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Selective Liquid-Phase Hydrogenation of Citral over Supported Palladium

M. A. Aramendía,[1] V. Borau, C. Jiménez, J. M. Marinas, A. Porras, and F. J. Urbano

Department of Organic Chemistry, Faculty of Sciences, University of Córdoba, Avenida San Alberto Magno s/n, E-14004 Córdoba, Spain

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Citral in the liquid phase was reduced in a low-pressure hydrogenator by using catalysts consisting of palladium supported on (a) a mixed 80 : 20 $SiO_2/AlPO_4$ system and (b) sepiolite from Vallecas (Madrid, Spain). A kinetic study provided the reaction orders in the substrate concentration and hydrogen pressure. Experimental variables such as temperature, hydrogen pressure and the type of solvent were adjusted in order to optimize the reduction process. The presence of additives of the Lewis acid type such as $FeCl_2$ was found to considerably alter the hydrogenation mechanism; under these conditions, the selectivity proved strongly dependent on the Fe^{2+}/Pd atomic ratio. The reaction products were characterized by using gas chromatography in combination with mass spectrometry.

INTRODUCTION

The selective reduction of α,β-unsaturated carbonyl compounds is one of the most important research areas in fine chemistry; an overview of the topic is provided in several compilations (1). Crotonaldehyde (2, 3), methacrolein (4), and, particularly, cinnamaldehyde (5–7) are the most widely documented compounds in this respect, particularly in relation to the use of single- and two-metal catalysts supported on various materials such as carbon, zeolites, sepiolites, etc. The chief problem lies in obtaining catalysts affording the selective reduction of C=O or C=C double bonds.

The hydrogenation of α,β-unsaturated carbonyl compounds with single-metal catalysts leads to the reduction of the conjugate C=C bond with a high selectivity (close to 100%) (8–11). On the other hand, the formation of unsaturated alcohols calls for two-metal catalysts (the best results are usually obtained with Ru–Sn catalysts supported on carbon (12)). However, Richard *et al.* (13), using Pt catalysts and a reaction medium containing $FeCl_2$, accomplished the highly selective reduction of the C=O group of cinnamaldehyde. Other authors obtained similar results for various α,β-unsaturated carbonyl compounds by using $SnCl_2$, $FeCl_3$, $MnCl_2$, or $CoCl_2$ as additive (14, 15). The favourable effect of the metal ions in these halides is related to their Lewis acid character, which activates the carbonyl group by inducing positive charge on the carbon atom (16). Poltarzewski *et al.* (7), who used $SnCl_2$ in conjunction with Pt catalysts, put forward a second effect related to the formation of solid aggregates of Pt–Sn particles that might decrease the electron density at Pt sites, as in the case of Ni–Cu reported by Noller *et al.* (17).

The textural properties of the support, particle size, extent of metal dispersion, and nature of the precursor used to synthesize the catalyst are also influential, to a smaller extent, on the selectivity of the reduction of α,β-unsaturated carbonyl compounds (5, 18).

On the other hand, small changes during the synthetic process affect the catalyst performance. Thus, the addition of some oxides such as ZnO (19) favours the reduction of the C=C double bond since it leads to the formation of a bond between the carbonyl compound and the oxide that leaves the C=C group in the optimal spatial orientation for access by hydrogen. Conversely, the prior reduction of the catalyst at a high temperature increases the affinity for the C=O group (20).

The reduction of α,β-unsaturated carbonyl compounds is also influenced by other experimental variables. Thus, Grass *et al.* (21) found temperature and the type of solvent used (ether, alcohol) to have some effect on the activity and selectivity of the process.

Prominent among α,β-unsaturated carbonyl compounds is citral (3,7-dimethyl-2,6-octadienal), a substrate of special interest inasmuch as it possesses an isolated C=C bond in addition to the conjugate C=O and C=C groups. Its potential reduction products are schematized in Fig. 1. Citronelal and citronelol are especially interesting to the perfume industry because of their highly pleasant odours (22). The presence of 3,7-dimethyloctanal and 3,7-dimethyloctanol detracts from this valuable quality; as a result, for a catalytic process to have the desired result, it should reduce the conjugate C=C bond first and then the C=O bond, without altering the isolated C=C bond. However, the highly selective reduction of the C=O group, which is unaffordable with a single-metal catalyst, is more interesting in chemical terms.

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[1] To whom all correspondence should be addressed. E-mail: qo1urnaf@uco.es.

