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Hydrogenation of 3-methyl-butenal on Pt(110); comparison with Pt(111)

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The gas-phase hydrogenation of 3-methyl-butenal or prenal, was studied, at temperature equal to 353 K, on the (110) plane of platinum and compared to previous results obtained on Pt(111). The selectivity was found to be very structure sensitive. This has been ascribed to steric factors which determine when the unsaturated bond is on a substituted carbon atom. The combination of the use of well characterized surfaces as catalysts, and of the determination of the kinetics of the reaction led us to propose a Langmuir–Hinshelwood type mechanism. The nature of the reaction intermediates, di-σ or tetra-σ activated adsorbed species, depends upon the reactant pressure and upon the geometry of the surface. This catalytic study on model surfaces is of particular interest in understanding the selectivity of real catalysts whose atomic arrangement is possibly defined and controlled.

Keywords: unsaturated aldehyde; hydrogenation; platinum; single crystals; structure sensitivity

1. Introduction

Improving the selectivity of the hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols is a challenging task. A better understanding of the reaction mechanism and of the factors governing the selectivity is essential to define more efficient catalysts.

An extensive study of the hydrogenation of 3-methyl-butenal or prenal on Pt(111) already made clear the importance of steric factors to the selectivity of the reaction [1]; it is directly related to the configuration of the adsorbed reaction intermediate. On the close-packed surface, the CH_3 groups, in the vicinity of the unsaturated C=C bond, induce a preferential activation of the C=O bond which is free of substituents [2,3]. We also reported a comparative study of the adsorption of the

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unsaturated aldehyde on Pt(111) and on Pt(553) and found that monoatomic steps can significantly modify the adsorption characteristics. Low coordination atoms were shown to be very reactive both towards the C=O and to the C=C bonds of the molecules [4]. To go further into the understanding of the mechanism of a reaction, and in particular to be able to predict what happens on a real catalytic surface, a study of the same reaction on a "rough" surface at the atomic scale, Pt(110), was carried out and is reported in this paper. We shall compare these results to the ones obtained on the (111) plane of platinum. The influence of the structure of the surface will be discussed, in particular regarding the selectivity.

2. Experimental

The experiments, cleaning, characterization of the surface and catalytic tests, were achieved in a UHV chamber connected to a quartz reactor for reactions in the atmospheric pressure range. The procedure for preparing the surface and measuring the reactivity has been described in detail in refs. [1,2]. LEED and Auger spectroscopy were used to analyze the surface before and after every catalytic test. The sample was transferred from the UHV chamber to the reactor, it was heated by Joule effect to the reaction temperature, and then, the gas mixture was admitted to the reactive cell. The reactions were carried out in a batch mode, the gas recirculation was ensured by a pump in order to avoid mass transfer limitation. The hydrogenation reaction was monitored by an on-line gas chromatograph. The reaction was performed in the presence of an equimolecular mixture of hydrogen and deuterium; the H_2-D_2 exchange was simultaneously monitored by a mass spectrometer in order to measure the rate of dissociation of hydrogen.

The catalytic activity was expressed by the turnover frequency, TOF, i.e. the number of reactant molecules transformed per second and per surface Pt atom.

After cleaning the surface by successive Ar ion sputtering and annealing, the LEED pattern was a p(1 × 1) indicating no reconstruction of the (110) surface. The absence of reconstruction has been attributed to a residual partial pressure of CO ($P_{\text{residual}} = 4 \times 10^{-9}$ Torr) which was difficult to eliminate after the reactions.

3. Results

The 3-methyl-butenal or prenal was hydrogenated on clean Pt(110), in the presence of a large excess of hydrogen and deuterium. The standard experimental conditions were $P_{\text{prenal}} = 7 \times 10^{-3}$ Torr, $P_{H_2} = P_{D_2} = 200$ Torr, $T = 353$ K.

