellol which corresponding to the cyclization of the ring and the hydrogenation of the car-
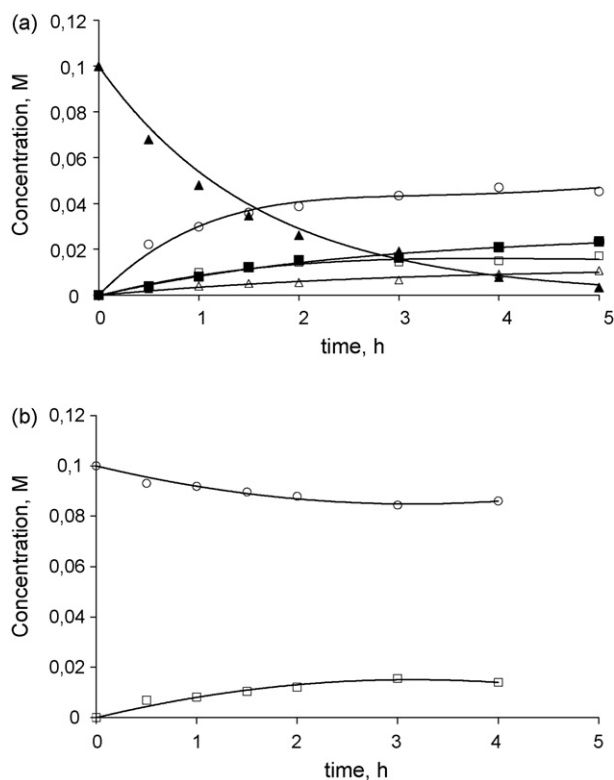
Fig. 3. (a) Citronellal conversion as function of time over Ir/TiO$_2$/SiO$_2$ catalysts: (▲) citronellal; (○) citronellol; (■) isopulegol; (△) 3,7-dimetil-octanal; (□) 3,7 dimethyloctan-1-ol. (b) Citronellol conversion.

bonyl function, respectively (Fig. 3a). Other products such as 3,7-dimethyl-octanal,3,7-dimethyl-octanol were also detected which can be produced as result of incomplete hydrogenation of citronellol. Recent reports [19] have suggested the possibility of citronellal cyclization to isopulegol due to the Brönsted acidity. Fig. 3(b) displays the selectivity during the hydrogenation of citronellol which is very selective for producing mainly 3,7-dimethyl-octanol. A summary of the reactions which take place over Ir/TiO$_2$/SiO$_2$ is displayed in Fig. 4.

An increase in the activity as well as the concentration of the substrate decreases was observed for all molecules (Fig. 5), it is in accordance with LH adsorption kinetics, in which at low concentrations the fractional occupancy of the catalyst surface increases linearly with the concentration and activity of the solutions. At higher reactant concentrations, however, the surface is almost fully occupied and the activity becomes independent of concentration initial of the molecule [20]. However, it can be observed in Fig. 5, that the conversion of geraniol, nerol and citronellol is lower that citronellal and citral, therefore the order of reactivity over Ir/TiO$_2$/SiO$_2$ catalyst is: citronellal > citral > citronellol > nerol > geraniol, which is explained considering that the Ir/TiO$_2$/SiO$_2$ catalyst possesses active sites in which the metallic component exhibits a partial decoration by the creation of Ir$^{\delta+}$ species, and this sites are more actives in the polarization of the C=O bond [6]. The lower catalytic activity and lower final conversion of nerol and geraniol over this catalyst can be explained due to the catalyst also present Ir° sites in a minor proportion.

Because of the complexity associated with catalytic reactions it is convenient that a study of the relative reaction rates be approached in the simplest way. Accordingly, only initial rates were considered in this work. To evaluate the reaction order with respect to the reagent concentration, the reaction rate was expressed as $r_0 = kr(PH_2)^m[R]_0^n$, and working at constant PH_2 in an excess of H_2, the equation can be write as: $r_0 = kr[R]_0^m$. By logarithmic correlation a plot of log r_0 against log $[R]_0$, where $[R]_0$ is the initial substrate concentration were obtained, from the slope at time near zero, and the initial reaction rate (r_0) expressed as (TOF)$_0$ were evaluated (Fig. 6). At initial reaction rates, the dependence of citral concentration is near zero-order indicating a strong adsorption of the molecule on the metallic surface.