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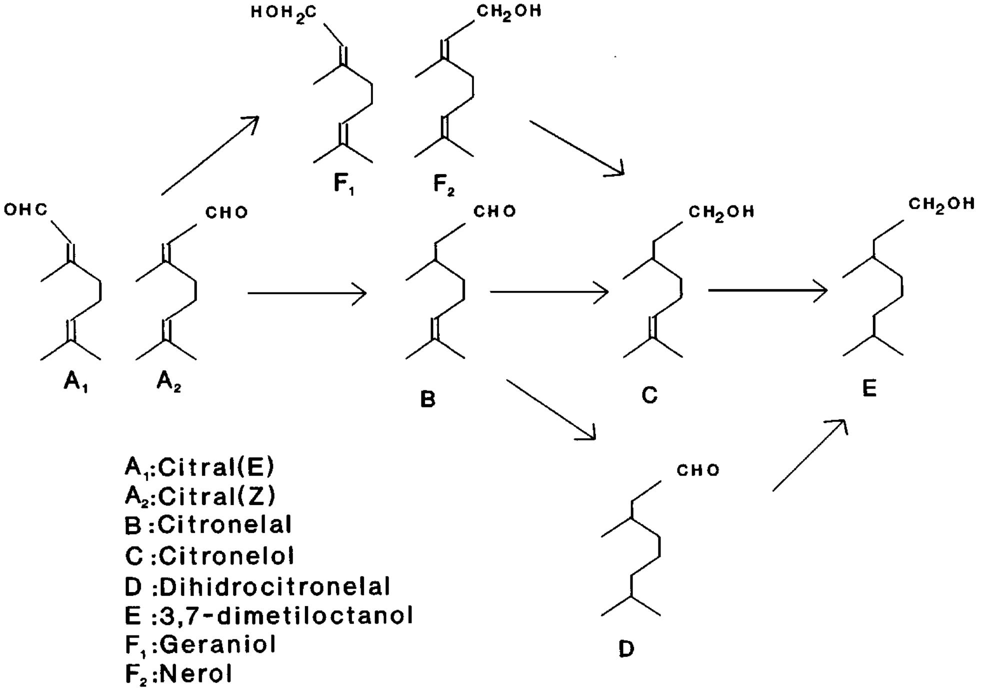

FIG. 1. Scheme of the products of citral reduction.

In this work, we studied the hydrogenation of citral with Pd catalysts supported on (a) a mixed 80 : 20 $SiO_2/AlPO_4$ system named PM2 and (b) sepiolite from Vallecas (Madrid, Spain) designated PS_{400}. We examined the influence of reaction variables (temperature, hydrogen pressure, type of solvent) on the reduction sequence. The addition of a small amount of $FeCl_2$ to the reaction medium was found to alter the sequence and increase the selectivity with which the C=O group was reduced.

EXPERIMENTAL

Procedure

Reactions were conducted in a Parr Instruments Co. model 3991 low-pressure reactor at a constant rate of 300 shakes/min. The reaction bottle, 500 mL, was wrapped in a metal jacket internally thermostated by circulating water. The apparatus was equipped with a pressure gauge from which the pressure inside the bottle could be read at any time. All reactions were carried out by using an overall solution volume of 20 mL, a 0.5 *M* citral concentration, an initial hydrogen pressure of 20–60 psi and a temperature in the range 283–323 K. Prior to each reaction, the catalyst (50 mg) was activated by passage of a hydrogen stream at a flow-rate of 120 mL min^{-1}. The temperature programme used comprised the following steps: (a) heating from room temperature to 393 K at 4 K min^{-1}; (b) holding 393 K for 30 min; and (c) cooling to room temperature. The hydrogen flow was maintained throughout the programme.

The procedure used in the experiments where $FeCl_2$ was added to the reaction medium was as follows: an amount of 50 mg of catalyst (pre-activated under a hydrogen stream) in 13.3 mL of dioxane was supplied with 5 mL of aqueous $FeCl_2$ at an appropriate concentration to ensure the required Fe^{2+}/Pd atom ratio. After the temperature had stabilized at 303 K, an H_2 pressure of 60 psi was set and the mixture was shaken for 2 h. Then, a volume of 1.7 mL of citral (for a 0.5 *M* concentration) was added, the reactor was filled up with H_2 and the shaking mechanism restarted.

Each reaction was preceded by tests intended to ascertain the absence of intra- and interparticle diffusion under the working conditions used. Thus, the absence of *intraparticle diffusion* was confirmed by checking that:

(a) The reaction rate did not depend on the shaking rate, which was the case above 200 shakes/min.

(b) The reaction rate was proportional to the catalyst weight. For this purpose, we plotted the reciprocal of the hydrogenation rate against the catalyst weight and obtained a straight line with a correlation coefficient better than 0.99. The reciprocal of the intercept was used to obtain the rate of hydrogen transfer from the gaseous phase to the liquid phase; because such a rate was higher than the highest hydrogenation rate obtained, we can state that the hydroen-transfer process was not the rate-determining step. These tests were repeated with every solvent studied and no signs of diffusion control were observed.

We used a small enough particle size to ensure that no *interparticle diffusion* occurred.

In addition, the absence of both internal and external heat and mass transfer constraints is apparent from the turnover frequencies obtained for two PM2 catalysts that differed in their metal loading by a factor of 3 but had similar dispersion. The absence of any significant change in these turnover frequencies (0.76 vs 0.81 s^{-1}) confirm that the reaction rates are correctly measured (23, 24).

Analysis of Reaction Products

Reaction products were analysed on a Hewlett–Packard 5890 gas chromatograph furnished with a Supelcowax-10 semi-capillary column of 30 m and 0.53 mm ID. Products were identified on a VG Autospec high-resolution mass spectrometer.

