

Liquid phase hydrogenation, isomerization and dehydrogenation of limonene and derivatives with supported palladium catalysts

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Abstract

The hydrogenation of limonene, using 5% Pd/C, 5% Pd/Al₂O₃ and 0.5% Pd/Al₂O₃ catalysts, was studied in a stirred slurry minireactor in a temperature range of 273–323 K, at 106.65 kPa of hydrogen pressure. In the absence of extraparticle and intraparticle mass transfer effects, side products, such as terpinolene, γ -terpinene and *p*-cymene, were formed besides *p*-menthene and *p*-menthane. A significant presence of terpinolene and γ -terpinene indicates that an extensive isomerization precedes hydrogenation, while the presence of *p*-cymene shows that a dehydrogenation occurs simultaneously. The virtual absence of intermediates, such as α -phellandrene, β -phellandrene and α -terpinene, can be attributed to the fact that conjugated cyclic dienes are too strongly adsorbed to desorb before reacting further. Possible mechanisms of reaction are discussed: the involvement of π -allyl-adsorbed species explains the isomerization process over palladium, but greater isomerization activity observed for alumina-supported catalysts is explained by mechanisms involving Lewis acid sites provided by the alumina. Two possible pathways for isomerization on alumina are recognized: one of them involves the formation of carbonium ions and the other may comprise double-bond migration via allyl route including carbanions. The results suggest that, over alumina, limonene isomerizes via the π -allylic mechanism, whereas terpinolene and terpinene isomerize via the carbonium ion mechanism. © 1999 Elsevier Science B.V. All rights reserved.

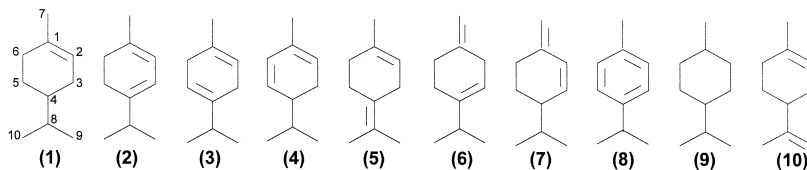
Keywords: Palladium/alumina; Palladium/carbon; Hydrogenation–isomerization–dehydrogenation reactions; Limonene hydrogenation; Reaction schemes

1. Introduction

In order to carry out hydrogenation studies of cyclic olefins, an extensive structural diversity could be found in monoterpenes directly available from more volatile fractions of some essential oils. Several monoterpenes, such as 1-methyl-4-isopropyl-1-cyclohexene or *p*-menthene (**1**), 1-methyl-4-isopropyl-1,3-cyclohexadiene or α -terpinene (**2**), 1-methyl-4-isopropyl-1,4-cyclohexadiene or γ -terpinene (**3**) and 1-methyl-4-isopropyl-1,5-cyclohexadiene or α -phellandrene (**4**), 1-methyl-4-isopropylidene-1-cyclohexene or terpinolene (**5**), 1-methylene-4-isopropyl-3-cyclohexene or β -terpinene (**6**),

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1-methylene-4-isopropyl-2-cyclohexene or β -phellandrene (7), 1-methyl-4-isopropyl-1,3,5-cyclohexatriene or *p*-cymene (8), and 1-methyl-4-isopropyl-cyclohexane or *p*-menthane (9), form a collection of isomers and derivatives of 1-methyl-4-isopropenyl-1-cyclohexene or limonene (10).



After considering the possibility of obtaining endocyclic monoenes (1), endocyclic dienes (2)–(3)–(4), endo-exocyclic dienes (5)–(6)–(7), endocyclic trienes (8), and saturated products (9) from an abundant endo-extracyclic diene as limonene (10), we decided upon the catalytic hydrogenation of limonene using supported palladium as catalyst for such purposes. There are extensive studies related to reaction mechanisms of cyclic olefins over palladium, but no specific reports seem to have been published about the hydrogenation of limonene [1,2]. Therefore, the information about the intrinsic selectivity and reaction schemes of the catalytic hydrogenation of limonene using supported palladium catalysts is scanty, if any.

Accordingly, the present paper attempts to focus on reaction mechanisms of limonene over palladium catalysts, as a way to provide plausible schemes to describe some aspects of the selectivity towards intermediates formed in the liquid-phase reaction with hydrogen, in which isomerization, hydrogenation and dehydrogenation reactions take place simultaneously. To throw some light on the complex mechanism by which these simultaneous reactions proceed, hydrogenations were carried out in a batch slurry reactor using 5% Pd/C, 5% Pd/Al₂O₃ and 0.5% Pd/Al₂O₃ catalysts, in a temperature range of 273–323 K and at 106.65 kPa of hydrogen pressure. Additional objectives were to determine the feasibility of obtaining intermediates, and to analyze the influence of the temperature on the selectivity in the absence of mass transfer limitation.