The effect of the hydrogen pressure on the hydrogenation activity was studied by varying the partial pressure (0.20 to 0.62 MPa), keeping constant the citral and intermediaries concentration (0.1 M) and the catalyst weight (0.2 g) at a temperature of 363 K. The results are shown in Fig. 7. It can be seen that the activity increases as hydrogen pressure increases. The selectivity was not affected by the pressure changes. After obtaining the initial reaction rate, an appropriate plot, log r_0 versus log hydrogen pressure (Fig. 8), allows obtaining the reaction order with respect to hydrogen. For citral, nerol and geraniol, an experimental order in hydrogen of approximately 0.5 was observed. This value of order implies involves one adsorbed hydrogen atom that it is originated from dissociative adsorption of molecular hydrogen, in accordance with obtained results described for other reactions [5].

3.3. Effect of the weight of catalyst

The effect of the catalyst weight was studied using 0.1, 0.2 and 0.3 g of catalyst, while keeping constant the other experimental conditions. The results indicate an increase in the conversion as the catalyst weight increases (Fig. 9). A linear dependency in the initial reaction rate with the catalyst weight demonstrated that the mass transfer effects does not play a significant role under the used experimental conditions due to behavior observed also the liquid-side mass-transfer coefficient and liquid–solid mass-transfer were minimized by the high turbulence in the liquid phase (agitation to 1000 rpm) and avoid the intraparticle mass-transfer resistance using a small catalyst particles size (<100 μm).

3.4. Kinetic modeling of citral and their hydrogenated products

The hydrogenation of α,β-unsaturated aldehydes is potentially a complex combination of series and parallel reactions, as it has been reported in the literature [1–8]. The results showed for Ir/TiO$_2$/SiO$_2$ catalyst in the citral hydrogenation at high conversion levels and selectivity towards unsaturated alcohols especially due to SMSI effect that present this type of supports [6]. The hydrogenation of unsaturated alcohols was lower, which can be attributed to the fact that Ir$^{\delta+}$ species are less active compared to the metallic Ir^0 sites in the hydrogenation of C=C bond.
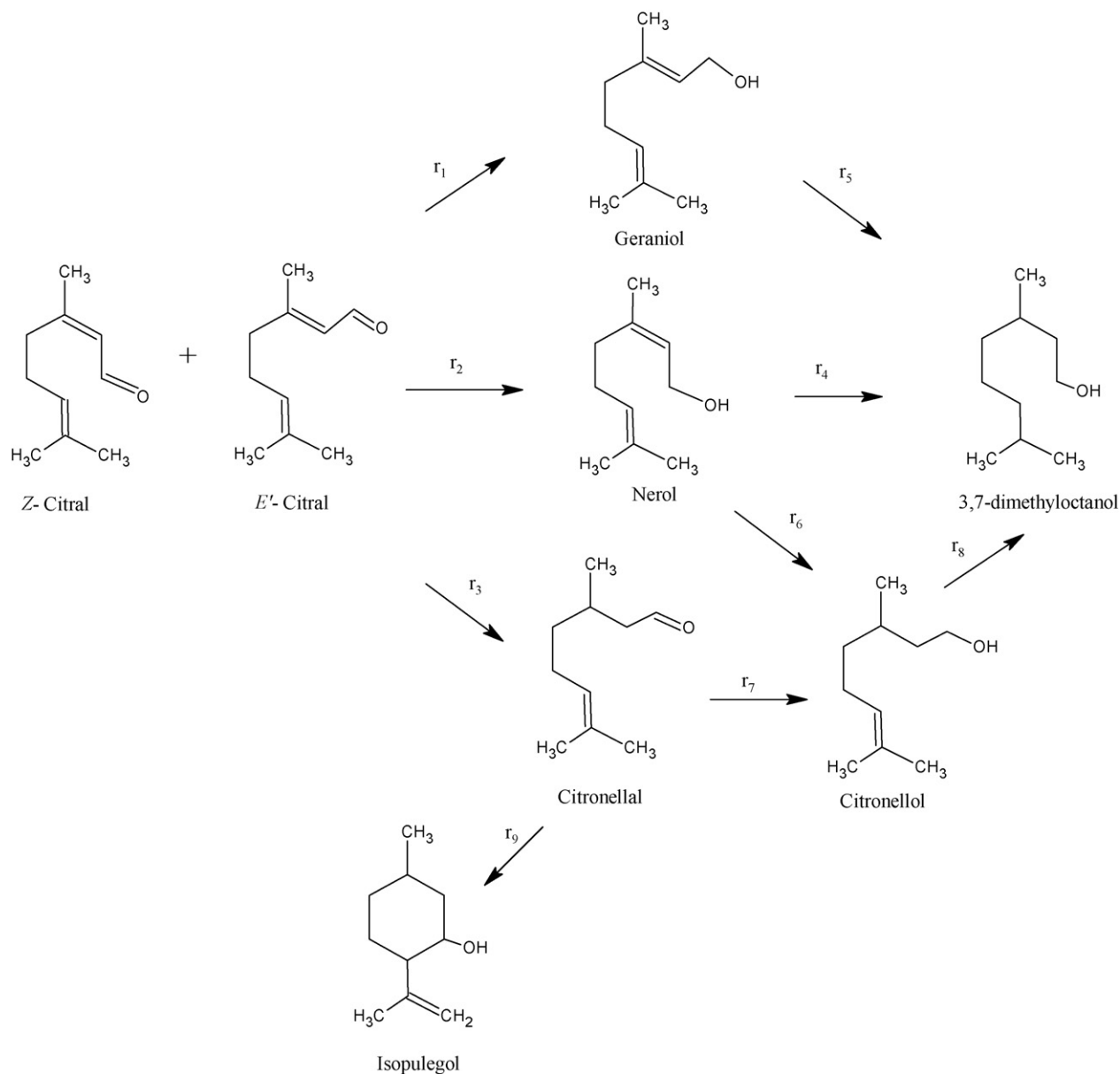
Fig. 4. Reaction network of citral and intermediaries during the hydrogenation reaction.