The composition of the gas phase has been plotted as a function of time in fig. 1. The turnover frequency, TOF, has been calculated at the initial stage of the reaction, and taking only the atoms of the above layer into account: $\text{TOF(hyd.)}_{0\%} = 8 \times 10^{-2}$ molecules at^{-1} s^{-1}.

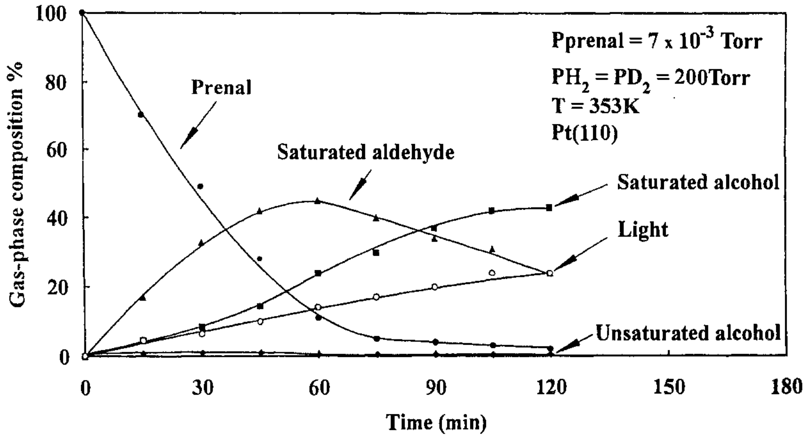


Fig. 1. Hydrogenation of prenal on Pt(110), at $T = 353$ K. Gas phase composition as a function of time.

The rate of prenal conversion slightly decreases along the reaction; it becomes very slow only at conversion higher than 90%. The rate of H_2-D_2 exchange, simultaneously measured, was also calculated at the beginning of the reaction: $\mathrm{TOF}(H_2-D_2)_{0\%} = 8 \times 10^2$ molecules at^{-1} s^{-1}. Let us note that the rate of hydrogen dissociation is four orders of magnitude higher than the one of prenal hydrogenation.

The distribution of products depends significantly on the conversion as shown in fig. 2:

At the beginning of the reaction:

- the most abundant product is the saturated aldehyde, selectivity extrapolated to 0% conversion, $s_0 = 65\%$;
- the fraction of saturated alcohol is very small, $s_0 = 18\%$, the one of unsaturated alcohol, which is the desirable product, is negligible, $s_0 \approx 1\%$!
- some hydrocarbons, mainly isobutene and isobutane, resulting from a decarbonylation or/and hydrogenolysis of the reactant, are formed, $s_0 = 16\%$.

At intermediate conversion, between 60 and 90%, the (110) plane is still selective to the saturated aldehyde, but the rate of formation of saturated alcohol increases significantly.

At high conversion, the main reaction responsible for hydrogen consumption is the hydrogenation of the saturated aldehyde. Saturated alcohol is the main product in the gas phase.

The rate of formation of light products is constant all along the reaction which results in an increase of the selectivity to hydrocarbons, with increasing conversion.