2. Experimental

Limonene (purity 99%) was isolated from lemon essential oil by fractionated distillation at low pressure, and redistillation at high vacuo in the presence of metallic sodium to remove oxygenated compounds. Hydrogen (UHP grade) was passed through a Deoxo unit and a drying column before use. Commercial 5% Pd/C, 5% Pd/Al₂O₃ and 0.5% Pd/Al₂O₃ powder catalysts were provided by Johnson Matthey. Some significant parameters of the catalysts used in this work are thus given in Table 1. All experiments were carried out using a catalyst loading of 0.2 wt./wt.% with respect to the mass of the liquid phase.

Batch hydrogenations were carried out in a 50-cm³ glass minireactor equipped with hydrogen reservoir, mechanical stirrer and a device for the sampling of slurry during the course of the reaction without stopping the agitation using a septum device. The temperature of reaction mixture was kept within ± 1 K using a heating mantle linked to a temperature PID controller. The typical procedure was as follows: 0.4 g of catalyst and 20 g of limonene were charged into the reactor. After purging with nitrogen, the temperature was increased under nitrogen gas until it reached the required reaction temperature. Nitrogen was then removed and hydrogen gas was introduced. Zero time was taken when the agitation began. Induction periods were not observed in any of the experiments, during

Table 1
Parameters for mass transfer estimations

Property	Pd/C	Pd/Al ₂ O ₃ ^d
Catalyst particle size ^a , m	12.0×10^{-6}	4.5×10^{-6}
Particle density ^a , kg m ⁻³	1.9×10^3	2.1×10^3
Pore volume ^a , m ³ kg ⁻¹	4.0×10^{-4}	4.2×10^{-4}
Porosity ^a	0.75	0.88
Surface area ^a , m ² kg ⁻¹	7.7×10^5	1.9×10^5
Palladium content ^b , %	5.0	0.5 or 5.0
Effective diffusivity of hydrogen ^c , m ² h ⁻¹	9.6×10^{-6}	3.8×10^{-5}
Effective diffusivity of limonene ^c , m ² h ⁻¹	6.4×10^{-7}	2.6×10^{-6}

^aExperimental data from our laboratory.

^bTechnical data from Johnson Matthey.

^cEstimated data from Ref. [3].

^dPhysical properties were quite similar for both 0.5 and 5% Pd/Al₂O₃ power catalysts.

which the hydrogen pressure was maintained constant. Liquid samples were withdrawn at different reaction times and analyzed after removing the catalyst by filtration.

Reaction products were separated by means of preparative GLC. The isolated compounds were identified by NMR analysis which showed the presence of *trans*-menthane, *cis*-menthane, *p*-menthene and *p*-cymene. When compared to authentic spectra, γ -terpinene and terpinolene were identified by GC-MS. The analyses of reaction samples were performed on a gas chromatograph equipped with a 30 m \times 0.53 mm HP-5 Megabore column (phase thickness: 0.88 μ m) and flame ionization detector using nitrogen as carrier gas.

3. Results and discussion

3.1. Mass transfer effects

Special care was taken to ensure that neither intraparticle nor extraparticle mass transfer rates affect the intrinsic kinetics [4–6]. In order to corroborate that gas–liquid and liquid–solid mass transfer resistances were negligible, the initial reaction rates were compared with the maximum rates which are possible at each mass transfer step. Table 1 shows the parameters for mass transfer estimations.

The gas–liquid resistance was evaluated according to the technique reported in a previous work [7]. The values of the hydrogen absorption resistance were found to be less than 5.7×10^{-2} s. Using 1×10^{-5} mol cm⁻³ as a cautious value of hydrogen solubility—the exact value was not available—the ratio between the highest initial reaction rate and the maximum mass transfer rate of hydrogen was less than 0.127. Thus, the experimental values reported for the initial stages of the hydrogenations with 5%Pd/C and 5%Pd/Al₂O₃ at 323 K are slightly affected by the gas absorption resistance. These undesirable effects were found to be almost negligible at 298 K, and completely negligible at 273 K, as consequence of the corresponding decrease of the hydrogenation rate.

Liquid–solid mass transfer coefficients were estimated from a widely used correlation [8]. The liquid–solid mass transfer resistances of hydrogen and limonene were found to be within the ranges 1×10^{-3} and 1×10^{-2} s, respectively. Thus, the values of the ratio between the maximal initial reaction rate and the maximum mass transfer rate ratios were lower than 2.7×10^{-3} and 3.3×10^{-5} , respectively, which indicate the absence of extraparticle mass transfer resistance.

