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Kinetic and mass transfer in the hydrogenation of polyunsaturated organic compounds in the presence of supported Pd catalysts

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Abstract

The hydrogenation of 1,5-cyclo-octadiene has been studied on well-defined Pd catalysts. The reaction is affected by internal diffusion of hydrogen into the catalyst particles. Despite this limitation, the reaction orders of the reactants have been determined. All the performed kinetic runs have been simulated and the kinetic and mass-transfer parameters giving the best fit of experimental data have been evaluated. The reaction occurs in two steps, in the first, a conjugate diene (1,3-cyclo-octene) is formed via isomerization, then, hydrogenation occurs quickly forming the monoene. The hydrogenation of the obtained cyclo-octene is relatively slow and strongly inhibited by the presence of the cyclo-octadiene. This last reaction has, therefore, been used for comparing the activities of different palladium catalysts showing an exponential behaviour of the reaction rate with the metal dispersion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Polyunsaturated organic compounds; Pd catalysts

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1. Introduction

In a previous work [1] on the partial hydrogenation of rapeseed oil, catalysed by supported palladium catalyst, we observed internal mass-transfer limitation despite the small mean size of the catalyst particles. For this reason and considering that at low temperature at which chemical regime could be operative, the viscosity of the oil strongly increases undergoing solidification, kinetics of hydrogenation can be studied only indirectly, i.e., also by considering the influence of the mass transfer. Reaction order with respect to hydrogen is zero, while a Langmuir–Hinshelwood kinetic law [2] was observed for the unsaturated molecules. In the same work, we observed that hydrogenation rates for trienes and dienes were identical, on the contrary, the rate of hydrogenation for monoene was quite lower. We interpreted this behaviour by assuming that polyunsaturated molecules firstly give place to conjugated double bonds as a consequence of shifting reactions occurring before hydrogenation. In order to verify this aspect, in the present work, we have studied the hydrogenation of model molecules such as 1,5-cyclo-octadiene, cyclo-octene and 1,7-octadiene. In this way, we have had the possibility of comparing the hydrogenation activity of dienes conjugated or not and of monoenes. The effect of the distance among the two double bonds of dienes has been tested too. As expected, we observed that the conjugated dienes are hydrogenated very quickly. On the contrary, non-conjugated dienes are firstly isomerized to conjugated ones and then hydrogenated faster than monoenes. By hydrogenating 1,5-cyclo-octadiene, e.g., 1,3-cyclo-octadiene is formed as an intermediate. The same behaviour occurs in the hydrogenation of 1,7-octadiene, but in this case, different dienic isomers are obtained and consequently many monoene isomers.

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Nomenclature

a	specific gas–liquid interface area (cm^2/cm^3)
a_s	specific external area of particles (cm^2/cm^3)
b_i	adsorption equilibrium constant of species i (cm^3/mol)
d_p	average diameter of catalyst particle (cm)
D_e	effective diffusivity (cm^2/s)
k_c	rate constant of diene isomerization ($cm^3\,(cm^3\,mol^{-1})^n\,g^{-1}\,s^{-1}$)
k_i	rate constant of i hydrogenation ($cm^3\,(cm^3\,mol^{-1})^n\,g^{-1}\,s^{-1}$)
k_S	liquid–solid mass-transfer coefficient (cm/s)
k_0	hydrogenation pseudo-constant (see Eq. (16)) ($cm^3\,(cm^3\,mol^{-1})^{n-1}\,g^{-1}\,s^{-1}$)
K_L	gas–liquid mass-transfer coefficient (cm/s)
r_c	rate of diene isomerization ($mol\,cm^{-3}\,s^{-1}$)
r_G	rate of hydrogen consumption, $r_G = r_1 + r_2 + r_3$ ($mol\,cm^{-3}\,s^{-1}$)
r_i	rate of i hydrogenation ($mol\,cm^{-3}\,s^{-1}$)
R	mean radius of catalyst particles (cm)
v_M	hydrogen molar volume (cm^3/mol)
V_L	volume of slurry (cm^3)
w	catalyst concentration (g/cm^3)