Synthesis and Characterization of Catalysts

The catalysts used contained 3% Pd supported on (a) a mixed 80 : 20 $SiO_2/AlPO_4$ system or (b) Spanish sepiolite supplied by TOLSA S.A. (Vallecas, Madrid, Spain); the supports were designated PM2 and PS_{400}, respectively. The procedures used to prepare the two solids were described in detail elsewhere (25, 26). The metal was deposited by using the method of "impregnation to incipient wetness," using Na_2PdCl_4 as the precursor salt. The pretreated support was placed in flask and supplied with appropriate amounts of precursor and aqueous sodium hydroxide. The flask was then placed on a rotavapor and stirred for 24 h, after which the solvent was vacuum-evaporated. Subsequently, the mixture was dried in a stove at 383–393 K for 24 h and ground to fine particles. Finally, the powder was calcined in a furnace at a linearly increasing temperature up to 483 K, which was held for 30 min.

The deposited metal salt was reduced in a hydrogen flow system consisting of a furnace into which the material to be reduced was inserted within a glass U-tube. The gas flow-rate was set at 120 mL min^{-1}. The reduction programme started at 373 K, which was held for 1 h and then raised linearly at 2 K min^{-1} up to 493 K, which was held for 10 min. Then, the U-tube was removed from the furnace and allowed to cool to room temperature under a constant flow of hydrogen. Thermal programmed reduction profiles confirmed that the temperature programme used ensured complete reduction of palladium on the surface of the support (27).

Supports and metal catalysts were characterized from nitrogen adsorption–desorption isotherms recorded on a Micromeritics ASAP 2000 porosimeter. Their specific surface area, was obtained by using the BET method (28). The acid–base properties of the supports were determined by using a thermal programmed desorption–mass spectrometry method with two different types of probe (pyridine for acid sites and CO_2 for basic sites) as described elsewhere (29, 30). The mean particle size (d), metal surface area (S), and metal dispersion (D) of the catalysts were determined by transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

Characterization of the Catalysts

The results are given in Table 1. Note that support PM2 exhibited greater S_{BET} and acidity values than did support PS_{400}. Regarding metal catalysts, the most salient finding was that Pd_3/PS_{400} had a larger particle diameter than $Pd_3/PM2$. The two histograms in Fig. 2 show the metal particle distribution in terms of inner diameter for both catalysts.

Hydrogenation of Citral

One of the essential steps in elucidating a reaction mechanism is determining the partial reaction order with respect to each reactant. The order in the hydrogen pressure was obtained from the initial reduction rate, r_g, at a variable initial hydrogen pressure (20–80 psi) and a temperature of 303 K, using a 0.5 M concentration of citral in tetrahydrofuran and an amount of 50 mg of catalyst $Pd_3/PM2$. The slope of a logarithmic r_g vs pressure plot provided the reaction order for hydrogen, which was found to be 1.25 ($r = 0.994$).

The reaction order in citral was obtained by using variable substrate concentrations in the range 0.3–0.9 M, an amount of 50 mg of catalyst $Pd_3/PM2$ and an initial hydrogen pressure of 60 psi. The order was found to be 0.36 ($r = 0.998$). This and the previous result are consistent with strong adsorption of citral and weaker adsorption of hydrogen (31).

In order to complete the kinetic study, activation parameters such as the energy (E_a), enthalpy ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were calculated from the Arrhenius and Eyring equations.

Table 2 lists the results obtained for catalyst $Pd_3/PM2$ in four different solvents, using a citral concentration of

TABLE 1

Textural, Acid–Base and Metal Properties of the Supports and Catalysts

	Properties							
	Textural			Acid–basic		Metalic		
Catalyst	S_{esp} $m^2 \cdot g^{-1}$	V_p Å	r_p Å	Acidity $\mu mol_{PY} \cdot g^{-1}$	Basicity $\mu mol_{CO_2} \cdot g^{-1}$	d Å	S $m^2 \cdot g_{Pd}^{-1}$	D %
PM2	402	0.36	141	115	—	—	—	—
$Pd_3/PM2$	241	0.30	50	—	—	62	81	18
PS_{400}	121	0.36	141	84	46	—	—	—
Pd_3/PS_{400}	71	0.32	180	—	—	144	35	8

Note. Specific surface area, S_{BET}; pore volume, V_p; mean pore radius, r_p; mean particle diameter, d, metal surface area, S; metal dispersion, D.

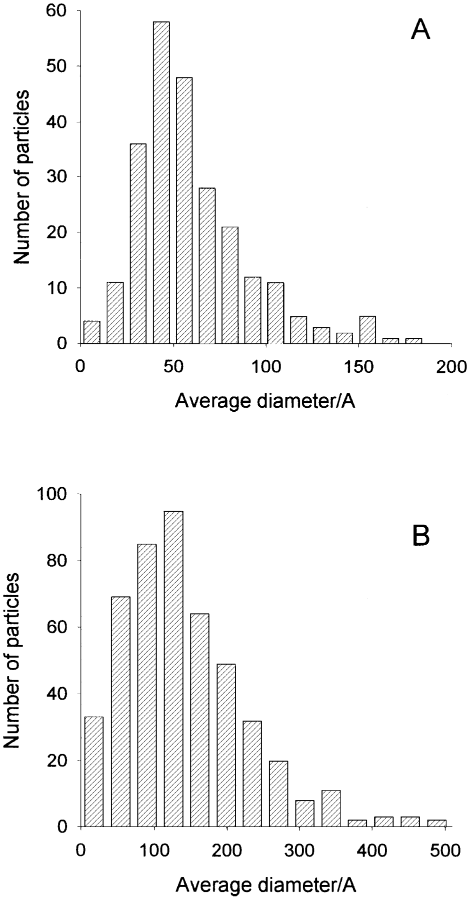

FIG. 2. Metal particle size distribution histograms for the two catalysts studied: (A) $Pd_3/PM2$; (B) Pd_3/PS_{400}.