The intraparticle diffusive limitations were estimated from well-known criteria. The overall reaction rate is first-order and zero-order with respect to hydrogen and limonene, respectively. Then, for hydrogen, the Weisz and Prater criterion establishes that $\phi_{\text{H}_2} \ll 1$ in the absence of intraparticle resistance [9]. For limonene, the criterion becomes $\phi_L \ll 2$ [10]. The values of the Weisz and Prater modules were found to be $\phi_{\text{H}_2} \ll 2.9 \times 10^{-3}$ and $\phi_L < 4.5 \times 10^{-4}$, which indicates that the chemical reaction is the rate-limiting step. The value of the critical concentration [11] for which the concentration of limonene drops to zero at some point within the catalyst was also estimated in view of the zero-order with respect to limonene. The critical value was found to be $7.6 \times 10^{-7} \text{ mol cm}^{-3}$ at 323 K. Then, the concentration of limonene does not become zero at any point within the catalyst since the corresponding bulk concentration is greater than the estimated critical value. Furthermore, it was confirmed that Pd/Al₂O₃ catalysts exhibit an intraparticle resistance lower than the one estimated for Pd/C catalysts.

Concluding, it was found that neither gas–liquid resistance, nor liquid–solid resistance or intraparticle diffusion resistance appreciably affected the kinetics of the reactions under the established reaction conditions.

3.2. Product distribution and initial reaction rates on Pd/C catalyst

The presence of limonene, *p*-menthene, *cis-p*-menthane, *trans-p*-menthane, γ -terpinene, terpinolene and *p*-cymene was confirmed by analysis of reaction samples. In some cases, a few additional tiny peaks were noted on the chromatogram. However, due to their very low quantity, they could not be identified, not even by mass spectrometry, so they were neglected. Then, the virtual absence of intermediates, such as α -phellandrene, β -phellandrene and α -terpinene, was assumed. The material balance was consistent up to 98.5% when all the side products were accounted for. The typical concentration profiles from hydrogenations with 5% Pd/C catalyst, at 273 and 323 K, are shown in Fig. 1. If we observe the evolution of the concentration profiles shown in Fig. 1a–f, the following points regarding the trend of individual plots may be highlighted.

(i) As regards limonene, a zero-order reaction takes place up to a conversion of 80–65% limonene (first step). This linear decrease is broken just as the concentration of terpinolene reaches a maximum close to 10% at either temperature. Afterwards, the disappearance rate of terpinolene appears also in zero order until a low concentration of terpinolene is reached (second step). A similar trend is then observed for the γ -terpinene reaction rate (third step). Thus, it seems that a competitive adsorption between non-conjugated cyclic dienes takes place. However, the total absence of any appreciable concentrations of intermediates, such as α -phellandrene, β -phellandrene and α -terpinene in the liquid phase, suggests that the conjugated cyclic dienes are adsorbed much more strongly than the non-conjugated ones. They therefore do not appear in the liquid phase since they cannot desorb before further reaction.

(ii) At the starting period, while the limonene concentration decreases at constant rate, the production of intermediates begins with initial rates decreasing in the order: *p*-menthene > terpinolene > *p*-menthane > γ -terpinene > *p*-cymene, at 273 K, and, terpinolene > *p*-menthene > γ -terpinene > *p*-menthane > *p*-cymene, at 323 K. Thus, an increase of the double bond migration rate compared to the hydrogenation rate is noticeable at higher temperatures.

(iii) Limonene and terpinolene are coupled by a fast isomerization reaction; otherwise, one would not be able to explain their disappearance. The production rate of *p*-menthene and the disappearance rate of limonene are coincidentally broken, and the maximum concentration of *p*-menthene is reached just as limonene and terpinolene disappear. Hence, it seems reasonable to postulate that *p*-menthene

