

Hydrogenation of 3-Methyl-crotonaldehyde on the Pt(553) Stepped Surface: Influence of the Structure and of Preadsorbed Tin

T. Birchem,* C. M. Pradier,*¹ Y. Berthier,* and G. Cordier†

*Laboratoire de Physico-Chimie des Surfaces, U.R.A. 425 associée au CNRS, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75005 Paris, France; and †Rhône-Poulenc Industrialisation, 24 avenue Jean Jaurès, 69151 Décines-Charpieu, France

Received May 27, 1994; revised January 2, 1996; accepted January 31, 1996

The hydrogenation of 3-methyl-crotonaldehyde was studied, in the gas phase, on a well-defined Pt(553) or Pt(S)-[5(111) × (111)] stepped surface and the results are compared with those of similar experiments on Pt(111). The selectivity is governed mainly by structural factors. Low-coordination step atoms create favorable hydrogenation sites for the production of saturated aldehyde, whereas (111) flat terraces lead to the formation of unsaturated alcohol. The influence of a preadsorbed submonolayer of tin was investigated on Pt(111) and Pt(553). The effect of this metallic additive depends on its local concentration and arrangement. Tin drastically changes the selectivity of Pt(553). At low coverage, tin, located in the vicinity of the steps, changes the selectivity to the benefit of the saturated alcohol. At higher coverage ($\theta > 0.3$), tin grows in islands on the terraces and the expected improvement in selectivity toward unsaturated alcohol was observed, suggesting a combination of electronic and geometric effects. © 1996 Academic Press, Inc.

1. INTRODUCTION

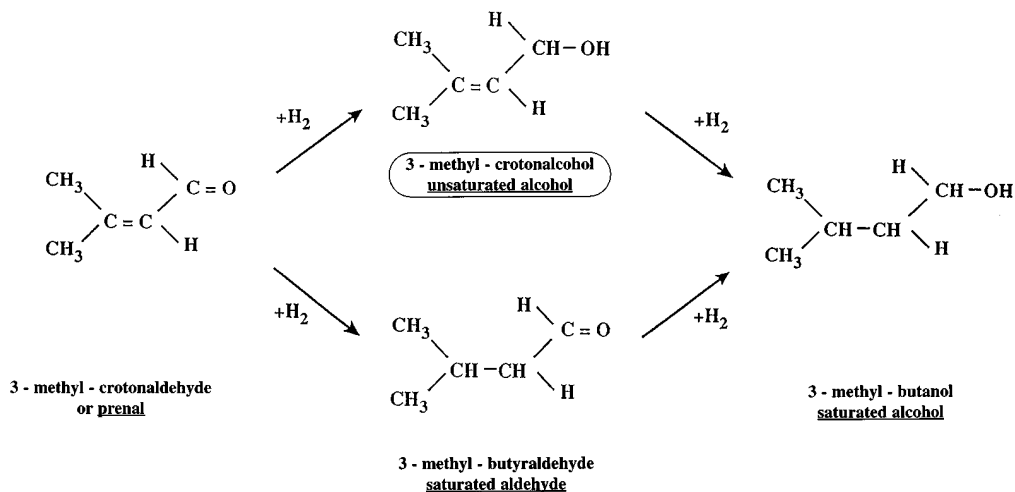
The selective hydrogenation of α,β -unsaturated aldehydes into corresponding unsaturated alcohols is a reaction of interest to the fine chemical industry (1, 2). From a theoretical point of view, this reaction raises interesting problems of selectivity for it is known that attempts to correlate the reactivities of these conjugated molecules to those of the monounsaturated ethylenic and carbonyl compounds have failed (3). Over the past 10 years, interest in this topic has been revived and many studies have been devoted to this nonfacile catalytic reaction (4–15). These studies, mostly carried out with catalysts based on dispersed group VIII modified metals, stressed the importance of electronic and, above all, steric effects on the selectivity of this reaction. Nevertheless, clear-cut conclusions are often difficult to draw with these complex catalysts and any attempt to gain further insight into the mechanism of this hydrogenation reaction is made easier by studying more simple catalytic systems.

In the course of an ongoing study, our group is investigating the gas-phase hydrogenation of 3-methyl-crotonaldehyde or prenal (Scheme 1), on different well-defined single-crystal platinum surfaces. This work clearly underlines the importance of the crystallographic orientation of the platinum surface on the selectivity: the hydrogenation of prenal on Pt(111) leads mainly to the unsaturated alcohol (16), whereas on Pt(110) the main product is the saturated aldehyde (17). This structure sensitivity was satisfactorily accounted for by a geometric effect: on the one hand, the close-packed structure of the (111) surface induces a steric hindrance for the accommodation of the two methyl groups; the molecule is thus mainly adsorbed and activated through its C=O unsaturation. On the other hand, the furrowed structure of the (110) surface removes this steric hindrance and enables the activation of the whole conjugated system of the molecule on the less coordinated atoms, leading to the formation of saturated aldehyde, via an enolic intermediary species.

To confirm and better understand this determining structure effect, we report, in this paper, a catalytic study of the hydrogenation of prenal on a stepped platinum surface. In this way, we studied the influence of surface defects, the location and concentration of which are known and controlled. We also investigated a catalytic surface that is closer to a real one than the low-index planes. We chose the Pt(553) surface, which is made up of a regular arrangement of (111) terraces and (111) monoatomic steps as depicted in Scheme 2. These (111) steps give the Pt(553) surface structural characteristics intermediate between those of Pt(111) and Pt(110). This enables valuable comparisons to be made with the two latter previously studied surfaces.