3.1. INFLUENCE OF 3-METHYL-BUTENAL PARTIAL PRESSURE

The influence of the prenal partial pressure on the hydrogenation reaction was

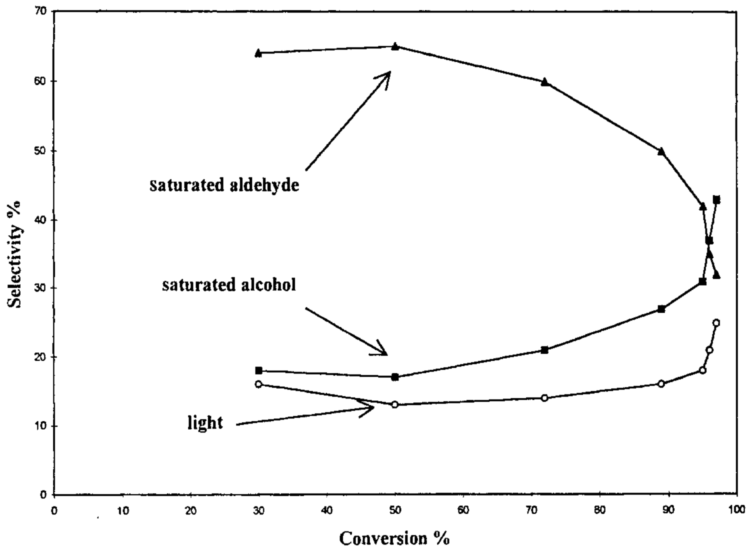


Fig. 2. Hydrogenation of prenal on Pt(110), selectivity as a function of conversion, same conditions as in fig. 1.

further investigated at a constant hydrogen + deuterium partial pressure of 400 Torr. Kinetic orders and variations of selectivity have been determined at $T = 353$ K:

The prenal partial pressure was varied in the range 1.7×10^{-3} Torr $\leqslant P_{\text{prenal}} \leqslant 34 \times 10^{-3}$ Torr. The kinetic order with respect to prenal, calculated from the initial activities, was equal to 0.2. A pseudo order was defined by the slope of the curve showing the rate of H_2-D_2 exchange as a function of the partial pressure of prenal; it is negative, close to -1, indicating a poisoning of the H_2-D_2 reaction by prenal. Let us note that, at the highest investigated prenal partial pressure, the rate of hydrogen dissociation is still three orders of magnitude higher than the one of hydrogenation.

The selectivity of the hydrogenation reaction, evaluated at 10% conversion, was found to be strongly influenced by the partial pressure of prenal, see fig. 3. The most important feature is the improvement of selectivity towards the unsaturated and the saturated alcohols, together with a decrease of the saturated aldehyde, when the partial pressure of prenal increases. Side reactions, cracking and/or decarbonylation, leading to light hydrocarbons, also diminish when the partial pressure of prenal increases.

3.2. INFLUENCE OF HYDROGEN PARTIAL PRESSURE

For a constant $P_{\text{prenal}} = 7 \times 10^{-3}$ Torr, the hydrogen partial pressure was varied in the range, 150 Torr $\leqslant P_{H_2} \leqslant 520$ Torr. The initial kinetic orders are equal to unity both for the hydrogenation and the H_2-D_2 exchange. No significant change of selectivity could be observed.

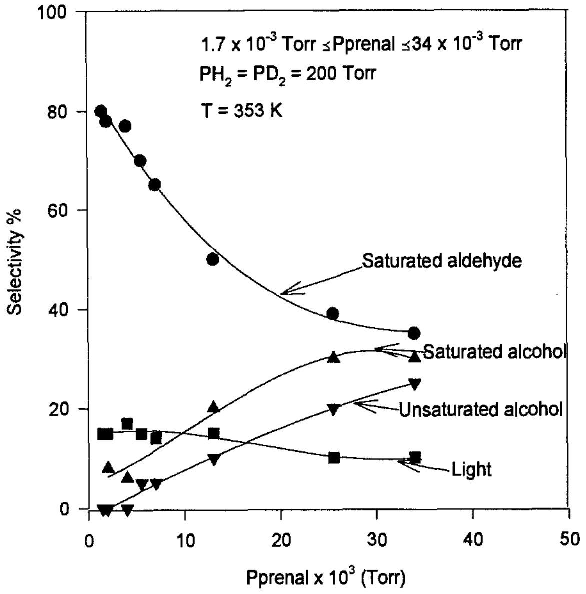


Fig. 3. Hydrogenation of prenal on Pt(110). Selectivity of the reaction, measured at 10% conversion, as a function of the partial pressure of prenal.

4. Discussion and comparison with Pt(111)

4.1. ACTIVITY

Exposing the clean Pt(110) surface to an hydrogen-rich mixture, $P_{H_2}/P_{prenal} = 10^5$, leads to a coverage of the surface, by organic molecules, close to saturation (order equal to 0.2), and a very low coverage by hydrogen (order equal to unity). Nevertheless, the H_2–D_2 exchange rate is four orders of magnitude higher than the one of hydrogenation, indicating that the reaction is not limited by the dissociation of hydrogen. It is rather limited by the amount of active hydrogen atoms available in the vicinity of the hydrogenation sites.