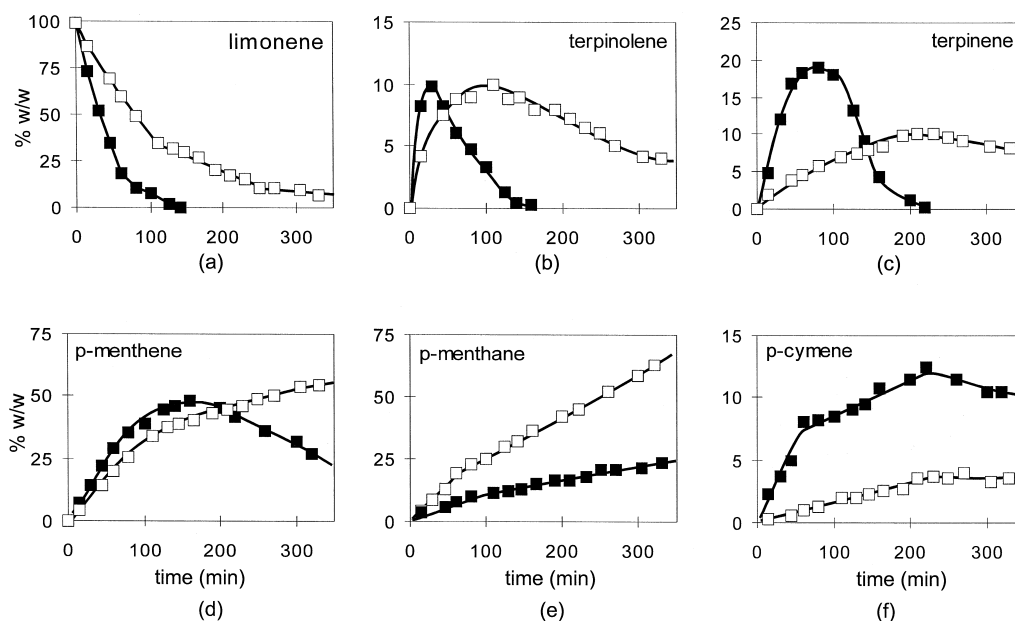


Fig. 1. Product distribution as a function of the reaction time during the hydrogenation of limonene for 5% Pd/C catalyst, at 106.65 kPa of hydrogen pressure: (□) 273 K; and (■) 323 K.

is formed from limonene and terpinolene. The initial production rate of *p*-cymene is broken just as the concentration of γ -terpinene reaches a maximum; thence, *p*-cymene is produced at a lower rate. From then on, γ -terpinene disappears and the concentration of *p*-cymene remains nearly constant. This behavior is consistent with the assumption that *p*-cymene is produced from γ -terpinene via dehydrogenation reactions.

(iv) In order to provide further information concerning the pathway reaction, the concentration profiles have been replotted as a function of the limonene conversion in Fig. 2. Temperature changes have a mild effect on the selectivity of terpinolene and *p*-menthane; so then, the selectivity of these products can only be marginally improved by changes in reaction temperature. Nevertheless, the selectivity toward γ -terpinene and *p*-cymene can be improved with increases of temperature at the expense of the selectivity of *p*-menthane.

The trend of the concentration profiles deserves some comments.

(v) Insignificant changes in the selectivity of terpinolene take place with temperature, as shown in Fig. 2a. Although there is no direct evidence, a strong adsorption of terpinolene with a significant departure from adsorption equilibria could be expected. If the slowest process involves the adsorption and not the surface reaction, a low level of terpinolene in the liquid phase with non significant changes on the selectivity are expected with temperature changes due to the lower dependence which has the adsorption constant with temperature respect to the reaction constant. The early production of terpinolene without any modification of its low concentration, which results from a significant increase of the reaction temperature, supports this suggestion.

When examining Fig. 2b, c and e, one may observe that the increase of γ -terpinene and *p*-cymene concentrations is counterbalanced by a comparable decrease of *p*-menthene concentration. A careful examination of these profiles reveals that there are no significant changes in the material balance of γ -terpinene, *p*-menthene and *p*-cymene with temperature, as it is shown in Fig. 2f. No modification of the values of this material balance could be expected if an increase of temperature favors the

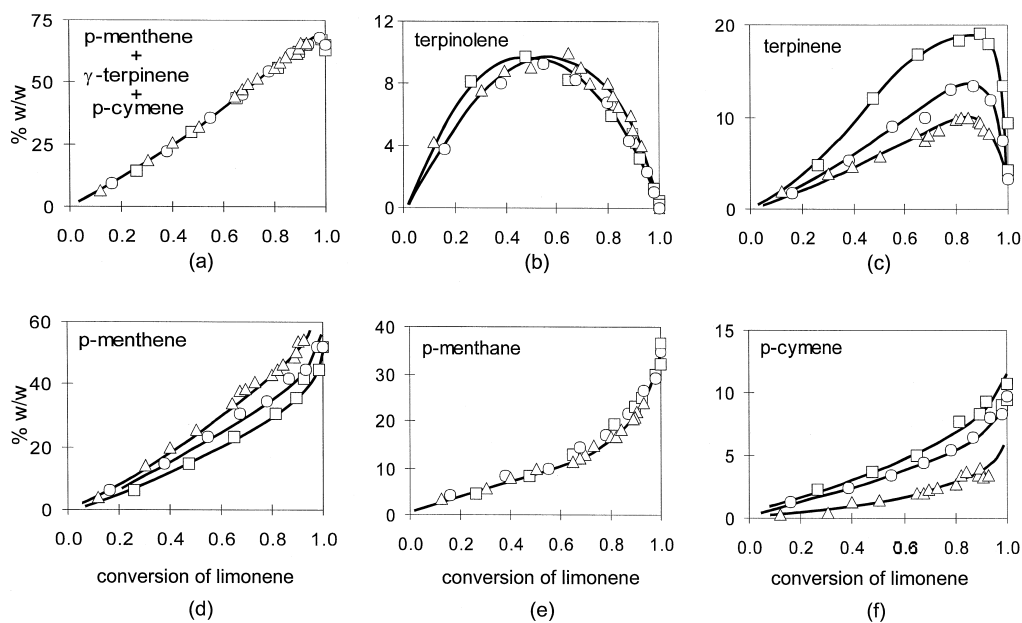


Fig. 2. Product distribution vs. conversion of limonene for 5% Pd/C catalyst, at 106.65 kPa of hydrogen pressure: (Δ) 273 K; (\circ) 298 K; and, (\square) 323 K.