To explain the results obtained in the citral hydrogenation and their hydrogenated products, two Langmuir–Hinshelwood models were proposed (Table 2); a first mechanism of a single site described by Vannice [1,10,18] with competitive adsorption between hydrogen and the organic compounds, and addition of the second hydrogen atom to each reactant as the rate determining step (RDS). The difference between models I and II is that in model II the reactions occur on different sites with different adsorption parameters.

Where S is an active site and S1 is a second active site in the second mechanism proposed. R is the organic reactant. RH_2 is the hydrogenated product. H-S, R-S, RHS and RH_2S are the adsorbed hydrogen, adsorbed organic species, adsorbed half-hydrogenated organic species and adsorbed product, respectively. In each model it was considered that the hydrogen shows dissociative adsorption, and that hydro-

Table 2
Elementary steps for L–H models of citral hydrogenation and their hydrogenated products

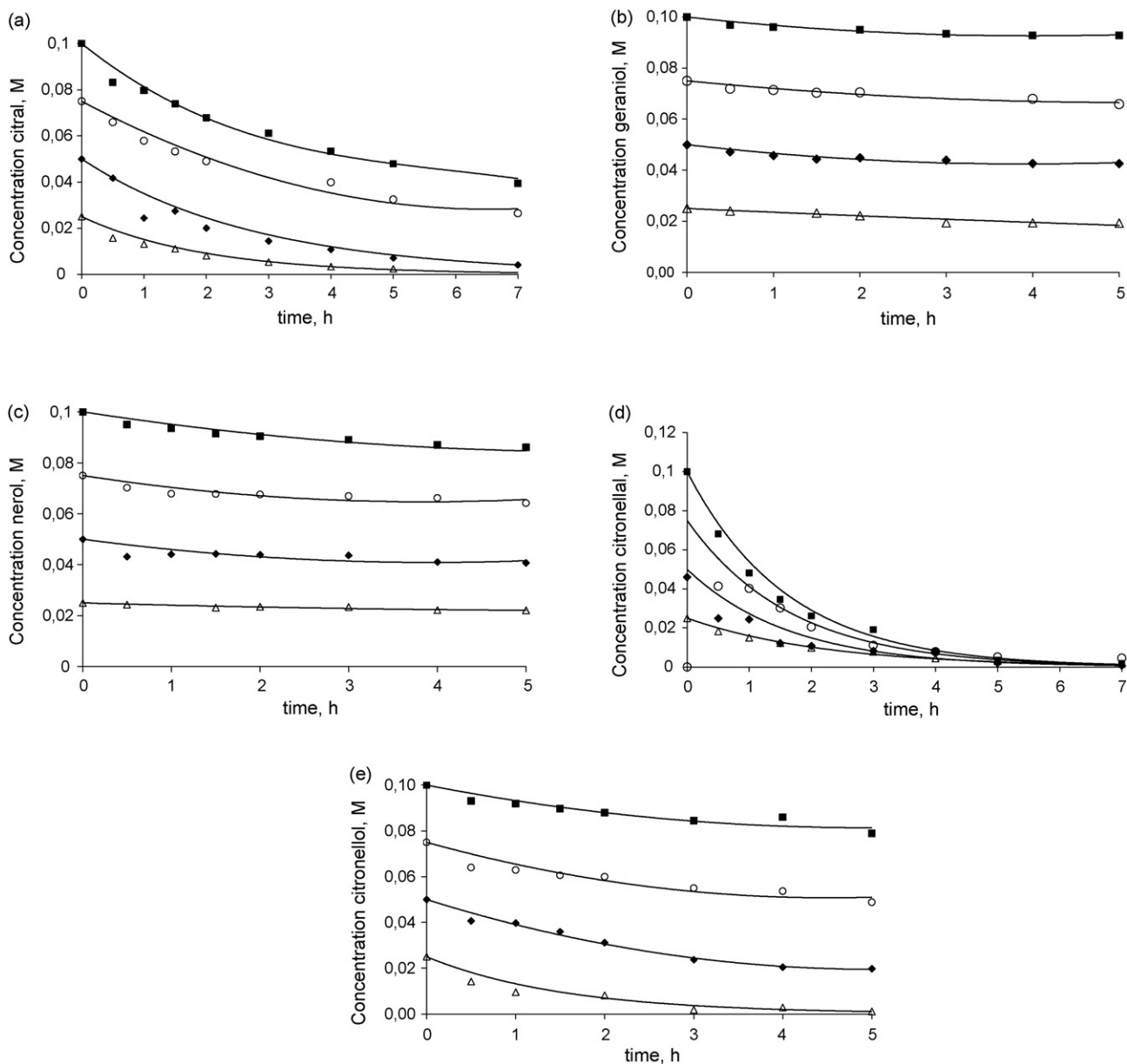| Mechanism I	Mechanism II
$H_2 + 2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2SH$	$H_2 + 2S_1 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2HS_1$