In the second part of this paper, we focus on the influence of a preadsorbed submonolayer of tin on Pt(111) and on Pt(553). Among bimetallic catalysts that have motivated intensive studies, the Pt–Sn system has attracted particular attention because of its interesting properties in reforming catalysis (18). Tin codeposited with platinum (15, 19, 20) or with ruthenium (21) on supported catalysts is also known to improve the selectivity to unsaturated alcohol due to preferential activation of the C=O bond.

¹ To whom correspondence should be addressed.



SCHEME 1. Reaction network for the hydrogenation of prenal.

Working on well-defined planes of platinum provides a better knowledge of the location of the tin atoms on the surface. The effect of addition of a controlled amount of tin on different faces of platinum has given rise to several publications (22–26). From these studies, it appears that tin on Pt(111) can lead to complex surface phase diagrams with, on annealing at 700–800 K, possible formation of a so-called surface alloy. Depending on the tin coverage, two models for surface alloys have been identified by Pafett and Windham on Pt(111), characterized by respectively a $p(2 \times 2)$ and a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern (22). Important is that these alloys have never been observed in the absence of heating the sample after tin evaporation (27). On Pt(100), ordered alloys have also been identified on annealing at 750–850 K (24, 26), and the authors concluded that the annealing, which is required to activate alloy phase conversion of the bimetallic surface, is mostly not dependent on the face orientation. To our knowledge, tin deposition has never been investigated on a stepped surface of platinum.

In the present work, the reaction of prenal hydrogenation has been carried out on clean platinum (553) and on platinum (553) covered with different levels of tin. For comparison, results on Pt(111) are recalled and some catalytic tests have been performed on Pt(111) in the presence of 0.5 monolayer (ML) of tin. The influence of tin on selecti-

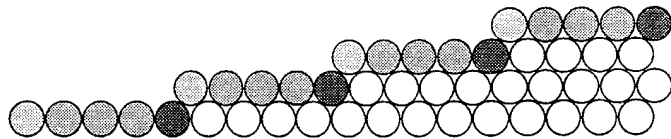
vity was carefully investigated and correlated with the most likely adsorption modes of the prenal molecule.

2. EXPERIMENTAL

The experimental procedure was previously described (16) and is only briefly reported in this paper. To obtain the Pt(553)-oriented sample, a 1-cm-thick, (111)-oriented disk of platinum, 5N purity, was cut at an angle of 12.2° from the surface plane by spark erosion. The correct orientation was checked by X-ray back-reflection diffraction and further on by LEED. The pattern of the (553) plane differed from that of the (111) plane in that the spots were split into doublets at certain voltages. The interdistance of the (10) doublet leads to a terrace length of 11.4 Å, in acceptable agreement with the value of 10.8 Å for an ideal Pt(553) plane.

To avoid any catalytic activity from the edge of the sample, the latter was coated with $\text{SiO}_2\text{-Al}_2\text{O}_3$ cement, heated at 1500 K to obtain a glasslike coating. This technique did not induce any contamination of the disk surface by silicon or aluminum, detectable by Auger spectroscopy.

The surface, which was mechanically polished to 0.5 μm , was subsequently introduced into UHV preparation chamber and was cleaned by repeated cycles of argon ion sputtering, low-pressure oxygen treatment, and annealing to 1200 K. The state of the surface was checked by LEED and Auger techniques before and after every catalytic test. At 353 K, the temperature at which the catalytic hydrogenation experiments were carried out, the cleaned Pt(553) sample exhibited a $p(1 \times 1)$ pattern in agreement with the high thermal stability of stepped platinum surfaces (28). The cleaned sample was then transferred, under UHV conditions, to an attached stainless-steel batch reactor connected to a glass reactor containing a homogeneous mixture of prenal and hydrogen ($P_{\text{H}_2}/P_{\text{prenal}} \sim 10^4$). The reaction was



SCHEME 2. The Pt(553) Surface is an array of (111) terraces represented by gray-colored atoms, with monoatomic steps represented by high-coordination dark-gray and low-coordination light-gray atoms.

monitored by an on-line gas-phase chromatograph, and to avoid any transport limitation phenomenon, the circulation of the gases was ensured by a pump producing a flow rate of 2 liters/min.

Tin (99.999%) was evaporated at room temperature, in the UHV chamber, from a Knudsen cell with a base pressure of 2×10^{-9} Torr. The $\text{PtN}_{6,7}\text{O}_{4,5}\text{O}_{4,5}$ (64 eV) and $\text{SnM}_5\text{N}_{4,5}\text{N}_{4,5}$ (430 eV) peak-to-peak Auger electron spectroscopy transitions were recorded during the evaporation process to determine the coverage, θ_{Sn} (29). In a preliminary series of experiments, the deposition of tin on Pt(111) and Pt(553) had been monitored by Auger electron spectroscopy and the monolayer evaluated as the break of the Pt Auger intensity curve as a function of time. Our Auger ratio-versus-coverage calibration is in good agreement with that reported by Pafett and Windham on the (111) plane of platinum (22).

To minimize the complex effects due to Pt–Sn alloying, in particular the possible role of subsurface atoms, in our experiments tin deposition was carried out at room temperature, followed by the hydrogenation tests at 350 K without any annealing of the sample.

3. RESULTS

3.1. Hydrogenation of Prenal on Pt(553)

The gas-phase hydrogenation of prenal was performed on Pt(553) under conditions identical to those used in our previous study on Pt(111), namely, $P_{\text{prenal}} = 22 \times 10^{-3}$ Torr, $P_{\text{H}_2} = 400$ Torr, and $T = 353$ K (1 Torr = 133.3 Pa). This enables a straightforward comparison to be made of the respective behaviors of the two faces. The composition of the gas phase as a function of time is shown in Fig. 1.