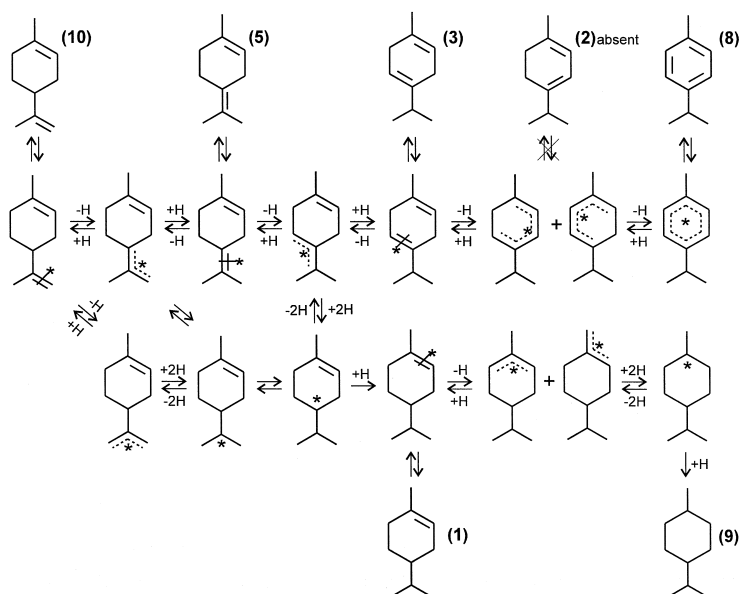
double bond isomerization from terpinolene toward γ -terpinene and further dehydrogenation to *p*-cymene, to the detriment of double bond saturation to *p*-menthene, or conversely. As regards this, we assume that a common intermediate must be involved in the reaction routes leading to γ -terpinene and *p*-menthene from terpinolene.

3.3. Reaction scheme over Pd / carbon catalysts

A plausible reaction scheme to explain the previously mentioned behavior is proposed in Scheme 1. It has been widely recognized that the olefin hydrogenation over palladium is promoted through π -allyl adsorbed species rather than through the 1,2- σ_2 entity involved in the classical Horiuti–Polanyi mechanism, which explains the overall behavior observed over platinum and similar metals [12–17]. Then, the involvement of π -allyl-adsorbed species is considered to explain the isomerization process.

On the basis of π -allyl-adsorbed species, the 4,8,9- π -allyl and 9,8,10- π -allyl species could be mainly formed from limonene. The formation of the 6,1,2- π -allyl, 7,1,2- π -allyl and 1,2,3- π -allyl species is also possible but unlikely, due to the fact that the adsorption of the endocyclic double bond has more steric hindrances than the exocyclic double bond. A support for this premise comes from the virtual absence of any appreciable quantity of 1-methylene-4-isopropenyl-cyclohexane and 1-methyl-4-isopropenyl-cyclohexane among the isomerization and hydrogenation products, respectively. Therefore, we think the 4,8,9- π -allyl species could be either desorbed, in a way leading to the predominant formation of terpinolene, or undergo hydrogenation to give a half hydrogenated-adsorbed intermediate involved in the formation of *p*-menthene which could also be formed from the 9,8,10- π -allyl species.

From Pd-catalyzed reactions of exocyclic monoenes (e.g., 4-*tert*-butyl-methylenecyclohexane and methylenecyclohexane) and endocyclic monoenes (e.g., 4-*tert*-butyl-methylcyclohexene, methyl cy-



Scheme 1.

clohexene, 3-methylcyclohexene and 4-methylcyclohexene) it has been determined that the exocyclic adsorbed species are minor components of the reaction mixture. The endocyclic adsorbed species are present on the catalyst surface to a greater extent, and then, the product saturation occurs through them [16,17]. However, although the formation of endocyclic adsorbed species such as the 6,1,2- π -allyl; 7,1,2- π -allyl and 1,2,3- π -allyl species is possible from adsorption of terpinolene, if it occurs, it would be expected to be to a minor extent. Again, as discussed above, the adsorption of the endocyclic double bond is not preferentially favored due to the lower steric hindrances of the exocyclic double bond. This assertion is supported by the virtual absence of 1-methyl-4-isopropylidene-cyclohexane among the hydrogenation products. Therefore, the predominant intermediacy of the 8,4,5- π -allyl species is expected, although the formation of the 1,2,3,4,8- π -allyl species could also be possible.