Greek letters

η	overall effectiveness factor of slurry reactor
η_c	catalytic effectiveness factor
ρ_p	catalyst particle density (g/cm^3)
σ_A	parameter defined by Eq. (13)
ϕ	Thiele parameter

Reaction order approaching zero, for hydrogen, has been confirmed for all the tested molecules, moreover, as observed in a previous work [1], for consecutive hydrogenations of polyunsaturated molecules, the slower hydrogenation such as that of monoene is strongly inhibited and practically does not occur in the presence of dienes. This behaviour has been explained and well reproduced on the basis of the Langmuir–Hinshelwood kinetic law. At last, the effect of palladium dispersion on the hydrogenation of cyclo-octene will be discussed.

2. Experimental

2.1. Methods, apparatus, techniques and reagents

Kinetic runs have been performed in a well-mixed stainless steel 0.5 l semibatch reactor. The reactor was equipped with a magnedrive stirrer able to develop a great interfacial area related to the rotating speed. The scheme of a similar reactor has already been reported in detail in a previous work [1]. Overall hydrogenation reaction rates were determined from the hydrogenation consumption rates directly measured with a flowmeter. Normally, we operated the stirrer at more than 1500 rpm to limit the external diffusion resistance.

The catalyst used in the kinetic runs contained 2 wt.% of palladium supported on sodium neutralized silica–alumina. Initially, palladium was in the oxidized form and was reduced inside the reactor. In Table 1, the main properties of the catalyst used in the kinetic runs are summarized.

Kinetic runs were performed both by monitoring the hydrogen consumption with a flowmeter connected to a computer and by withdrawing small samples of the reaction mixture at different times. The samples were analysed by gas chromatography using an FID detector and Poraplot Q column of 25 m length and 0.32 mm diameter. Helium was used as a carrier gas.

Kinetic runs have been made starting from, respectively, 1,5-cyclo-octadiene and cyclo-octene. Runs have been made also starting from 1,7-octadiene for

Table 1
Main properties of the catalyst used in the kinetic runs

Average diameter	0.013 cm
Support	Neutralized silica–alumina
Specific surface area	178 m^2/g
Palladium	2 wt.%
Metallic surface area	149 m^2/g
Specific weight	2.25 g/cm^3
Bulk density	0.77 g/cm^3
Porosity	0.80 cm^3/g

Table 2
Main properties of the catalysts used in the cyclo-octene hydrogenation, D is the average dispersion of palladium, S the specific surface area of the metal, d the mean diameter of the palladium particles, r the rate of cyclo-octene hydrogenation

Support	Pd (wt.%)	D (%)	S (m^2/g Pd)	d (nm)	r (Nml H$_2$/(g Pd h))
Silica	0.32	69	325	1.54	18.22
Silica	1.0	34	160	3.12	4.92
Alumina	1.0	75	373	1.34	22.78
Alumina	1.0	38	180	2.77	4.54
Silica–alumina	0.30	55	260	1.92	13.6
Silica–alumina	1.0	26	122	4.01	3.87

a useful comparison. As from 1,5-cyclo-octadiene, 1,3-cyclo-octadiene is formed, as an intermediate, also the kinetic of the hydrogenation of the conjugated double bond has consequently been studied. Cyclo-octene hydrogenation have also been studied on several types of palladium catalysts characterized by different supports and palladium dispersion. Catalysts have been prepared by using different techniques and their properties are summarized in Table 2.

Kinetic behaviour in cyclo-octene hydrogenation has been studied only by monitoring the hydrogenation consumption. The dispersion of palladium has been measured with the technique described by the author in a recent published paper [3]. All the reagents employed have been supplied by Aldrich at the highest level of purity available.