Activity. The activity was characterized by the turnover frequency (TOF), i.e., the number of molecules of prenal converted per second and per surface platinum atom, at the

origin of the reaction, assuming a surface atomic density of 1.6×10^{15} atoms cm^{-2} for Pt(553): $\text{TOF}_{(553)} = 40 \times 10^{-2}$ molecules $\text{atom}^{-1} \text{s}^{-1}$.

Under identical experimental conditions, the stepped Pt(553) surface is twice as active as the flat Pt(111) surface. This result is in agreement with the increase in activity with surface roughness already observed between Pt(111) and Pt(110) (17). To better understand this structure sensitivity, one may ask whether the surface concentration of hydrogen or that of the organic molecules is rate limiting.

To answer that question, the reaction was performed first at constant prenal partial pressure, varying the hydrogen partial pressure, and then the other way round. In the two series of experiments, the temperature of the reaction was maintained constant at 353 K. In the range 100 to 500 Torr, the initial activity increased with hydrogen pressure, which leads to a partial kinetic order toward hydrogen: β_{H_2} equal to 0.5. In the range 4×10^{-3} to 31×10^{-3} Torr, the initial acidity was found to be insensitive to the prenal partial pressure: α_{prenal} equal to 0.

Selectivity. Figure 2 shows the selectivities to the main products of the reaction at 10% conversion for both Pt(553) and Pt(111). The general tendency is the same; the hydrogenation of prenal both on Pt(111) and on Pt(553) leads mainly to the formation of unsaturated alcohol. Noticeable is that the fraction of saturated aldehyde is higher on the stepped surface than on the flat plane of platinum (18% instead of 5%).

As the hydrogenation reaction is carried out in a batch reactor, the selectivities change with conversion. Figure 3 reports the evolution of the selectivities on Pt(553) for each product with increasing conversion. The trends are the same as those observed for the hydrogenation of prenal on Pt(111) (16). From the very beginning of the reaction the unsaturated alcohol is hydrogenated into saturated alcohol through a competitive hydrogenation process with prenal.

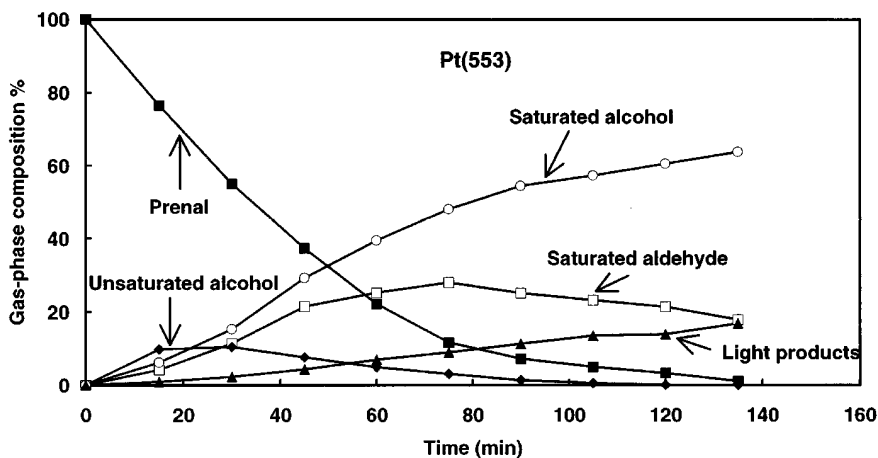


FIG. 1. Hydrogenation of prenal under the standard conditions: $P(\text{H}_2) = 400$ Torr, $P(\text{prenal}) = 2.2 \times 10^{-2}$ Torr, and $T = 353$ K on Pt(553).

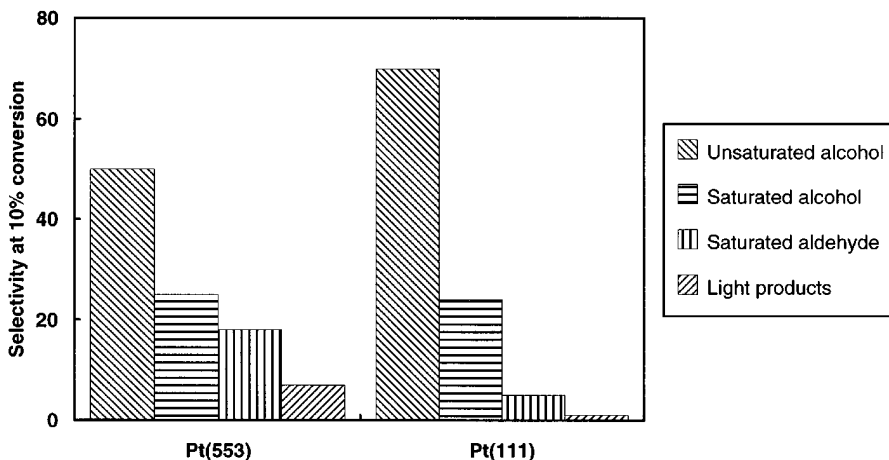


FIG. 2. Comparison of the selectivities at 10% conversion on Pt(111) and Pt(553) under the standard conditions. The error on the selectivity values was evaluated to be less than 10%.

The hydrogenation of the C=O double bond of the saturated aldehyde is a much more difficult reaction, and occurs only when this molecule is the most abundant unsaturated product in the gas phase (conversion >70%).