At that point, the 8,4,5- π -allyl species undergoes either double bond migration, followed by desorption to give γ -terpinene, or hydrogenation leading to half hydrogenated-adsorbed species which then completes its hydrogenation to yield *p*-menthene by desorption. The intermediacy of this common adsorbed species in the pathways leading to γ -terpinene and *p*-menthene seems to be necessary to explain the increase of selectivity to γ -terpinene, which is observed to the detriment of selectivity to *p*-menthene when the temperature increases.

The γ -terpinene is a nonconjugated endocyclic diene from which *p*-cymene could be formed, as already noted from the experimental data. By comparison of the hydrogenation rates of conjugated and nonconjugated endocyclic dienes (e.g., 1,3-cyclooctadiene and 1,3-cyclohexadiene, and, 1,4-cyclohexadiene and 1,5-cyclooctadiene, respectively) over palladium, it has been observed that the nonconjugated dienes have a lower rate of hydrogenation than the conjugated dienes with the same ring size. It was explained by the fact that the conjugated species have a higher adsorptivity on the catalyst surface as it was corroborated by direct measurement [18]. Furthermore, the desorption of the cyclohexadienes has never been observed in the heterogeneous catalytic hydrogenation of benzene over group VIII metals (e.g., Ni, Pd, Pt) [19]. Thus, it seems that the dehydrogenation route from

γ -terpinene to *p*-cymene would proceed via species strongly adsorbed and stabilized by π -electron delocalization through resonance.

Potentially, there are four possible π -allyl species from adsorption of γ -terpinene. Two of them are exocyclic adsorbed species, as the 7,1,2- π -allyl and the 8,4,5- π -allyl species. The other ones are endocyclic adsorbed species as the 1,2,3,4,5- π -allyl and the 4,5,6,1,2- π -allyl species. Since the inductive effect of the methyl and isopropyl substituents can cause a certain increase of the π -electron cloud density at the ring, the π -allyl endocyclic species could be expected to be strongly adsorbed. Whether a strong π -complex bond leads to either a lower or a higher reactivity of the adsorbed species is a controversial question which still remains to be solved [19]. Then, the virtual absence of α -terpinene among the reaction products would be due to the fact that conjugated dienes are desorbed in an extremely slow way or in a very reactive one. We think that the higher the adsorption of species on the catalyst surface the lower the ratio between the desorption and reaction rates. Thus, the conjugated endocyclic adsorbed species undergo dehydrogenation before desorption.

The hydrogenation of *p*-menthene to give *p*-menthane would proceed via the 6,1,2- π -allyl species, 1,2,3- π -allyl species and 7,1,2- π -allyl species. It has been previously found that the 1,2,3- π -allyl species is not involved in the hydrogenation of 4-*tert*-butylmethylcyclohexene and methylcyclohexene [16,17]. It has also been found that the endocyclic adsorbed species are present to a much greater extent than the exocyclic adsorbed species, and the product formation occurs by means of their saturation [17]. It is therefore possible that the hydrogenation of *p*-menthene takes place mainly through the 1,2,6- π -allyl species.

3.4. Product distribution and initial reaction rates on Pd/Alumina catalyst

To provide further information concerning the reaction mechanism, attention shifted to hydrogenation of limonene over Pd/Al₂O₃ catalysts. The catalytic activity for 5% Pd/C, 5% Pd/Al₂O₃ and 0.5% Pd/Al₂O₃ catalysts is summarized in Table 2 for comparison purposes. The alumina-supported catalyst exhibits higher initial activity than the carbon-supported catalyst under comparable conditions. The initial consumption rate of limonene over 5% Pd/Al₂O₃ catalyst (column b) is 45% higher than that over 5% Pd/C catalyst (column a). Likewise, the initial production rates of *p*-menthene, *p*-menthane, *p*-cymene, γ -terpinene and terpinolene increase 17, 38, 76, 81 and 98%, respectively, showing that the isomerization increases markedly on the alumina-supported catalyst. By examining the initial activity values for 5% Pd/C (column a) and 0.5% Pd/Al₂O₃ (column c), a higher isomerization level for alumina-supported catalyst is evident despite the fact that the palladium loading decreases by one order of magnitude. The initial consumption rates of limonene are comparable but the hydrogenation rates (to give *p*-menthene and *p*-menthane) decline while the

Table 2
Initial reaction rates over supported Pd-catalysts, at 298 K

Species	Initial reaction rate (mol g cat ⁻¹ s ⁻¹) over		
	5% Pd/C (a)	5% Pd/Al ₂ O ₃ (b)	0.5% Pd/Al ₂ O ₃ (c)
Limonene	6.30	9.14	6.73
<i>p</i> -Menthene	2.57	3.02	1.14
<i>p</i> -Menthane	1.16	1.61	0.85
<i>p</i> -Cymene	0.48	0.85	0.68
γ -Terpinene	1.03	1.87	1.58
Terpinolene	1.28	2.53	2.28