2.2. Results and discussion

In Figs. 1 and 2, kinetic runs of 1,5-cyclo-octadiene hydrogenation are reported. Runs have been performed both at 50°C, in the presence of 0.2 g of the catalyst, whose characteristics are reported in Table 1, and, respectively, at 3 and 4 atm of pressure.

As it can be seen, 1,3-cyclo-octadiene is formed as an intermediate. Therefore, it is reasonable to assume, on the basis of this experimental observation, a

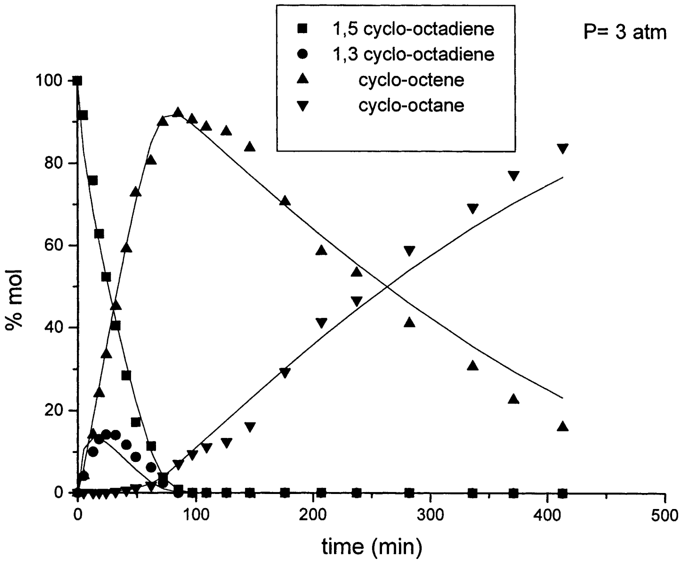
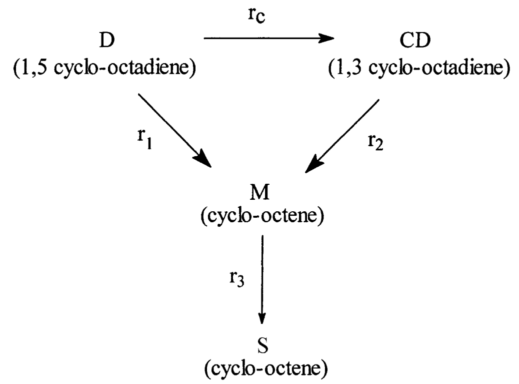


Fig. 1. Kinetic run of 1,5-cyclo-octadiene hydrogenation. $T = 50°C$, $w = 1.33\,mg/cm^3$, $[D]^0 = 1.3\,mmol/cm^3$, $P_{H_2} = 3\,atm$. Dots are experimental, lines are calculated.

reaction scheme of the type:



In a previous work [1] on the hydrogenation of fatty oils, we observed: (i) a Langmuir–Hinshelwood kinetic model which can be adopted for the organic substrate; (ii) that the reaction order for hydrogen is about zero; (iii) internal diffusion is always operative. We confirm the same behaviour in this system. In fact, by considering the reciprocal of the hydrogenation initial reaction rates determined from the hydrogen absorption rate curves (Fig. 3) as a function of the reciprocal of the catalyst concentration w, we obtained for 1,5-cyclo-octadiene the plot reported in Fig. 4. It is possible to recognize a behaviour that is typical for zero order reaction in the presence of internal mass-transfer limitation [4,5]. However, in a first approach, we considered the reaction order of hydrogen like a parameter of the model and submitted it to mathematical regression analysis.