The influence of hydrogen partial pressure on selectivity was studied under the following conditions: $100 \text{ Torr} < P_{\text{H}_2} < 500 \text{ Torr}$, $P_{\text{prenal}} = 20 \times 10^{-3} \text{ Torr}$, and $T = 353 \text{ K}$. Hydrogen partial pressure has no significant influence on selectivity. The same result was found on the two previously studied surfaces, Pt(111) (16) and Pt(110) (17).

Much more important is the influence of prenal partial pressure on selectivity. Figure 4 reports the evolution of the selectivities in the following range of pressure: $P_{\text{H}_2} = 400 \text{ Torr}$, $4 \times 10^{-3} \text{ Torr} \leq P_{\text{prenal}} \leq 31 \times 10^{-3} \text{ Torr}$, and $T = 353 \text{ K}$. The saturated alcohol is the major product of the reaction at low pressure of prenal; it decreases to the benefit of the unsaturated alcohol when the pressure of prenal increases.

3.2. Influence of Tin

It is clear from the results presented above that only 20% of low-coordination step atoms can induce significant changes in activity and selectivity compared with a flat (111) surface. In the second part of this work, the effect of tin was investigated on Pt(111) at 0.5 monolayer (ML) coverage and on Pt(553) at 0.5, 1, "2" monolayer coverages. The coverage on Pt(553) was estimated by taking the same calibration as that of Paffett and Windham on Pt(111) (22); the "2" ML coverage was also based on their curve, assuming a three-dimensional and not a layer-by-layer growth. This assumption was further confirmed by the drop in activity observed in the presence of tin. A coverage equal to 0.5 monolayer, corresponding to $\theta_{\text{Sn}} = 0.3$, was chosen first for it is close to the theoretical amount necessary to occupy the step atoms of the (553) plane. The metallic additive was evaporated *in situ*, and its adsorption,

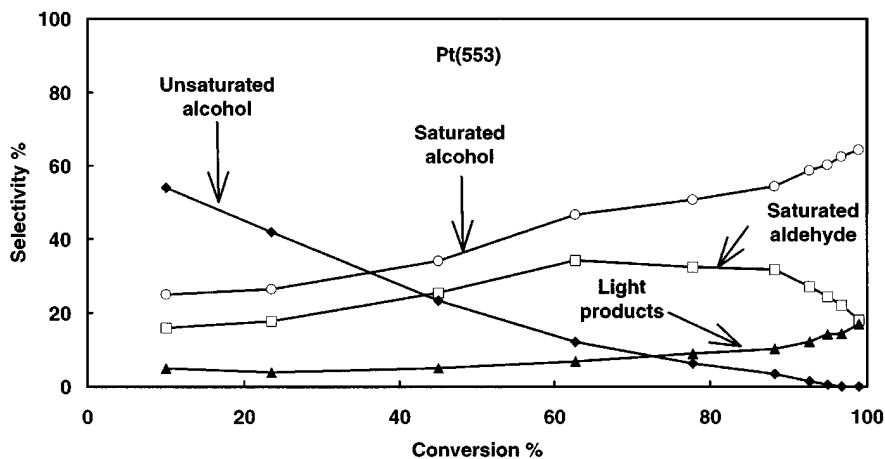


FIG. 3. Selectivity versus conversion for the hydrogenation of prenal under the standard conditions: $P(\text{H}_2) = 400 \text{ Torr}$, $P(\text{prenal}) = 2.2 \times 10^{-2} \text{ Torr}$, and $T = 353 \text{ K}$.

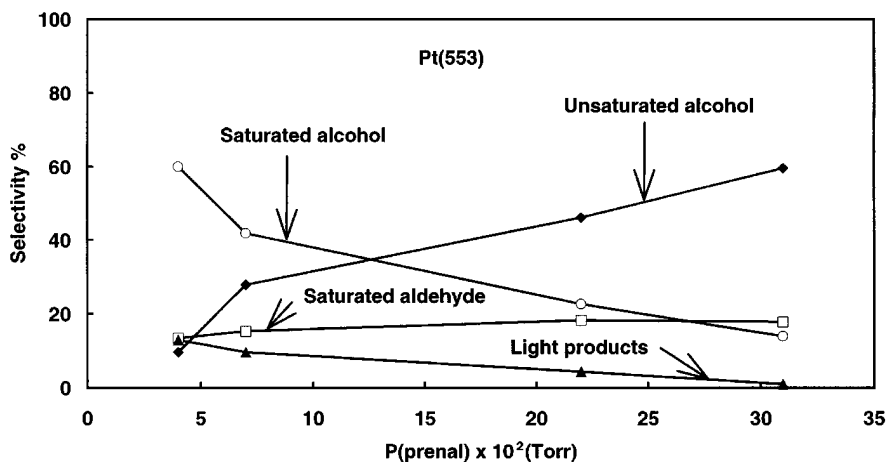


FIG. 4. Influence of the partial pressure of prenal on the selectivity at 10% conversion, under the standard conditions.