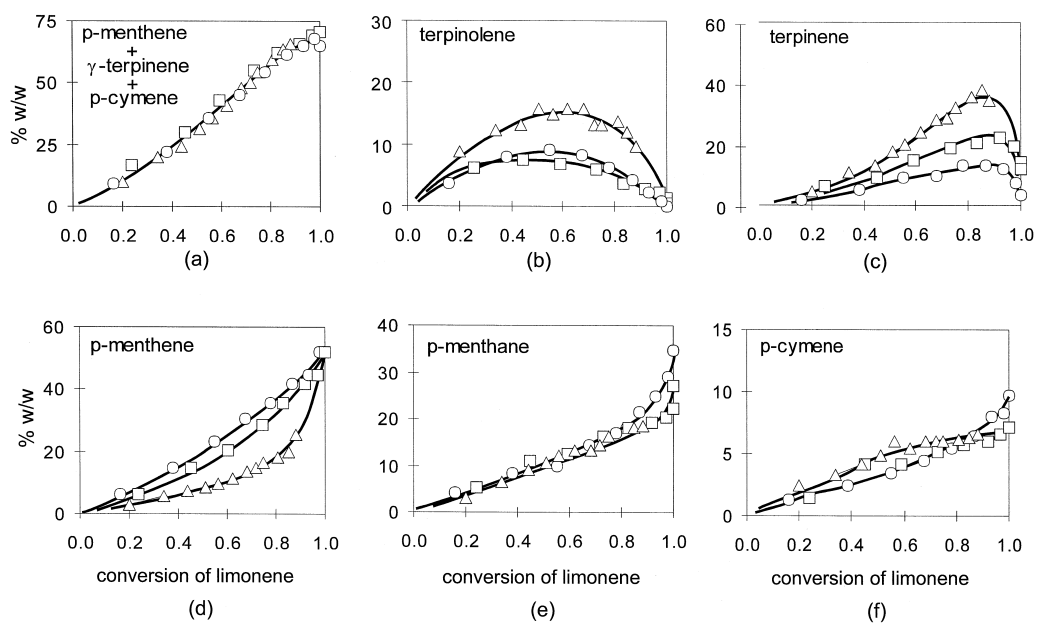
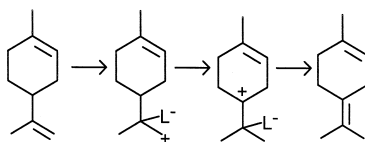


Fig. 3. Product distribution vs. conversion of limonene in the hydrogenation at 298 K and 106.65 kPa of hydrogen pressure: (Δ) 0.5% Pd/C catalyst; (\circ) 5% Pd/Al₂O₃; and, (\square) 0.5% Pd/Al₂O₃, at 106.65 kPa.

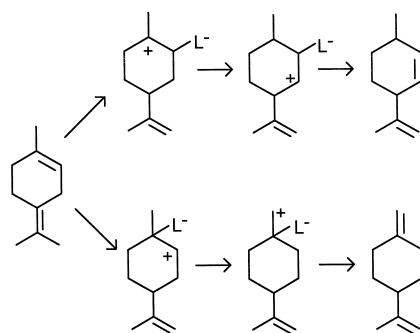
isomerization rates toward γ -terpinene, terpinolene and *p*-cymene increase 42, 53 and 78%, respectively.

The enhancement of the catalytic activity could be explained by effects of the support in view of the capability of the alumina for alkene isomerization. However, an additional contribution due to changes in the metal location and dispersion would play a significant role. We are not sure whether these properties significantly influence the observed catalytic activity, due to the fact that quantitative measurements were not performed. Nevertheless, the relatively greater isomerization capability of the alumina-supported catalyst is suggestive with respect to carbon-supported catalysts even if the palladium loading is 10 times lower. The small decrease of the isomerization level when the palladium load on alumina decreases 10 times is also noticeable, as shown in Table 1 (see columns b and c). It seems, then, that the enhancement of the catalytic activity for the isomerization of Pd/alumina catalysts could be mainly attributed to effects of the catalyst support. Further insight into the role of alumina can be gained by a more careful analysis, as follows.

Fig. 3 shows the concentration profiles vs. limonene conversion for 5% Pd/C, 5% Pd/Al₂O₃ and 0.5% Pd/Al₂O₃ catalysts, at 298 K. The comparable distribution of the hydrogenation products (i.e., *p*-menthene and *p*-menthane), which is obtained for the same palladium loading (5%) on different supports, could be taken—if it is not accidental—as an indicator of the enhancement of the isomerization by effects of the support, rather than to differences in both metal location and dispersion; otherwise, one would also expect dissimilar hydrogenation product profiles.



Scheme 2.



Scheme 3.