The Langmuir–Hinshelwood kinetic model [2] for the organic substrate can be deduced by observing in Figs. 1 and 2 that hydrogenation of cyclo-octene is strongly inhibited by the presence of the cyclo-octadiene, this corresponding to the same behaviour observed in the hydrogenation of fatty oils [1]. The kinetic experimental results, therefore, were interpreted by solving the following set of ordinary differential equations:

$$\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = -(r_1 + r_\mathrm{c}) \tag{1}$$

$$\frac{\mathrm{d}[\mathrm{CD}]}{\mathrm{d}t} = r_\mathrm{c} - r_2 \tag{2}$$

$$\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = r_1 + r_2 - r_3 \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{S}]}{\mathrm{d}t} = r_3 \tag{4}$$

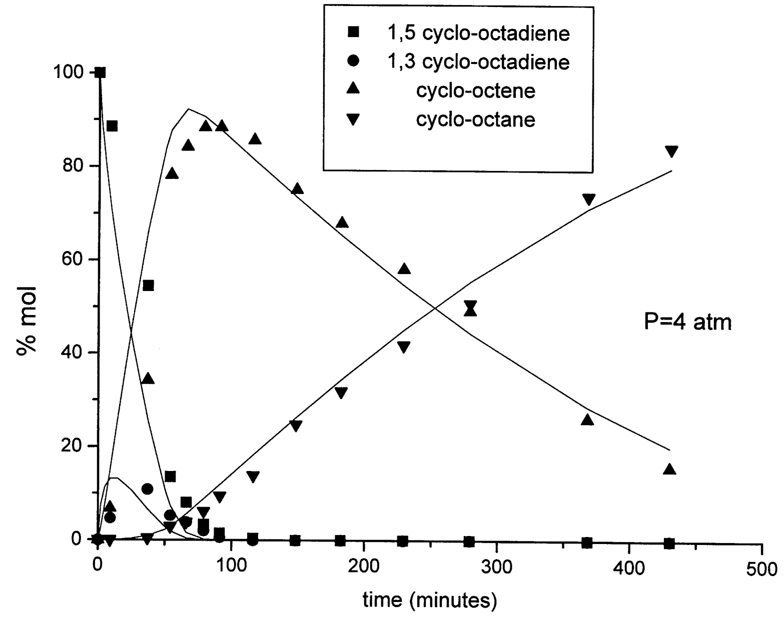


Fig. 2. Kinetic run of 1,5-cyclo-octadiene hydrogenation. $T = 50°\mathrm{C}$, $w = 1.33\,\mathrm{mg/cm^3}$, $[\mathrm{D}]^0 = 1.3\,\mathrm{mmol/cm^3}$, $P_{\mathrm{H_2}} = 4\,\mathrm{atm}$. Dots are experimental, lines are calculated.

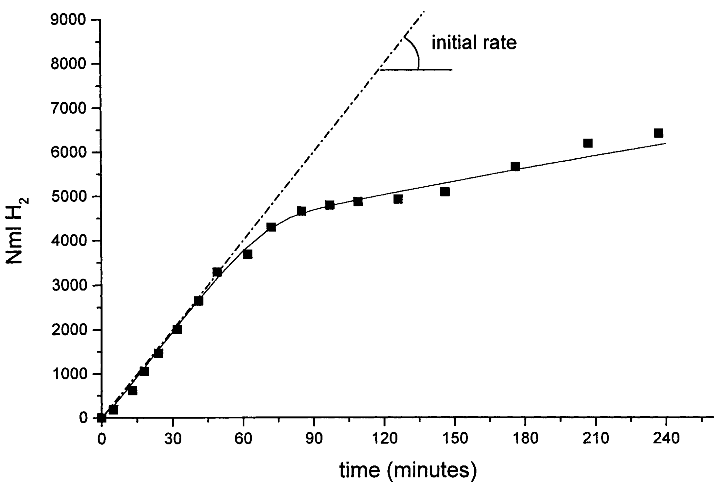


Fig. 3. Hydrogen adsorption. $T = 50^{\circ}C$, $w = 1.33\,mg/cm^3$, $[D]^0 = 1.3\,mmol/cm^3$, $P_{H_2} = 3\,atm$. Dots are experimental, lines are calculated.