$R + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RS$	$R + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RS$
$RS + HS \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RHS$	$RS + 2HS_1 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RH_2S + 2S_1$
$RHS + HS \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} RH_2S$	$RH_2S \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} RH_2 + S$
$RH_2S \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} RH_2 + S$	

Fig. 5. Effect of the initial concentration on hydrogenation of (a) citral, (b) geraniol, (c) nerol, (d) citronellal and (e) citronellol, as a function of time over $Ir/TiO_2/SiO_2$ catalysts: (■) 0.1 M; (○) 0.075 M; (♦) 0.05 M; (△) 0.025 M.
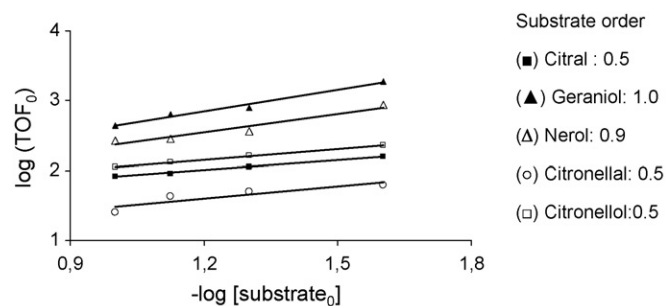

Fig. 6. Hydrogenation of different substrates on $Ir/TiO_2/SiO_2$ catalyst; plot log TOF vs. log (TOF)$_0$. (■) Citral; (▲) geraniol; (△) nerol; (○) citronellal; (□) citronellol.

genation surface reactions are all irreversible, the surfaces reactions were considered as rate determining step, whereas adsorption and desorption were considered to be in quasi-equilibrium.