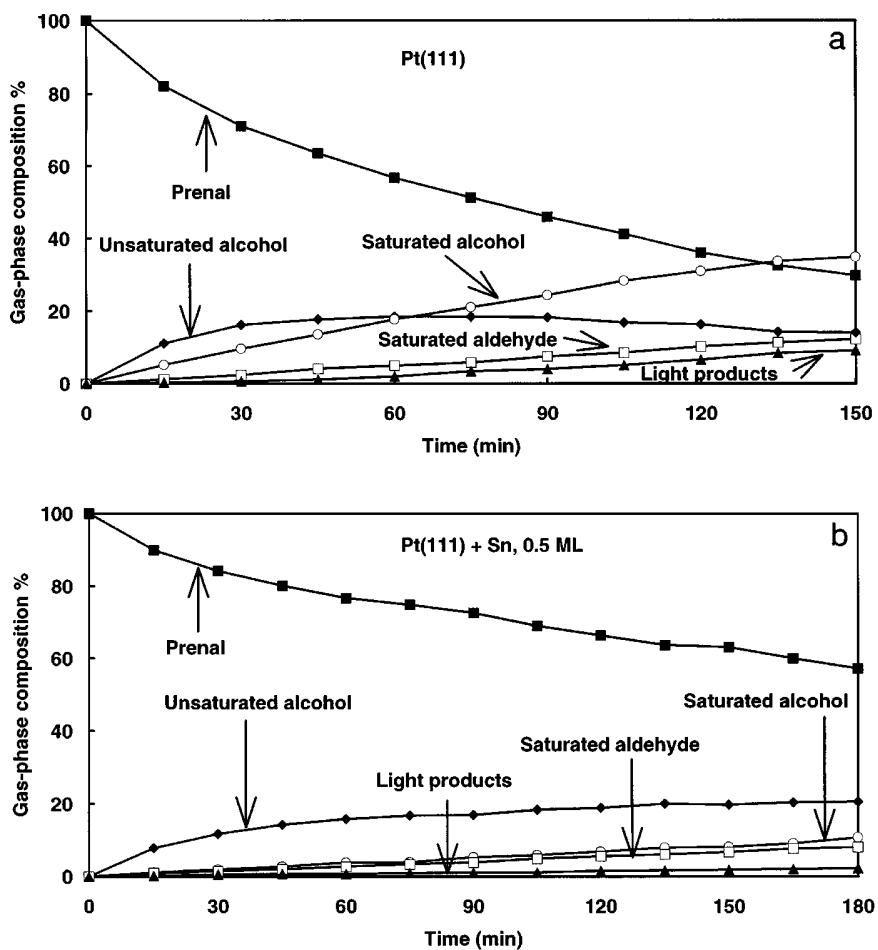


FIG. 5. Hydrogenation of prenal on clean Pt(111) (a) and on Pt(111) covered with 0.5 monolayer of Sn (b). $P(\text{H}_2) = 400$ Torr, $P(\text{prenal}) = 2.2 \times 10^{-2}$ Torr, and $T = 353$ K.

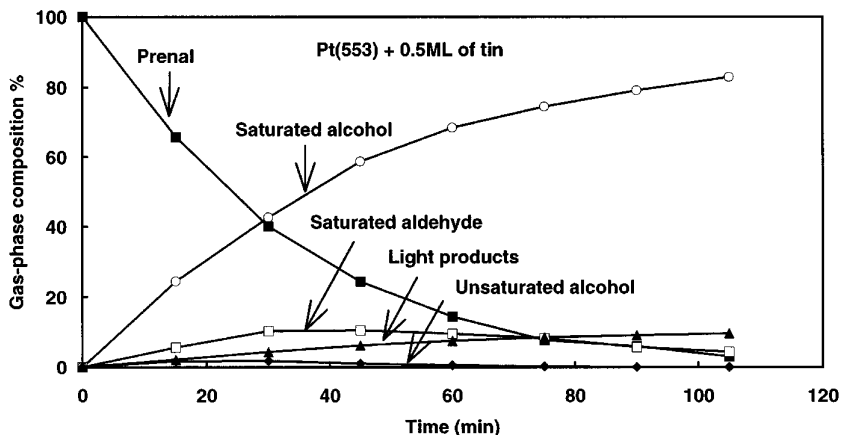


FIG. 6. Hydrogenation of prenal on Pt(553) in the presence of 0.5 monolayer of tin. $P(\text{H}_2) = 400$ Torr, $P(\text{prenal}) = 1.8 \times 10^{-2}$ Torr, and $T = 353$ K.

coverage, and arrangement were checked before the catalytic tests.

0.5 ML of tin on Pt(111), $\theta_{\text{Sn}} = 0.3$. The hydrogenation of prenal on Pt(111) + 0.5 ML(Sn), $\theta_{\text{Sn}} = 0.3$, was carried out under the standard experimental conditions: $P_{\text{H}_2} = 400$ Torr, $P_{\text{prenal}} = 22 \times 10^{-3}$ Torr, and $T = 353$ K. The influence of tin on the hydrogenation of prenal on Pt(111) is clearly demonstrated in Fig. 5.

In the presence of 0.5 ML of tin on Pt(111), a 30% decrease in activity was observed. At the same time, the selectivity toward the unsaturated alcohol was slightly improved (80% instead of 70%), compensated by a lower formation of saturated alcohol.

0.5 ML of tin on Pt(553). The hydrogenation reaction was carried out under the following experimental conditions: $P_{\text{prenal}} = 18 \times 10^{-3}$ Torr, $P_{\text{H}_2} = 400$ Torr, and $T = 353$ K. These conditions are close to the standard conditions previously used.

The TOF at the origin of the reaction was found to be

equal to 31×10^{-2} molecules atom $^{-1}$ s $^{-1}$, corresponding to a 25% drop in activity.

The kinetics of the reaction changed due to the presence of tin as indicated by the orders with respect to both reactants. The partial kinetic orders were now equal, respectively, to 0.7 and 0.2 for prenal and hydrogen (0 and 0.5 in the absence of tin).