$$\frac{dV_{H_2}}{dt} = v_M V_L (r_1 + r_2 + r_3) = v_M V_L r_G = \text{hydrogen consumption rate} \quad (5)$$

where

$$r_c = w\eta k_c \frac{[D][H_2]^n}{(1 + b_D[D] + b_{CD}[CD] + b_M[M])} \quad (6)$$

$$r_1 = w\eta k_1 \frac{[D][H_2]^n}{(1 + b_D[D] + b_{CD}[CD] + b_M[M])} \quad (7)$$

$$r_2 = w\eta k_2 \frac{[CD][H_2]^n}{(1 + b_D[D] + b_{CD}[CD] + b_M[M])} \quad (8)$$

$$r_3 = w\eta k_3 \frac{[M][H_2]^n}{(1 + b_D[D] + b_{CD}[CD] + b_M[M])} \quad (9)$$

The overall efficiency factor, incorporating all the transport effect η has been calculated as suggested by Chaudari and Ramachandran [5,6]. For a reaction of a generic n order, we have to solve the following

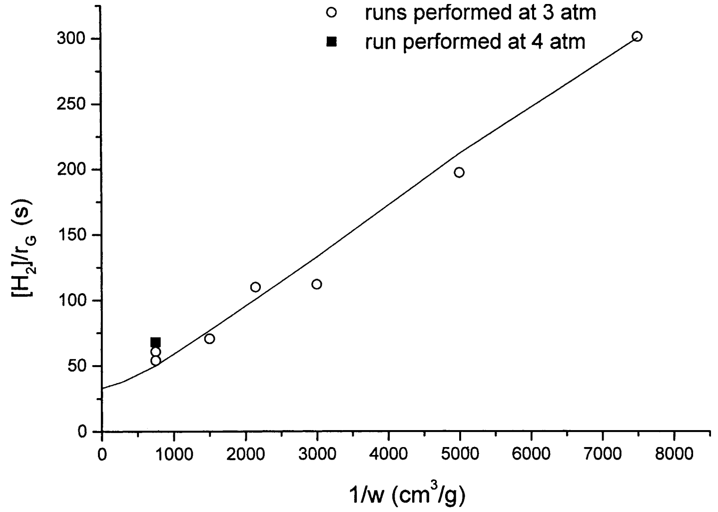


Fig. 4. Plot of $[H_2]/r_G$ against $1/w$. $T = 50^{\circ}C$, $[D]^0 = 1.3\,mmol/cm^3$. Dots are experimental, lines are calculated.

equations:

$$\eta = \eta_c \left(1 - \frac{\eta}{\sigma_A}\right)^n \tag{10}$$

$$\eta_c = \frac{1}{\phi}\left[\coth 3\phi - \frac{1}{3\phi}\right] \tag{11}$$

$$\phi = \frac{R}{3}\left[\frac{n+1}{2}\frac{\rho_p k_0 [H_2]^{n-1}}{D_e}\left(1 - \frac{\eta}{\sigma_A}\right)^{n-1}\right]^{1/2} \tag{12}$$

where

$$\sigma_A = \frac{[(1/K_L a) + (1/k_S a_p)]^{-1}[H_2]}{w k_0 [H_2]^n} \tag{13}$$

When reaction order for hydrogen is zero, the calculation of the overall efficiency factor is simplified and can be calculated with the relation

$$\eta = \sigma_A\{1 - \tfrac{1}{6}\phi^2[1 - 3(1-\eta)^{2/3} + 2(1-\eta)]\} \tag{14}$$

where

$$\phi = R\left[\frac{\rho_p k_0}{D_e [H_2]}\right] \tag{15}$$

In both cases, a pseudo-kinetic constant can be introduced:

$$k_0 = \frac{k_1[D] + k_2[CD] + k_3[M]}{1 + b_D[D] + b_{CD}[CD] + b_M[M]} \tag{16}$$