0.5 *M*, an initial hydrogen pressure of 60 psi and temperatures between 293 and 323 K. As a rule, the higher the dielectric constant of the solvent was, the higher was the activation energy obtained. These results suggest a strong influence of the solvent on the reduction temperature. According to Grass *et al.* (21), the effect arises from (a) the acid–base properties of the solvent; (b) its electrical properties (a high dielectric constant favours alternative reactions over hydrogenation owing to polarity effects); and (c) the substrate–solvent reaction.

Our attempts at correlating r_g values with the acid–base properties of the solvent led to no conclusive results, so the latter can have no appreciable effect on the reaction. On the other hand, the dielectric constant was found to significantly affect the results, which differed markedly at a given temperature depending on the solvent. Thus, the solvents with low ϵ values (dioxane and cyclohexane) led to high reduction rates that decreased with increase in the solvent polarity (e.g., in methanol).

The effect of the substrate–solvent reaction is interesting when the solvent is an alcohol, which forms an acetal with the carbonyl group of citral (compunds characterized by mass spectrometry) thereby decreasing the reduction rate. The effect arises from sterically hindered access of the substrate to the catalytic site. In any case, the exact nature of the solvent effect on the reduction of citral is rather complex and requires further investigation (32, 33).

The time course of the hydrogenation process was monitored by recording hydrogen uptake and product distribution profiles (Figs. 3a and 3b, respectively) at an initial citral concentration of 0.5 *M* in THF and an initial H_2 pressure of 60 psi, using 50 mg of catalyst $Pd_3/PM2$ and a temperature of 303 K. The hydrogen uptake profile (Fig. 3a) consists of three distinct portions of different slope that correspond to as many reduction rates. The first portion (the steepest), corresponds to the reduction of the C=C bond conjugated with the C=O bond, which takes place at the highest rate. The second, of gentler slope, represents the period during which the isolated C=C bond is reduced. Finally, the third portion corresponds to the reduction of the carbonyl group to an alcohol function. Therefore, the reduction of the conjugate C=C bond takes place first, at a high rate that

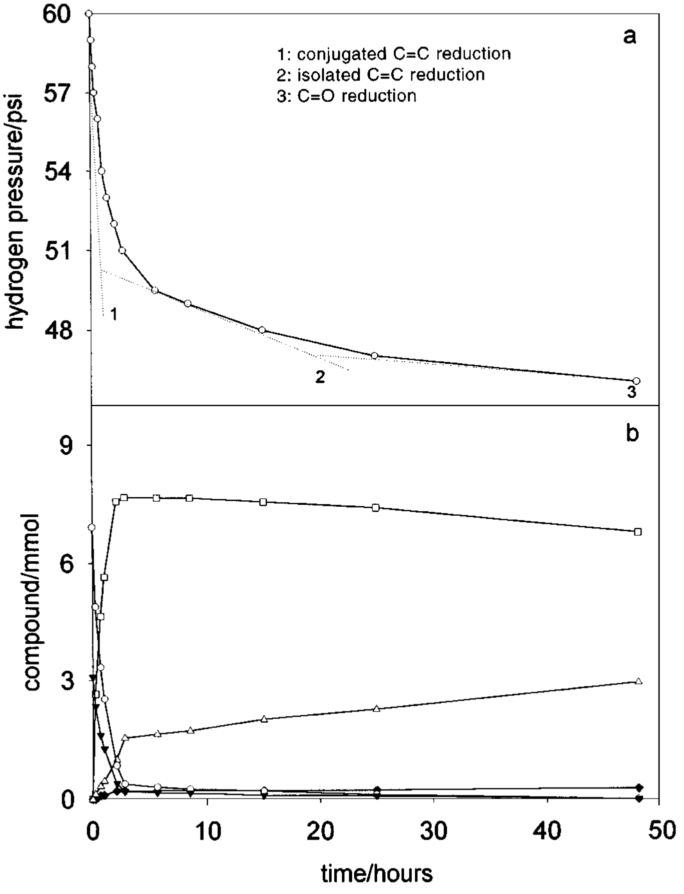

FIG. 3. Hydrogen uptake (a) and product distribution profiles (b) for the reduction of citral with molecular hydrogen. Reaction conditions: amount of catalyst ($Pd_3/PM2$), 50 mg; solvent, tetrahydrofuran; temperature, 303 K; citral concentration, 0.5 *M* (○, E-citral; ▼, Z-citral; □, citronelal; △, dihydrocitronelal; ◆, citronelol).