The negative value of the order of the H_2–D_2 exchange towards prenal suggests competitive adsorptions of hydrogen and prenal on the low coordinated atoms of the surface; it is commonly assumed that the dissociation of hydrogen preferentially occurs on bridge sites and requires free atoms in the topmost layer of a (110) plane [5].

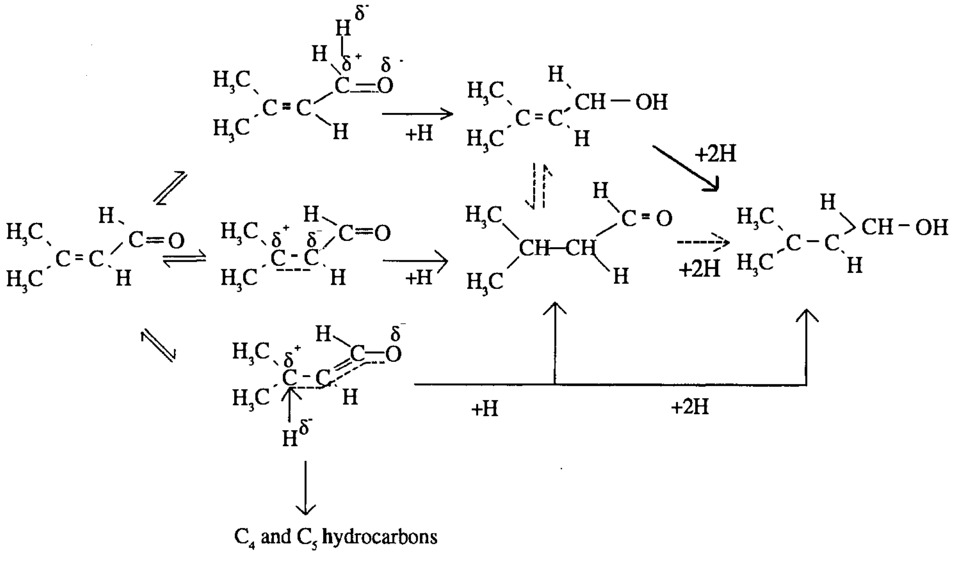
Comparing the turnover frequencies of the (111) and (110) surfaces, the latter is twice as much active as the flat surface. This ratio is about the same as the one found for the hydrogenation of butadiene on the same surfaces [5], and is likely to be related to the mobility of hydrogen on the surface. That means that the rate is governed by the surface reaction between adsorbed hydrogen and organic species.

4.2. SELECTIVITY AND MECHANISM

At low conversion, the selectivity on Pt(110) is strongly in favor of the saturated aldehyde; it is totally different from the one on Pt(111) on which the unsaturated alcohol was predominant. On that close-packed surface, the accommodation of the methyl groups was difficult and this steric hindrance was responsible for the preferential activation of the C=O bond. On the "open" (110) plane, a flat adsorption of the whole conjugated system is possible on the low coordinated atoms, the accommodation of the methyl groups being easy on top of the lower atomic layer. On such a conjugated and planar system, a 1,4 addition of hydrogen is the most likely mechanism, as represented in scheme 1: the main route leads to a keto-enolic equilibrium, strongly displaced in favor of the aldehyde. It also explains the formation of saturated alcohol as a primary product of the reaction, and the possible cracking of the molecule which leads to isobutene. This type of mechanism, governed by a first addition of one H atom on the C_4, was proposed by Germain and Jenck for the unsaturated aldehydes when the flat adsorption is possible [6].

The cracking of the molecules is important compared to the (111) plane, 14% on Pt(110), less than 5% on Pt(111) under identical conditions, and this is clearly related to the cracking properties of low-coordinated atoms [7]. These electron deficient atoms also favor the activation of the ethylenic bond which is electron enriched by the two methyl groups [8].