Table 3
Kinetic and mass-transfer parameters giving best fitting of runs reported in Figs. 1 and 2. Kinetic parameters (k_c, k_1, k_2, b_d) have been obtained by mathematical regression on experimental data, while diffusion ones have been calculated with Sano equation [7] (k_S) or experimentally determined ($K_L a$) [4,5]

k_c (cm^3 g^{-1} s^{-1})	4.6 ± 0.5
k_1 (cm^3 g^{-1} s^{-1})	0.19 ± 0.03
k_2 (cm^3 g^{-1} s^{-1})	22.5 ± 2
k_3 (cm^3 g^{-1} s^{-1})	$\frac{1}{2}k_1$
b_d (cm^3/mol)	3100 ± 150
b_c (cm^3/mol)	b_d
b_m (cm^3/mol)	$\frac{1}{2}b_d$
k_S (cm/s)	0.25
$K_L a$ (s^{-1})	0.03 ± 0.01

The result of the mathematical regression analysis made on experimental data concentrations ([D], [CD], [M] and [S]) of the runs reported in Figs. 1 and 2 gives the hydrogen reaction order $n = -0.006$, i.e., $n \approx 0$. Therefore, runs have been again submitted to mathematical regression analysis by assuming $n = 0$. The kinetic parameters giving the best fitting are reported in Table 3.

In the same table, the external mass-transfer coefficient ($K_L a$), determined by the intercept of Fig. 4 [4,5] has also been reported, k_S has been calculated by using the correlation recommended by Sano et al. [7], while the external surface area of the catalyst can be

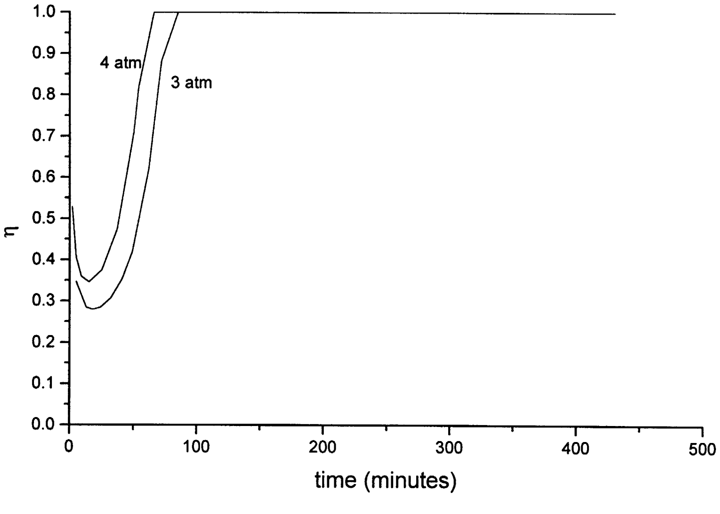


Fig. 5. Evolution of calculated overall effectiveness factor. $T = 50°C$, $w = 1.33\,mg/cm^3$, $[D]^0 = 1.3\,mmol/cm^3$.

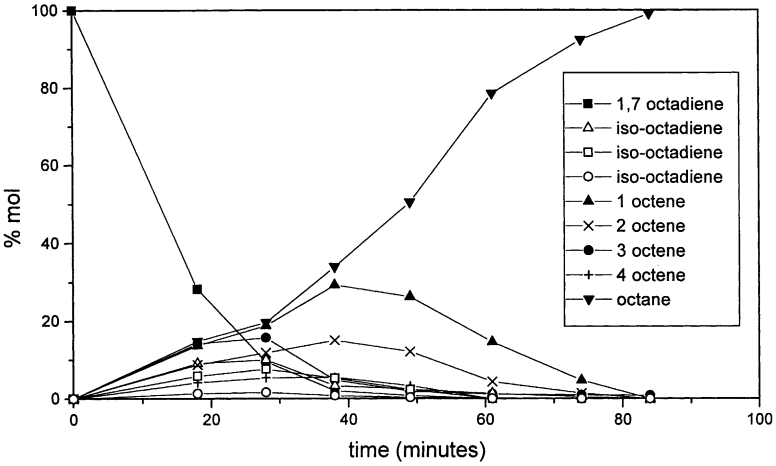


Fig. 6. Kinetic run of 1,7-octadiene hydrogenation. $T = 50^\circ C$, $w = 1.33\,mg/cm^3$, $[1,7\text{-octadiene}] = 1.3\,mmol/cm^3$, $P = 3\,atm$.

calculated by the relation:

$$a_p = \frac{6w}{\rho_p d_p} \tag{17}$$

Hydrogen solubility in n-hexane can be obtained by extrapolating data reported by Brummer [8]. The diffusion coefficient has been calculated by using the Wilke method [9].