TABLE 2

Kinetic and Activation Parameters for the Hydrogenation of Citral with Catalyst Pd_3/PM2 in Different Solvents

		Kinetic parameters		Activation parameters		
Solvent ϵ	T/°C	r_g $\text{mmol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Pd}}^{-1}$	TON s^{-1}	E_a $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta H^{\#}$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S^{\#}$ $\text{J} \cdot \text{k}^{-1} \cdot \text{mol}^{-1}$
MeOH	293	1.0	0.59	40.0 ± 7.2	36.5 ± 7.2	-9.6 ± 2.5
32.6	303	1.3	0.76			
	313	2.5	1.47			
	323	3.5	2.05			
CHA	293	7.7	4.52	20.0 ± 2.5	17.9 ± 2.5	-166.2 ± 8.4
2.0	303	11.7	6.87			
	313	13.8	8.10			
	323	17.3	10.16			
DIO	293	13.4	7.87	8.7 ± 0.4	6.1 ± 0.4	-202.0 ± 1.5
2.2	303	14.6	8.57			
	313	16.3	9.57			
	323	17.8	10.45			
THF	293	3.9	2.29	22.4 ± 5.2	19.8 ± 5.2	-165.8 ± 16.9
7.6	303	5.1	2.99			
	313	5.7	3.35			
	323	9.9	5.81			

Note. MeOH, metanol; CHA, cyclohexane; DIO, dioxane; THF, tetrahidrofurane; ϵ, dielectric constant; r_g, initial rate; TON, turnover frequency; E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$, energy, enthalpy, and entropy, of activation, respectively. Reaction conditions: amount of catalyst (Pd_3/PM2), 50 mg; hydrogen pressure, 60 psi; citral concentration, 0.5 *M*.

decreases as the reaction develops and the isolated C=C bond and carbonyl group are reduced.

The product distribution profile (Fig. 3b) shows changes in the reactant and product concentrations as a function of the reaction time. At the beginning, citral is reduced highly selectively to citronelal via the double bond conjugated with the carbonyl group. The amount of product formed peaks (change of slope, in Fig. 3a) and then decreases, concomitantly with an increase in the amount of dihydrocitronelal, which suggests that the former is reduced to the latter. The proportion of citronelol (obtained by reduction of the carbonyl group of dihydrocitronelal) is very low but increases slightly as the hydrogenation proceeds.

In examining the influence of variables such as temperature, initial hydrogen pressure, solvent, and catalysts on the process, we defined the selectivity towards reaction products (i) that show in Fig. 1, as

$$S_i = \frac{\text{mmol i}}{\text{mmol products of reaction}} \times 100, \qquad [1]$$

where (i) is citronelal, dihidrocitronelal, citronelol, geraniol, nerol, and 3,7-dimetiloctanol.

On the other hand, citral has two geometric isomers, Z and E. It was thus also interesting to determine the influence of the previous parameters on the changes in both isomers during the reduction process. To this end, we defined the E/Z selectivity, $S_{E/Z}$ as

$$S_{E/Z} = \frac{\text{mmol of E consumed}}{\text{mmol of E consumed + mmol of Z consumed}} \times 100. \qquad [2]$$

As noted earlier, citronelal is the reaction product of the highest industrial interest of all obtained in the process. Table 3 illustrates the influence of solvent, temperature, and hydrogen pressure on $S_{\text{citronelal}}$ and $S_{E/Z}$. Selectivities were determined at 10 and 25% of conversion. The standard reaction conditions were 0.5 *M* citronelal in dioxane, 303 K, 50 mg of catalyst Pd_3/PM2, and 60 psi (initial H_2 pressure). From the results it follows that low pressures and temperatures, in combination with methanol as the solvent, are the best in order to ensure high values of both types of selectivity.

As regards the influence of the support, the last section in Table 3 shows initial rate (r_g), turnover frequency (TON) and selectivity data ($S_{\text{citronelal}}$ and $S_{E/Z}$) for reactions conducted with 0.5 *M* citral in dioxane, an initial H_2 pressure of 60 psi, a temperature of 303 K and 50 mg of catalyst Pd_3/PM2 or Pd_3/PS_{400}. The turnover, TON, was greater for catalyst Pd_3/PS_{400} because it had a smaller metal surface and larger Pd particles (i.e., a lower electron density) than catalyst Pd_3/PM2. However, neither the reaction sequence nor selectivity differed between the two catalysts (citronelal

TABLE 3

Influence of the Temperature, Hydrogen Pressure, Solvent, and Metal Support on the Initial Rate (r_g), Turnover Frequency (TON), and Selectivities ($S_{citronelal}$ and $S_{E/Z}$) of the Process

		r_g mmol · s^{-1} · g_{Pd}^{-1}	TON s^{-1}	$S_{citronelal}$/%		$S_{E/Z}$/%	
				a	b	a	b
Temperature °C	293	13.4	7.87	94	84	79	74
	303	14.6	8.57	88	81	77	69
	313	16.3	9.57	80	73	73	60
	323	17.8	10.45	76	69	68	60
$P_{hydrogen}$ psi	20	11.3	6.63	97	86	83	78
	40	12.9	7.57	94	83	81	76
	60	14.6	8.57	88	81	77	69
	80	15.7	9.22	82	75	76	61
Solvent	MeOH	1.3	0.76	99	96	78	74
	THF	5.1	2.99	97	91	85	73
	CHA	11.7	6.87	92	87	81	69
	DIO	14.6	8.57	88	81	77	69
Catalyst	$Pd_3/PM2$	14.6	8.57	88	81	77	69
	Pd_3/PS_{400}	8.7	11.82	82	73	75	67

Note. Conversion: a = 10%; b = 25%. Standard conditions: amount of catalyst ($Pd_3/PM2$), 50 mg; hydrogen pressure, 60 psi; temperature, 303 K; citral concentration, 0.5 *M*; solvent, dioxane.

and dihydrocitronelal were the main reaction products with both).