Figure 6 shows the time course of the reaction on Pt(553) covered with 0.5 ML of tin. It is clear from a comparison with Fig. 1 that 0.5 ML of tin induces a drastic change in the selectivities: the saturated alcohol is now the main product from the beginning of the reaction, and the fraction of unsaturated alcohol is reduced to less than 10% at 10% conversion.

1 and "2" ML of tin on Pt(553). The influence of tin on activity and selectivity was investigated up to "2" ML on the stepped surface. The hydrogenation reaction was carried out under the standard conditions and the results are reported in Fig. 7. The activity decreases with increasing

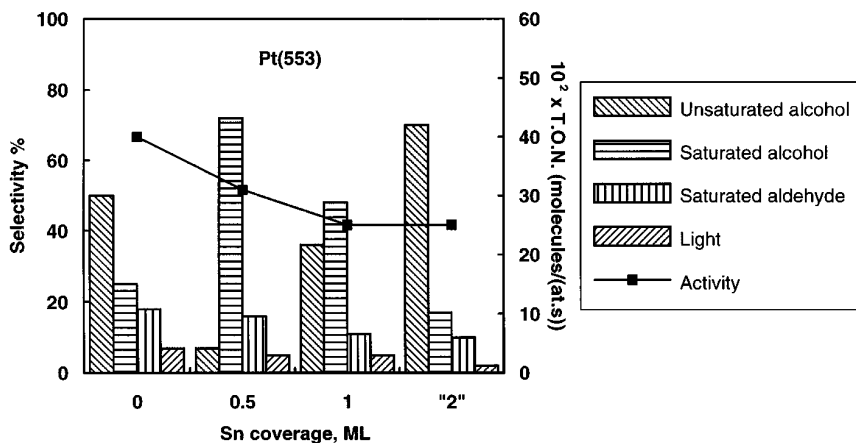


FIG. 7. Hydrogenation of prenal on Pt(553) under the standard conditions: $P(\text{H}_2) = 400$ Torr, $P(\text{prenal}) = 2 \times 10^{-2}$ Torr, and $T = 353$ K. Influence of the coverage of tin on the activity and the selectivity.

TABLE 1

Decrease in Activity and Changes in Selectivity Induced by Various Coverages of Tin on Pt(553)

	Sn coverage (ML)			
	0	0.5	1	"2"
Decrease in activity (%)	—	25	40	40
Unsaturated alcohol (%)	50	9	36	70
Saturated alcohol (%)	25	70	47	18
Saturated aldehyde (%)	18	16	12	10
Light products (%)	7	5	5	2

Sn coverage. Nevertheless, in the presence of 1 ML of tin ($\theta_{\text{Sn}} = 0.6$), the initial activity is only 40% lower than that measured on the clean Pt(553) surface. When the tin coverage increases beyond 1 ML, the rate of prenal hydrogenation remains constant, 40% lower than in the absence of tin.

As regards the selectivity, an increase in Sn coverage beyond 0.5 ML induces an improvement in the selectivity to unsaturated alcohol, which reaches 35% for $\theta_{\text{Sn}} = 0.6$, a lightly higher value than in the absence of tin, and 70% for "2" ML, a value even higher than that on clean Pt(553).

The catalytic activity and selectivity of the reaction on Pt(553) and their variations with tin are summarized in Table 1.

4. DISCUSSION

As mentioned in the Introduction, hydrogenation of unsaturated aldehydes has given rise to extensive studies on supported and unsupported platinum catalysts. The influence of the size and structure of the molecule has been elucidated, but little is known about the influence of the catalyst structure itself. The present work involving a study of the reaction on two planes of platinum of different structures and the influence of tin adatoms on both surfaces is discussed in terms of activity and selectivity. The results show considerable change with the structure and with the amount of tin adatoms.

Activity of the Hydrogenation Reaction on Pt(553) and Comparison with Pt(111)

The Pt(553) surface leads to an increase in the rate of hydrogenation by a factor of 2 compared with the flat (111) plane. Considering the kinetic order toward prenal, equal to zero both on Pt(111) and on Pt(553), one can say that, under reaction conditions, the surfaces are saturated with organic molecules in the entire pressure range. The rate of hydrogen dissociation is known to be enhanced by a factor of 10 in the presence of steps (30, 31), but this is not determining in view of the rate of $\text{H}_2\text{-D}_2$ exchange, one order of magnitude higher than that of prenal hydrogenation on

Pt(111) (16) and consequently not rate limiting. We rather ascribe the two fold increase in the hydrogenation rate to the diffusion of hydrogen atoms from the sites of dissociation to the adsorbed organic intermediate being more rapid on Pt(553) than on a flat, close-packed, surface. We believe that the rate-limiting factor of the reaction is the amount of dissociated hydrogen in the vicinity of the adsorbed molecules of prenal. This fits well with the positive order of the reaction toward hydrogen.

Selectivity of the Reaction on Clean Pt(553) and Comparison with Pt(111)

Steric considerations have often been put forward to explain the selectivity of hydrogenation of unsaturated aldehydes. Size and number of substituents, for instance, were shown to be determining on supported platinum catalysts (15, 21). Also, the structure of the catalyst may induce a "chemoselectivity" (32). In that respect, the size of zeolite micropores (33) or the geometry of the active sites (16, 17) can be determining. The present results, obtained on two closely related surfaces, differing only in the presence of monoatomic steps, will give new insights into this domain of comprehension.