In Figs. 1 and 2, the obtained fittings can be appreciated, while in Fig. 5, the evolution of the overall efficiency factor with time for the performed kinetic runs is reported.

It is surprising to observe that the hydrogenation of 1,7-octadiene is faster than the one of 1,5-cyclo-octadiene, as it can be seen in Fig. 6, nevertheless, double bonds in the molecules are, in this case, more distant. Probably, for linear molecules, the double bond shift reaction is very easy and fast.

As it can be seen, in Fig. 6, we recognized four monoene isomers, as expected, and we attributed the position of the double bond on the basis of kinetic considerations. On the contrary, we have found only four diene isomers, that are probably, non-conjugated dienes, conjugated dienes are too much reactive and does not accumulate in the reaction mixture in a detectable amount.

As it has been seen that the hydrogenation of cyclo-octene (M) is a relatively slow process, therefore, starting from cyclo-octene as reagent, the system is always in chemical regime. Therefore, we have made this reaction in the presence of several Pd catalysts prepared by using different precursors, techniques of preparation and different supports. These catalysts are characterized by different palladium dispersions. Catalysts used are reported in Table 2, together with their characteristics and related performances. The obtained results, as reaction rates as a function of palladium specific surface area, are reported in Fig. 7.

As it can be seen, catalytic activities increase exponentially with the specific palladium surface area, i.e., hydrogenation of cyclo-octene seems to be a structure

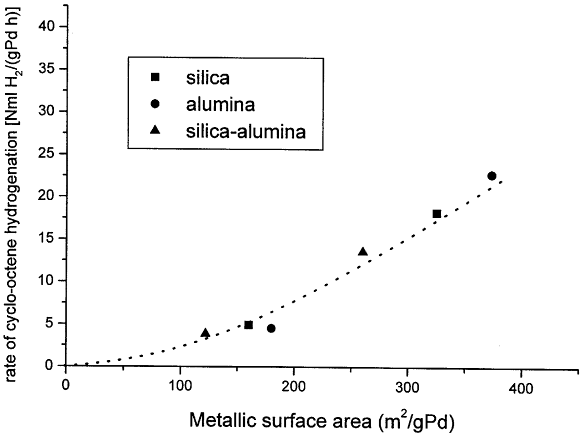


Fig. 7. Rate of cyclo-octene hydrogenation against the metallic surface area.

sensitive reaction and catalytic sites involved would, probably, be located mainly at the vertex or at the edge of the dispersed palladium microparticles.

3. Conclusion

The hypothesis proposed in a previous work [1] according to which the hydrogenation of dienes occurs following two different parallel pathways as in the scheme previously reported is confirmed. Conjugated dienes are formed as a consequence of double bond isomerization and then hydrogenated to monoenes more quickly than non-conjugated dienes.

The Langmuir–Hinshelwood kinetic model for the organic substrate and a pseudo-zero reaction order for hydrogen have been confirmed too.

The effect of mass-transfer reaction rate limitation has been described by introducing an overall effectiveness factor considering both external and internal hydrogen diffusion. It is important to point out that diene hydrogenation is a fast reaction and is very difficult to operate in the absence of mass-transfer limitation.

Then hydrogenation rate of linear dienes is much faster than cyclic dienes, probably, because isomerization to conjugated dienes is facilitated in the case of linear molecules.

At last, we observed that the hydrogenation of an isolated double bond on palladium catalysts is a structure sensitive reaction being promoted by the dispersion of metallic particles.

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