For citral hydrogenation, the selectivity to any product does not change with the reaction time, which can indicate that hydrogenation of nerol and geraniol to citronellol, are negligible under the citral hydrogenation reaction conditions. Hydrogenation reactions at 363 K showed that addition of the unsaturated alcohols (geraniol and nerol) as well as citronellol to the reaction mixture at the beginning of reaction had no effect on the rate of reaction and for this reason the product term ($\sum K_{RH2} C_{RH2}$) in the denominator in rate expressions was omitted. In agreement of the mechanisms proposed the rate expression can be written as is displayed in Table 3.where Lk is the rate con-
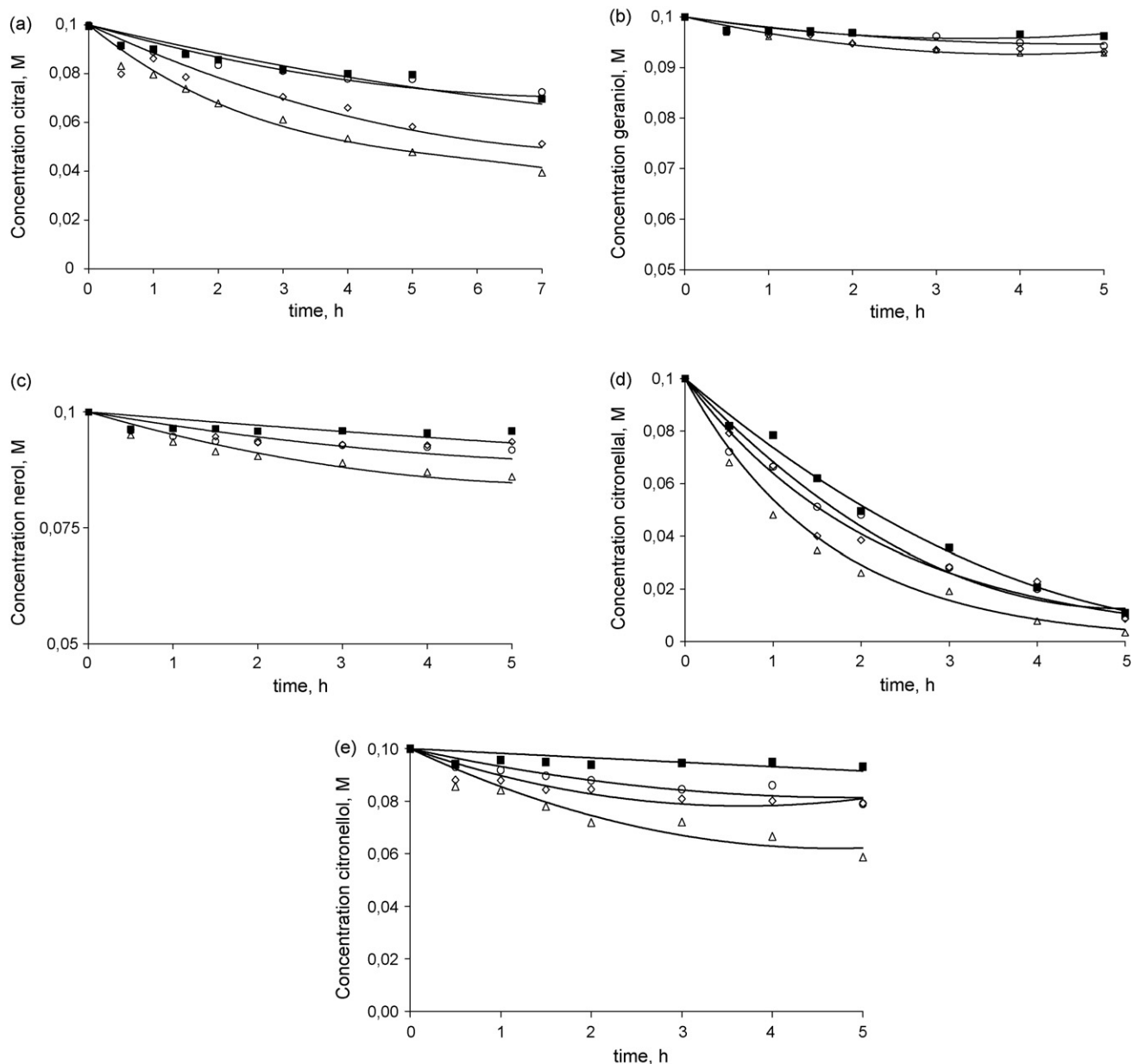
Fig. 7. Effect of hydrogen partial pressure on hydrogenation of (a) citral, (b) nerol, (c) geraniol, (d) citronellal and (e) citronellol, as a function of time over Ir/TiO$_2$/SiO$_2$ catalysts: (■) 0.62 MPa; (○) 0.48 MPa; (◇) 0.34 M; y (△) 0.20 MPa.
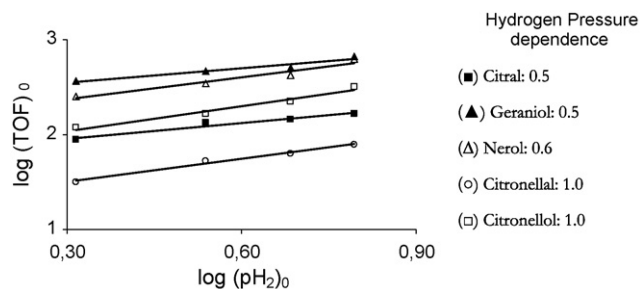