At this point, it is interesting to report on a recent theoretical determination of the preferential adsorption modes of unsaturated aldehydes on various planes of platinum. Delbecq and Sautet (34) have shown that, depending on the face orientation, the adsorption geometries are totally different: on Pt(111), the di- σ -CO mode is preferred, whereas on a stepped surface, the $\pi\text{CC}(\perp)$ and the di- σ -CO geometries are in competition. Note that the authors did not consider the (553) plane as their model stepped surfaces but one having (100) instead of (111)-type steps. This may slightly change the tilt angle of the adsorbed molecules on the step edges, but not the tendency in favor of $\pi\text{CC}(\perp)$ activation of the molecule. These calculated adsorption geometries are of great interest since they confirm that, though adsorption is only an elementary step of the reaction mechanism, it may govern the selectivity of the whole reaction. Moreover, in the case of prenal, the C=C bond, enriched in electrons due to the donor effect of the methyl groups, is likely to interact strongly with the atoms of low coordination on the edges of the steps. Assuming that the bond involved in the adsorption of a molecule is the first one to be hydrogenated, one may easily explain the observed initial selectivity of the reaction. On the Pt(553) surface, the di- σ -CO activation on the (111) terraces accounts for the unsaturated alcohol as the main product and the $\pi\text{CC}(\perp)$ mode, favored by the steps, accounts both for the saturated aldehyde as the second most abundant product of reaction and for the non-negligible fraction of "light" products (mainly isobutene), coming from hydrogenolysis reactions. In fact, hydrogenolysis reactions are known to be particularly easy on atoms of low coordination (28).

The above-discussed results on Pt(553) are in full agreement with the conclusions drawn for the hydrogenation of prenal on Pt(111) and on Pt(110), the surface exhibiting the highest steric hindrance toward a CC adsorption mode, and the one having low-coordination atoms that favor the formation of saturated aldehyde and hydrogenolysis products. Let us note that the products of hydrogenolysis do not poison the surface because this reaction is run in the presence of a huge excess of hydrogen. We think that light alcohols desorb and could not be detected with our gas chromatograph setup for C₄ and C₅ compounds.

The nondependence of selectivity on P_{H_2} simply implies that increasing the hydrogen partial pressure does not change the adsorption mode of the prenal molecules. Conversely, variations of selectivity with P_{prenal} can be related to a change in the surface coverage. At low prenal pressure the higher selectivity toward the saturated alcohol can be explained by an easier and quicker addition of two H₂ molecules to the unsaturated aldehyde or by immediate readsorption and second hydrogenation of the monohydrogenated product; when the partial pressure of prenal increases, activation of the C=O bond becomes preferential and we again observe a regime in which the selectivity is governed by the steric hindrance of the two methyl groups.

Influence of Tin

When tested on tin-modified platinum surfaces, the reaction showed little decrease in activity but considerable changes in selectivity.

0.5 ML of tin. The improvement in selectivity in the presence of tin on Pt(111) observed at $\theta_{\text{Sn}} = 0.3$ is in agreement with results reported in the literature (15–19, 21). This enhancement of selectivity is generally accounted for by an electronic effect. Adsorbed tin is in a slightly oxidized state Sn^{δ+} due to an electronic transfer toward platinum atoms (the difference in electronegativity between Pt and Sn, 2.2 and 1.8 respectively on the Pauling scale, is in agreement with this interpretation). These slightly oxidized species have Lewis acid properties, which activate the C=O polarized bond of the unsaturated aldehyde.

A structural effect induced by tin may also account for changes in selectivity. Whether Sn is present in a surface alloy or as an overlayer may be questioned. Our tin deposition was performed at room temperature and no subsequent heating of the sample was carried out before reaction. Moreover, no LEED substructure has ever been observed after tin deposition. These features and results from the literature led us to assume that our catalytic tests were performed over *unalloyed* tin overlayers. Tin atoms adsorbed on a flat (111) surface reduce the areas of free platinum atoms, making even more difficult the accommodation of the substituted CC bond. These considerations apply to Pt(111) and to the flat terraces of Pt(553).

As regards Pt(553), whether tin is located on the flat (111) terraces or along the steps is a difficult question. The effect of tin on selectivity, totally different from what had been observed on Pt(111), rules out the possibility that tin is simply adsorbed on the flat terraces. Moreover, in the presence of tin, the activity of the (553) plane decreases only by a factor of 25%, indicating that the additive atoms are not located on top of the most active low-coordination atoms. If it was so, the addition of tin would approximately kill the effect of the step atoms; i.e., a much more considerable decrease in activity would have been observed. This leaves the hypothesis that the hot tin atoms, impinging the surface, diffuse on the surface until they reach an energetically favorable position, i.e., along the steps. We can now assume that the tin atoms are adsorbed on top of the highest coordinated atoms of the surface, i.e., on the bottom of the steps. Localization of tin on the highest coordinated atoms of the stepped surface is the most energetically favorable position (35) and is in total agreement with the experimental results obtained by Yeates and Somorjai for the evaporation of Cu on Pt(553) (36).

Due to the reduced coordination of the atoms on top of the steps, a localized alloying phenomenon may occur under reaction conditions, which involves strong interactions between Sn and Pt atoms, and a possible induced atomic roughness in the vicinity of the steps. Losing the flat, 5-atom-long terraces induces a change in the preferential adsorption mode. The reactant coverages are also modified as shown by the kinetic orders, which are now equal respectively to 0.7 and 0.2 for prenal and hydrogen. The surface is no more saturated in organic species; at the same time, it is enriched in hydrogen. The observed increase in selectivity toward the saturated alcohol can be accounted for by a change in the adsorption mode of the molecule and possibly also by the rapid addition of a second H₂ molecule to the enolic form of monohydrogenated intermediate, possibly stabilized by Sn^{δ+} species.