Richard *et al.* (5), using cinnamaldehyde and Pt catalysts, found the selectivity to be markedly dependent on particle size. Thus, large particles led to the unsaturated alcohol preferentially, whereas small particles led to the saturated aldehyde. On the other hand, our experiments with citral showed neither turnover nor selectivity to depend on particle size, consistent with the previous findings of Galvagno *et al.* (34) for citral. The explanation for the divergence with the results of Richard *et al.* lies in steric factors related to the molecule to be reduced. Thus, the stiffness of the cinnamaldehyde molecule (where the phenyl ring is conjugated with C=C and C=O bonds) favours its adsorption via the C=C bond on small particles and the C=O bond on large particles. On the other hand, the citral molecule can rotate freely about the C_4–C_5 bond, thus facilitating adsorption via the C_2=C_3 bond, whatever the particle size.

$S_{E/Z}$ always exceeded 50%, so isomer E was reduced to a greater extent than was isomer Z. This is logical, taking into account that the reduction rate, calculated from the distribution profiles for the two isomers at similar concentrations, was greater for isomer E than for isomer Z (e.g., 6.2 vs 4.1 mmol/s · g_{Pd} as calculated from the distribution profile of Fig. 3b at a 0.15 *M* concentration of each isomer).

As a rule, the reduction of an α,β-unsaturated carbonyl compounds with a single-metal catalyst is influenced by various types of factors, namely: (a) *geometric* (e.g., support structure, extent of metal dispersion, accessibility of catalyst pores, all dependent on the morphology of the metal surface) (5, 6); (b) *electronic*, which arise from the differential electron density of palladium metal particles (high in small particles and low in small ones) (35, 36); and (c) *steric*, or related to the molecule of the structure to be reduced (37–40). The reduction of citral with Pd catalysts is affected by geometric and steric factors, but scarcely by electric factors, which are highly influential on the reduction of cinnamaldehyde, however. All this favours the reduction of C=C double bonds over the C=O group, as is the case in most reductions of α,β-unsaturated carbonyl compounds with a single-metal catalyst (8–11).

Effect of $FeCl_2$ in the Reaction Medium

Citral was also reduced in a reaction medium containing $FeCl_2$ in an Fe^{2+}/Pd ratio of 0–2. Figures 4a, b show the variation of the TON and the selectivity of the different reaction products (citral, citronelal, dihydrocitronelal,

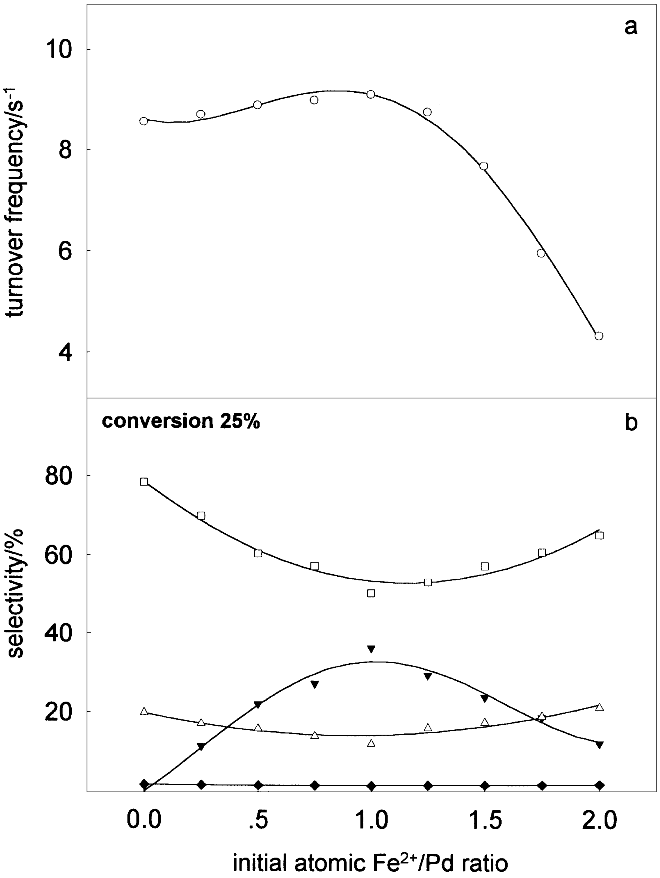

FIG. 4. Variation of the turnover frequency (TON) (a), and selectivity (b) in the reduction of citral with $Pd_3/PM2$ in the presence of variable amounts of $FeCl_2$. Reaction conditions: amount of catalyst ($Pd_3/PM2$), 50 mg; solvent, dioxane; temperature, 303 K; citral concentration, 0.5 *M*; conversion, 25% (○, (E + Z)-citral; □, citronelal; △, dihydrocitronelal; ◆, citronelol; ▼, unsaturated alcohol (geraniol + nerol)).