Fig. 8. Effect of hydrogen partial pressure in the hydrogenation reactions over a Ir/TiO$_2$/SiO$_2$ catalyst; plot log (pH$_2$) vs. log (TOF)$_0$.
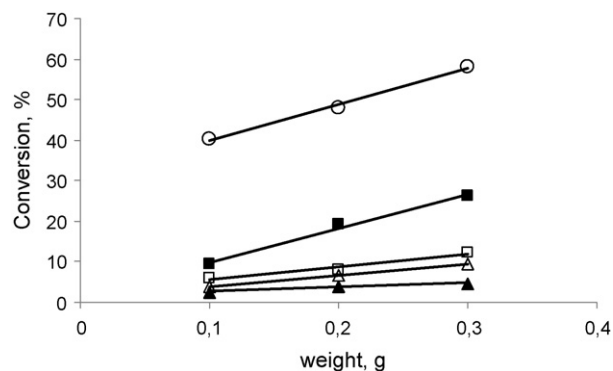

Fig. 9. Effect of the weight of Ir/TiO$_2$/SiO$_2$ catalyst in hydrogenation reactions: (■) citral; (▲) geraniol; (△) nerol; (○) citronellal; (□) citronellol.

Table 3
Rate expressions for the mechanisms proposed

Model I	$r_1 = \dfrac{Lk_{r1} K_{RH} K_{H_2} C_R pH_2}{[1 + K_R C_R + K_{H_2}^{1/2} pH_2]^2}$
Model II	$r_1 = \dfrac{Lk_{r1} K_R K_{H_2} C_R pH_2}{[(1 + K_R C_R)(1 + K_{H_2}^{1/2} pH_2^{1/2})]^2}$

stant for the substrate hydrogenation on the surface and K_R and K_{H_2} are the equilibrium adsorption constants. The values of the rate constants were determined using a non-linear regression program with an iterative Gauss–Newton method of the experimental concentration versus time profiles of the chemical species involved in the reaction. The objective function to be minimized was $RSS = \sum (C^* - C^{calc})^2$ where C^* is the experimental relative concentration, C^{calc} is the relative concentration calculated with the model, at a reaction time with i components.

The estimated parameters of Lk, K_R and K_{H_2} for the different expressions at various temperatures (Table 4) were calculated under the restriction that the three parameters must be positive [21–23]. To evaluate the validity of the rules established by Boudart and Vannice [24,25] the fitting parameters were
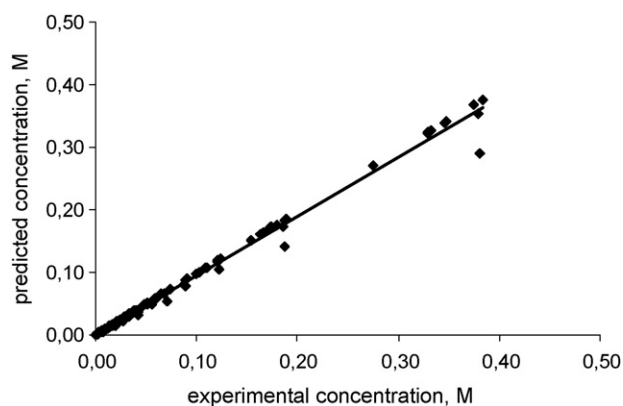

Fig. 10. Comparison of predicted concentrations (model II) with experimental concentrations at various temperatures and reactant concentrations for citral hydrogenation.

considered, consequently the k obtained should follow the order $k_{citronelal} > k_{citral} > k_{citronelol} > k_{geraniol} > k_{nerol}$ for all temperatures studied.