1 ML of tin. The activity on Pt(553) + 1 ML of tin decreases by only 40%. This indicates that for $\theta_{\text{Sn}} = 0.6$, there are still free hydrogenation sites. On the basis that a random distribution of tin atoms would induce a more severe drop in activity, we believe that hydrogen adsorption induces tin island formation, as already evidenced for the Bi/Pt(111) system (37).

Let us add that tin may also reduce the poisoning of the surface by carbon deposition during the reaction. This was shown to be significant in the case of dehydrogenation of cyclohexene on Pt(111) and Sn/Pt(111) (38).

As regards the selectivity, a totally reverse effect of tin is now observed at high coverage, to the benefit of unsaturated alcohol. This promoter effect on selectivity when tin is gathered in clusters may be accounted for by a combination of geometric and electronic effects. First, these clusters induce a steric hindrance for a flat adsorption of the prenal

molecules, and hence the least hindered C=O unsaturation is preferentially hydrogenated. Second, at the interface between tin clusters and platinum atoms, a positive electronic effect due to partially oxidized $\text{Sn}^{\delta+}$ species activates the polar carbonyl group of the prenal molecule. Such an explanation was previously proposed by Poltarzewski *et al.* to account for the promoter effect of tin during the hydrogenation of acrolein and cinnamaldehyde on Sn–Pt/nylon (19).

“2” ML of tin. Activity does not decrease any further, confirming an island-type growth mode of tin adatoms, which leaves roughly the same free platinum area. The selective hydrogenation of the C=O bond of prenal is even more favored than in the presence of 1 ML of tin, due to an enhanced electronic effect. Note that the fraction of unsaturated alcohol reaches 70%, slightly higher than on clean Pt(553).

In comparison with the literature, the observed influence of tin, when it is not restricted to a perturbation of the steps, i.e., for $\theta_{\text{Sn}} > 0.3$, can be related to two recent studies, one dealing with CO and H_2 adsorption (39) and the other dealing with isobutane hydrogenolysis (40) on Sn–Pt(111). In the former study, the chemisorption of CO on Sn–Pt(111) surface alloys exhibiting the characteristic $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED patterns has been investigated. The CO uptake is larger than expected if Sn only acted as a 1 per 1 site blocking atom [only 5% decrease in CO coverage on the $p(2 \times 2)$ alloy]. Moreover, let us note that the authors do not consider a possible adsorption of CO on tin atoms. In contrast, tin is a drastic poison for hydrogen adsorption. The alloy surfaces are practically inert toward H_2 dissociation at 150 K, assigned to the removal of active ensembles of adjacent Pt atoms; similar behavior was observed for supported Pt–Sn alloy catalysts (19). This result appears contradictory to our finding concerning hydrogen coverage, at least at $\theta_{\text{Sn}} = 0.3$, or simply confirms that our catalytic surface is a nonalloyed Pt–Sn bimetallic. Opposite behavior of alloyed or nonalloyed surfaces have already been evidenced in oxygen chemisorption (39): tin totally blocks oxygen chemisorption on Pt–Sn alloys, whereas the authors showed an increase in oxygen uptake on a bimetallic nonalloyed Pt–Sn(111) surface compared with Pt(111); this was attributed to the oxidation of tin atoms. Similarly, strong hydrogen–tin interactions may enable hydrogen dissociation despite the reduction in the number of free platinum atom ensembles. We cannot exclude either that, in our experiments, when a prenal molecule approaches the surface, the oxygen terminal atom interacts with tin surface atoms and that this also contributes to improving the reactivity of the CO bond.

In the latter study (40), Xu *et al.* explained the decrease in hydrogenolysis on *n*-butane for the Sn–Pt(111) alloy compared with Pt(111), by a reduction in equilibrium coverage; tin-induced selectivity was ascribed to the large reduction in the heats of adsorption of olefins (41).

Our results, in particular the increase in selectivity toward the preferential hydrogenation of the C=O bond of prenal, and in perfect agreement with these literature results.

5. CONCLUSION

The gas-phase hydrogenation of 3-methyl-crotonaldehyde (prenal) was investigated on a well-defined stepped Pt(553) surface at pressures near 1 atm. This surface is twice as active as the (111) plane, which underlines the higher activity of the low-coordination step atoms for the dissociation and diffusion of hydrogen.

The influence on selectivity of a preadsorbed submonolayer of tin depends on the concentration and local arrangement of this metallic additive. On Pt(111), at low coverage, the influence of tin is, as expected, in favor of the unsaturated alcohol and is ascribed to a mainly electronic effect. On Pt(553), at low coverage ($\theta_{\text{Sn}} = 0.3$), Sn atoms are likely to be located in the vicinity of the steps and induce a local reconstruction of the platinum surface. Under these conditions, the surface is not saturated in organic species but is enriched in hydrogen, and the reaction leads mainly to the formation of saturated alcohol. At higher coverage, 1 or 2 ML, tin grows in islands on the (111) terraces of the surface and these clusters induce a change in the activation mode of the molecule due to steric and electronic effects. The metallic additive then recovers its well-known promoter effect, leading to a higher selectivity toward unsaturated alcohol.

This study of the influence of a metallic additive on a stepped surface has enabled us to distinguish steric or structural effects, prevailing at low coverage, from electronic effects, which are determining at high coverage.

ACKNOWLEDGMENTS

The authors are indebted to E. Margot for her competence and thank Professor J. Oudar for fruitful discussions. The financial support of Rhône-Poulenc is gratefully acknowledged.

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