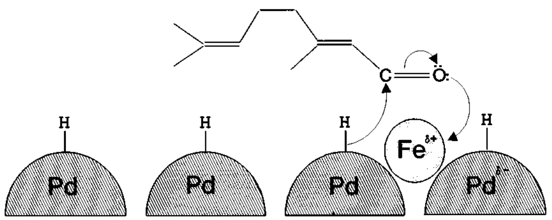

FIG. 5. Model for the selective adsorption–reduction of citral on a Pd catalyst doped with $FeCl_2$.

geraniol, and nerol) as a function of the Fe^{2+}/Pd ratio at 25% of conversion.

The effect of Lewis acids on the reduction of carbonyl compounds with Pd catalysts was previously studied (41). The selectivity change introduced by $FeCl_2$ arises from the presence of positively charged ferrous ions on the surface of Pd particles. These species may originate from unreduced Fe^{2+} ions or electron-deficient Fe^0 atoms resulting from electronegativity differences between iron and palladium (Fig. 5). Surely, only a few of initial ferrous ions appear either as Fe^0 atoms over palladium or unreduced Fe^{2+} ions associated with palladium particles. The rest of ferrous ions stay in solution, far from the palladium, and they do not take part in the reaction. In futher works, we will attempt to determine the percentage of initial ferrous ions that take part in the reaction. The interaction of positively charged iron with the carbonyl group causes an electron to be transferred from the oxygen atom in the C=O group of citral, which is thus made electron-deficient. Next, an electron rearrangement takes place by which one of the electrons in the pair that forms the double bond is transferred to the oxygen atom while the other is used to form a C–H bond between the carbonyl carbon and a proton bonded to the more electronegative metal (Pd). Finally, the formation of a bond between the second proton and the oxygen causes the alcohol to be released (13, 42). In this context, Coq *et al.* (32) claim that low-coordinated acid sites ($Sn^{\delta+}$, Zr^{3+}) involved in a two-metal catalyst (usually with Ru) favour anchoring via the C=O double bond and, hence, its reduction.

The reduction rate and the proportion of each reaction ingredient varied with the Fe^{2+}/Pd ratio. Thus, the maximum amount of unsaturated alcohol (geraniol + nerol) was obtained at an initial atomic Fe^{2+}/Pd ratio close to unity. On the other hand, r_g increased linearly with increase in such a ratio up to $Fe^{2+}/Pd = 1$, above which it decreased sharply with further increases. The origin of this variation pattern for r_g lies in the above-described mechanism. Thus, below an Fe^{2+}/Pd ratio of 1, the presence of Fe^{2+} facilitates the emergence of electric factors, which are absent from the single-metal catalyst. On the other hand, in the presence of a large amount of Fe^{2+} (*viz.* at an Fe^{2+}/Pd ratio above unity), the dissociative cleavage of H_2 on Pd atoms is hindered and the reduction rate decreased as a result. On the other hand, an excessive proportion of Fe atoms (an Fe^{2+}/Pd mole ratio above 1) would turn the two-metal catalyst into a single-metal (Fe) catalyst of selectivity similar to that obtained with the single-metal Pd catalyst (initial Fe^{2+}/Pd ratio = 0) (see Fig. 4b).

Figure 6 shows the hydrogen uptake (a) and products distribution (b) profiles for a reaction carried out at 303 K and an initial Fe^{2+}/Pd ratio of 1. As can be seen, the amount of unsaturated alcohol (geraniol + nerol) increased with increasing hydrogen uptake, whereas that of citronelal peaked and then decreased. The amount of citronelol obtained was very small, consistent with the results in the absence of $FeCl_2$.

For easier comparison of the performance of the three most frequently used catalysts, Fig. 7 shows the selectivity profiles (obtained from Eq. [1]) for Pd_3/PS_{400} (a), $Pd_3/PM2$ (b), and $Pd_3/PM2$ doped with $FeCl_2$ in a unity Fe^{2+}/Pd mole ratio (c). Catalyst $Pd_3/PM2$, was the most selective towards