The enhancement of the catalytic activity for the isomerization of terpinolene and γ -terpinene could be explained by mechanisms involving Lewis acid sites provided by alumina, although the Brønsted mechanism is potentially possible, too. Nevertheless, since the experiments were carried out at low temperatures (≤ 323 K), it is presumable that the eventual contribution via the Brønsted mechanism is negligible. Working from the mechanistic aspects, we recognize two possible pathways for isomerization on alumina: one of them involves the formation of carbonium ions, and the other one, if it occurs, comprises double-bond migration via allyl route involving carbanions.

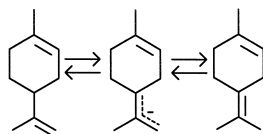
For limonene, three Lewis mechanisms are accessible if the formation of enantiomeric species are not accounted for. The first of them involves adsorption of the extracyclic double-bond with formation of a primary carbonium ion, followed by a proton shift leading to a tertiary carbonium ion from which terpinolene could be formed (see Scheme 2).

The other two routes could proceed via adsorption of the endocyclic double-bond, but both routes are unlikely since they have steric hindrances and involve the unfavorable formation of secondary and primary carbonium ions from tertiary and secondary ones, respectively (see Scheme 3).

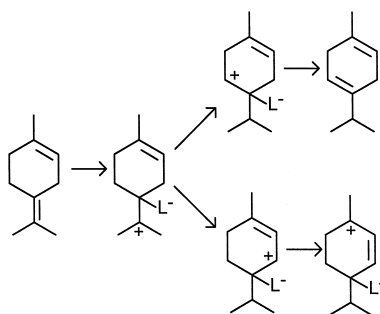
In the light of the assertion which establishes that the isomerization activity over alumina depends on the ability of the olefinic structure to form tertiary carbonium ion \gg allylic intermediate $>$ secondary carbonium ion [20], it seems that the carbonium ion mechanism shown in Scheme 3 is not probable.

The allyl mechanism is also possible, and if it occurs, it would be expected to lead the formation of some terpinolene through the mechanism shown in Scheme 4.

Then, the slight modification of the selectivity toward the formation of terpinolene, during the hydrogenation of limonene over 5% Pd/C and 5% Pd/Al₂O₃, can be accounted for citing the intermediacy of π -allyl-intermediates adsorbed predominantly on palladium. While the relative increase of terpinolene production for 0.5% Pd/Al₂O₃ catalyst suggests an increase of the migration of extracyclic double-bond via carbonium ion intermediates (Scheme 2) and/or via allyl route involving carbanions (Scheme 4).



Scheme 4.



Scheme 5.

For terpinolene, four Lewis mechanisms are viable besides the π -allylic route. Two of them comprise carbonium ions, similar to those derived from the endocyclic double-bond adsorbed species previously described for the limonene adsorption. Once more, we argue that the formation of such intermediates has more steric hindrances in relation to the adsorbed exocyclic species and, consequently, lower occurrence possibilities. The other routes involve the adsorption of the exocyclic double-bonds followed by the formation of secondary and tertiary carbonium ion stabilized by resonance, as shown in Scheme 5.

Therefore, the occurrence of two mechanisms is possible, one involving π -allylic route on palladium, with a great predominance over the similar mechanism, which could be taking place on alumina, and another, Lewis-acid induced, taking place when Pd/Al₂O₃ catalysts are used. Our results suggest that limonene isomerizes over alumina via π -allylic mechanism, while terpinolene and terpinene isomerize via the carbonium ion mechanism.

4. Conclusions

The hydrogenation of limonene using 5% Pd/C, 5% Pd/Al₂O₃ and 0.5% Pd/Al₂O₃ catalysts was studied under mild reaction conditions in the absence of extraparticle and intraparticle effects. It was observed that, besides *p*-menthene and *p*-menthane, side products such as terpinolene, γ -terpinene and *p*-cymene were also formed. A significant presence of terpinolene and γ -terpinene indicates that an extensive isomerization precedes the hydrogenation, while the presence of *p*-cymene evidences that a dehydrogenation occurs simultaneously. The virtual absence of intermediates, such as α -phellandrene, β -phellandrene and α -terpinene, was attributed to the fact that conjugated cyclic dienes are strongly adsorbed to desorb before further reaction. Reaction schemes have been proposed by examining the products distribution and taking into account mechanistic aspects of hydrogenation and isomerization of cyclic olefins over palladium catalysts.

It seems that the enhancement of the catalytic activity for isomerization of terpinolene and γ -terpinene for Pd/Al₂O₃ catalysts could be explained by mechanisms involving Lewis acid sites provided by alumina. Therefore, the occurrence of two mechanisms is possible, one involving π -allylic route on palladium—in weak competence on alumina—and the other, Lewis acid-induced on alumina, taking place when Pd/Al₂O₃ catalysts are employed. The obtained results suggest that, over alumina, limonene isomerizes via the π -allylic mechanism, whereas terpinolene and terpinene isomerize via the carbonium ion mechanism.

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