Interesting to note is that cracking or decarbonylation reactions, though more considerable on Pt(110) than on Pt(111), do not induce a significant poisoning of the reaction, as they do on the flat surface, stopping the conversion to 50%. Schröder and Andersson showed that side reactions, on Pt/Al_2O_3, are due to CO adsorp-



Scheme 1. Surface reaction mechanism on Pt(110).

tion on active sites [9]. It is possible that, on Pt(110), the decomposition rate to isobutene and carbon monoxide and/or alcoholic residues, selectively poisons one type of sites, leaving free atoms for the activation of the C=C bond of prenal or of the C=O bond of the saturated aldehyde. It is reasonable to assume that, on that surface, known to be very active for the reduction of C=C bonds, carbonaceous residues are more quickly hydrogenated than on any other surface. Hydrocarbons desorb instead of blocking sites.

At high conversion, the very small fraction of unsaturated alcohol undergoes a fast rehydrogenation, in agreement with the high reactivity of the C=C bond on that surface. The increase of hydrocarbons and saturated alcohol in the gas phase is due to a readsorption and the hydrogenation of the saturated aldehyde becomes the majoritary product in the gas phase. Let us note that, on Pt(111), the selectivity towards saturated alcohol also increased with conversion.

The dominant formation of C_4 hydrocarbons as light products can be explained either by an activation and breaking of the C_2-C_3 bond of prenal or by an activation of the C=C bond in α position of the OH group on the enolic form of the aldehyde. Both routes are favored by increasing conversion.

4.3. INFLUENCE OF REACTANT PRESSURES

Assuming the above mechanism, based upon competitive adsorptions of the reactants, one needs to explain why both the fractions of saturated and unsaturated alcohols increase when the initial partial pressure of prenal increases. We suggest a progressive change of the chemisorption mode of the molecule. At low and intermediate pressures of prenal, organic molecules are adsorbed on top of the upper atomic layer; that configuration facilitates an activation of the whole conjugated system, followed by a preferential C=C hydrogenation. At high initial pressure, the upper atomic rows become saturated, and the lower atoms start to be occupied. We think that the surface dipole, now involved, enhances the activation of the C=O bond and also the simultaneous activation of both unsaturations. Such a change of adsorption states could not be observed on Pt(111) which exhibits only one type of sites.

Though the kinetic order toward prenal is lower than the one toward hydrogen, 0.2 compared to 1, changes in the selectivity are more significant when the pressure of the organic reactant varies. This proves the determining role of the adsorption configuration of adsorbed prenal molecules, which is likely to change by an increase of the prenal pressure, all the more at coverage close to saturation, but which is insensitive to P_{H_2}.

5. Conclusion

Similar studies of the hydrogenation of the prenal, a C_5 α,β-unsaturated aldehyde, on the (111) and the (110) planes of platinum make clear that the selectivity of a catalyst may be extremely structure sensitive. The selectivity is directly correlated to the chemisorption mode of the molecule. On Pt(110), when the surface is not saturated, a global activation of the non-planar conjugated molecule is possible on the low coordination atoms; the molecule undergoes a classical 1,4 hydrogenation; at higher pressure, the change of selectivity has been attributed to the activity of the second atomic row; the C=O bond is then more likely to be hydrogenated. On Pt(111), the selectivity was governed by the steric hindrance of the two methyl groups which prevented a global activation of the molecule. The difference in the specific activities, only a factor 2, is not significant and could be overestimated due to the number of atoms considered in our calculation.

These two basic catalytic studies on model surfaces, show the importance of the geometry and coordination of the active sites. Such effects could be made clear by hydrogenating a non-symmetric molecule. We are now pursuing some investigations, using vibrational techniques, in order to determine the adsorption configurations of unsaturated aldehydes on low index planes of platinum. These studies are necessary to confirm our hypotheses.

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