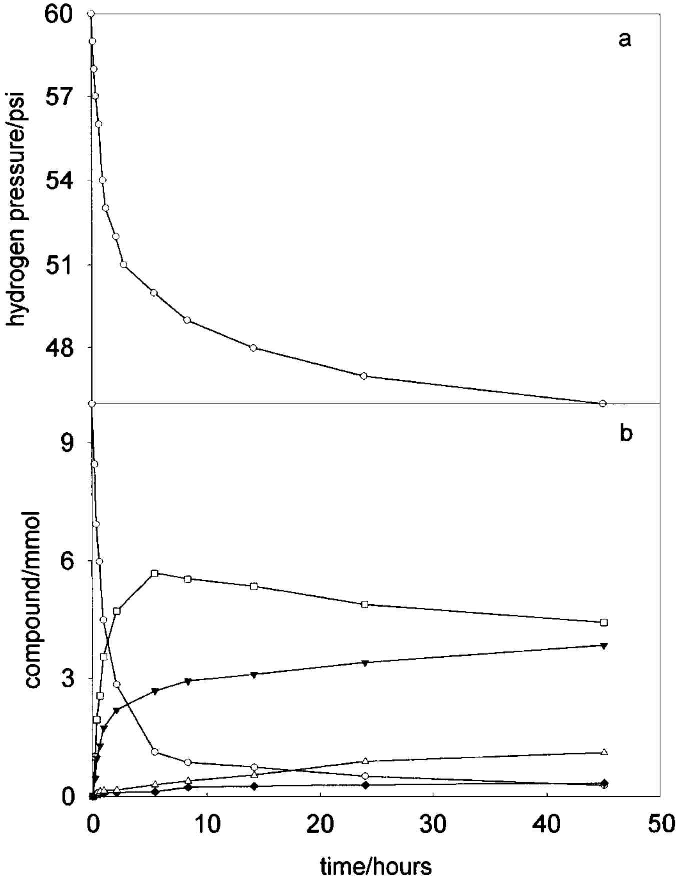

FIG. 6. Hydrogen uptake (a) and product distribution (b) profiles for the reduction of citral with catalyst $Pd_3/PM2$ in a reaction medium containing $FeCl_2$ at an Fe^{2+}/Pd ratio of 1. Reaction conditions: amount of catalyst ($Pd_3/PM2$), 50 mg; solvent, dioxane; temperature, 303 K; citral concentration, 0.5 *M* (○, (E + Z)-citral; □, citronelal; △, dihydrocitronelal; ◆, citronelol; ▼, unsaturated alcohol (geraniol + nerol)).

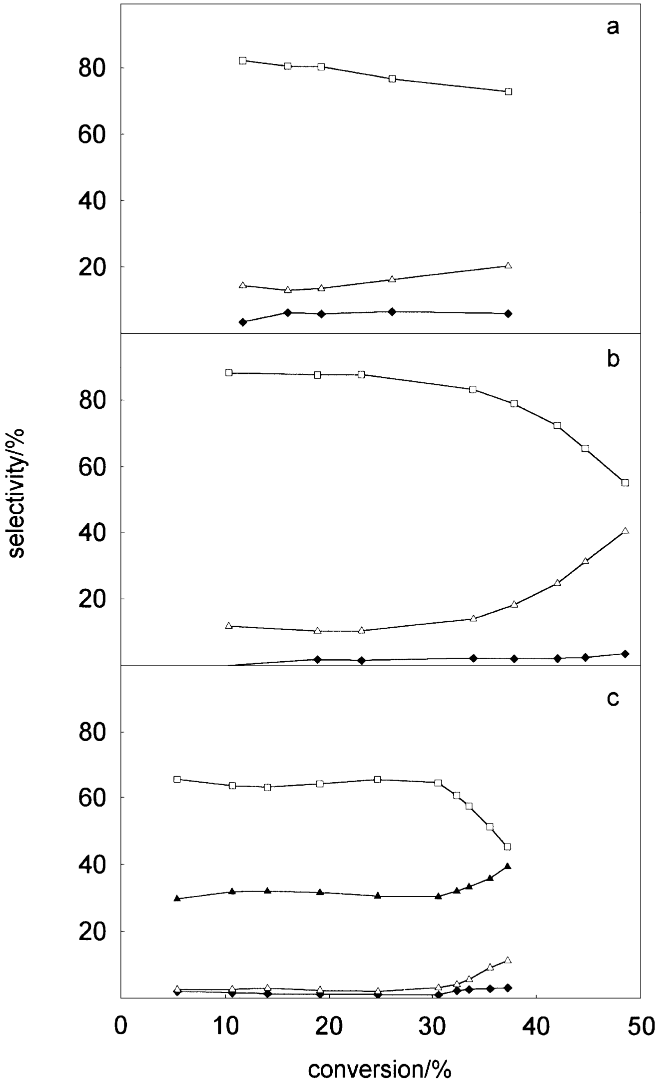

FIG. 7. Selectivity versus conversion profiles for the catalysts Pd$_3$/PS$_{400}$ (a), Pd$_3$/PM2 (b), and Pd$_3$/PM2 with FeCl$_2$ (relation molar Fe^{2+}/Pd = 1) (c). Reaction conditions: amount of catalyst (Pd$_3$/PM2), 50 mg; solvent, dioxane; temperature, 303 K; citral concentration, 0.5 *M* (□, citronelal; △, dihydrocitronelal; ◆, citronelol; ▲, unsaturated alcohol (geraniol + nerol)).

citronelal at any conversion and the catalyst doped with FeCl$_2$ the most selective towards the unsaturated alcohol (geraniol + nerol).

CONCLUSIONS

The reduction of citral with a single-metal Pd catalyst yields the saturated aldehyde; the selectivity towards citronelal is especially high at low pressures and temperatures. The solvent has a marked effect on the reduction rate; thus, nonpolar solvents lead to greater reduction rates. The use of alcohols gives rise to the formation of acetals between the solvent and citral, the reduction process being accompanied by side reactions which, together with steric hindrance, decrease the rate at which the substrate can access active sites.

The hydrogenation of the E (*trans*) isomer is favored over that of the Z (*cis*) isomer as a result of the adsorption of the latter on the catalyst surface being sterically hindered.

The presence of Lewis acid additives such as FeCl$_2$ induces an electron transfer between the two metals (Fe and Pd) arising from their differential electronegativity; the effect favours adsorption of citral via the $C=O$ group and, hence, increases the selectivity towards geraniol and nerol.

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