The sum of the residual squares as the variance gives information about the quality of the fit of the models proposed. Thus the comparison of the RSS or the variance indicates for the hydrogenation of citral, geraniol, nerol and citronellol that

Table 4
Optimized rate parameters for the hydrogenation of citral and intermediaries at different temperatures, RSS and variance for the LH model selected

Substrate	Temperature (K)	Lk (μmol min^{-1} g cat^{-1})	K_R (atm^{-1})	K_{H_2} (atm^{-1})	RSS	Variance
Citral model 1	323	1.8	0.48	1.17	3.08×10^{-5}	3.69×10^{-4}
	343	4.9	0.26	0.91	5.78×10^{-6}	7.01×10^{-4}
	353	6.9	0.24	0.38	2.53×10^{-6}	9.64×10^{-4}
	363	10	0.18	0.24	1.01×10^{-6}	1.01×10^{-4}
Citronellal model 2	323	2.6	1.87	0.23	1.55×10^{-5}	9.78×10^{-4}
	343	4.3	1.1	0.17	1.20×10^{-5}	5.45×10^{-4}
	353	6.4	0.67	0.21	4.80×10^{-6}	3.20×10^{-4}
	363	11	0.37	0.18	1.69×10^{-6}	3.34×10^{-4}
Citronellol model 1	323	0.2	0.09	0.99	2.10×10^{-6}	3.45×10^{-6}
	343	0.7	0.06	0.94	5.24×10^{-6}	5.87×10^{-6}
	353	1.2	0.02	0.37	5.81×10^{-6}	3.93×10^{-6}
	363	2.7	0.01	0.2	3.42×10^{-6}	2.33×10^{-6}
Geraniol model 1	323	1.09	0.55	1.84	2.39×10^{-6}	3.26×10^{-4}
	343	1.74	0.4	0.5	7.66×10^{-6}	4.26×10^{-6}
	363	2.13	0.35	0.41	9.49×10^{-6}	5.39×10^{-6}
Nerol model 1	323	0.92	0.51	1.75	1.15×10^{-6}	5.4×10^{-6}
	343	1.18	0.47	1.03	2.16×10^{-6}	2.61×10^{-6}
	363	1.93	0.36	0.47	1.4×10^{-6}	4.9×10^{-6}

Table 5
Thermodynamic parameters for adsorption K_R from expression of model II for different substrates

Substrate (R)	E_{ap} (kcal mol^{-1})	ΔH_R (kcal mol^{-1})	ΔS_R (kcal mol^{-1})	ΔH_{H_2} (kcal mol^{-1})	ΔS_{H_2} (kcal mol^{-1})
Citronellal	8	−9	−26	−11.4	−6.5
Citral	10	−5	−18	−9.4	−28
Geraniol	3.9	−2.6	−9.4	−7.6	−22.4
Nerol	4.2	−20	−7.5	−8.9	−26.5
Citronellol	14	−12	−43	−9.2	−28

mechanism I based on single site gives the best fit to the experimental data. A comparison of the concentrations predicted by this model and the experimentally observed concentrations for citral hydrogenation is shown in Fig. 10. The predicted values are in reasonable agreement with each other. While the model II was considered the best model for representing the hydrogenation of citronellal.

From the kinetic parameters obtained at different temperatures, the activation energy for the rate determining step and the enthalpy and entropy of adsorption for citral and each reactant were determined. These values are listed in Table 5. The enthalpies and entropies of adsorption for citral, citronellal, geraniol, nerol and citronellol were estimated over the range of temperatures studied. The enthalpies of adsorption are negative, as they should be, and the entropies of adsorption are also negative and quantitatively satisfy guidelines established indicating their thermodynamic consistency [21,22]. This does not prove that the reaction mechanisms proposed are correct, but it does show that they are possible and physically consistent.

4. Conclusions

The kinetics of the hydrogenation of citral and intermediaries were described using a Langmuir–Hinshelwood model. A single site model can describe satisfactorily the kinetics for citral hydrogenation as well as the hydrogenation of geraniol, nerol and citronellol. For citronellal the model II with the assumption of dual site gives the best fit to the experimental data. Both models present thermodynamic consistency. Ir/TiO$_2$/SiO$_2$ catalyst possess a high proportion of active sites in which the metallic component exhibits a partial decoration with the creation of Ir$^{\delta+}$ species, which are more active in the polarization of the C=O bond. The lower catalytic activity and lower final conversion in the nerol and geraniol hydrogenation over this catalyst can be attributed to the fact that this catalyst displays a low proportion of Ir$^{\circ}$ sites.

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