

## Crotonaldehyde and Methylcrotonaldehyde Hydrogenation over Pt(111) and Pt<sub>80</sub>Fe<sub>20</sub>(111) Single Crystals

P. BECCAT,\* J. C. BERTOLINI,\* Y. GAUTHIER,† J. MASSARDIER,\* AND P. RUIZ\*

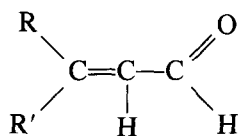
\*Institut de Recherches sur la Catalyse (CNRS), 2 Avenue Albert Einstein, 69626 Villeurbanne Cédex, France, and †Laboratoire de Spectrométrie Physique, Université Joseph Fourier, BP 87, 38402 Saint Martin d'Hères Cédex, France

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Hydrogenation reactions of crotonaldehyde and methylcrotonaldehyde have been carried out on Pt(111) and Pt<sub>80</sub>Fe<sub>20</sub>(111) single crystals. The reactions have been performed in the gaseous phase with a large excess of hydrogen. A noticeable enhancement of activity has been observed by alloying the platinum with iron. The additional methyl group present in the methylcrotonaldehyde greatly increases the selectivity toward formation of the unsaturated alcohol, while only a slight increase of such selectivity is induced by alloying. The results have been compared with the previous experimental results on crotonaldehyde hydrogenation on Pt/SiO<sub>2</sub> catalysts and cinnamaldehyde hydrogenation on Pt and Pt<sub>80</sub>Fe<sub>20</sub> particles supported on carbon. © 1990 Academic Press, Inc.

### INTRODUCTION

The ability of catalysts to hydrogenate preferentially the carbonyl groups rather than the unsaturated C=C bond in  $\alpha,\beta$ -unsaturated aldehyde molecules can be important in the production of specific chemical products in industrial hydrogenation processes. It has been shown that such a selectivity may depend upon both the nature of the metal catalyst and the substituents *R* and *R'* of the unsaturated molecule (1):



Such a selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes into unsaturated alcohols often needs specific conditions. For example, in the liquid phase, the addition of Fe metallic salts increases the selectivity of Pt for unsaturated alcohols (1, 2) while the hydrogenation rate of cinnamaldehyde is higher on metallic Pt-Fe/C catalysts than on Pt/C (3). In the second case, the activity is the highest for a composition of Pt<sub>80</sub>Fe<sub>20</sub>

particles although the selectivity toward hydrogenation of the aldehyde group increases only slightly compared to that for supported Pt catalysts (3). X-ray analysis and STEM measurements have shown that the catalysts are alloy particles showing the fcc structure and a uniform composition. The modifications induced by Fe atoms in the catalytic properties of Pt have not yet been seriously studied. In addition there are other effects like the mutual electronic influence (4), surface composition, and the support and solvent effects.

In the present work we have studied the catalytic properties of Pt<sub>80</sub>Fe<sub>20</sub>(111) and Pt(111) surfaces for hydrogenation of two unsaturated aldehydes differentiated by the substituent on the C<sub>3</sub> carbon, namely crotonaldehyde (CROALD) and methylcrotonaldehyde (MeCROALD). In order to gain complementary information, the hydrogenation reaction of the half-hydrogenated products like the aldehydes (butyraldehyde (BUTALD) and methylbutyraldehyde (MeBUTALD)) and the alcohols (crotyl alcohol (CROALC) and the alcohol with an additional methyl

group (MeCROALC)) have also been studied.

## EXPERIMENTAL

### Preparation of Samples

The alloy single crystals of 20 at.% Fe were grown by the Czochralski method. They exhibited the  $\gamma_3$ -ordered cubic  $L1_2$  type structure (5, 6). The net composition checked by atomic absorption spectroscopy was 20 at.% Fe with an error of  $\pm 0.5\%$ . The crystal was cut in the shape of a thin slab by the spark erosion technique along the (111) orientation and this was monitored by X-ray diffraction.

The crystal was then mechanically polished up to  $1 \mu\text{m}$  in a position well defined by the X-ray goniometry techniques. The orientation so obtained is better than  $\pm 0.2^\circ$  with respect to the (111) plane. It was confirmed by X-ray emission under scanning electron microscope conditions that the composition was perfectly uniform along the sample.

The surface recrystallization was obtained by simply heating the sample to 1300 K in vacuum. From the quantitative analysis of the LEED results it was found that the outer layer was quasi-complete with Pt atoms (7).

The cleaning of the sample was achieved by repeated cycles of Ar ion etching, short-time low-pressure oxygen treatments and annealings at about 1100 K.

### The Preparation/Reaction Chamber

A schematic representation of the system is given in Fig. 1. It was checked that the experimental apparatus (without Pt or Pt/Fe sample) has no significant activity at 300 K.

The surface cleanliness and the surface composition of the samples were measured by using a CMA Auger spectrometer included in the UHV chamber working in the  $10^{-10}$  Torr ( $10^{-8}$  Pa) pressure range.

The samples were transferred from the UHV sample holder to a quartz reactor of volume  $365 \text{ cm}^3$  separately pumped with an

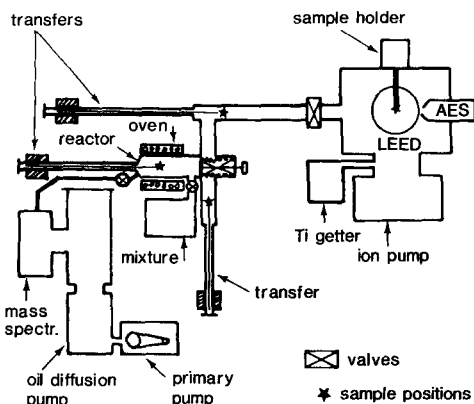


FIG. 1. Schematic representation of the experimental arrangement.

oil diffusion pump fitted with a liquid nitrogen cold trap. The reactants (about  $5.3 \times 10^{-3}$  Pa for the organic product and 3 Pa for hydrogen) and the samples were heated by a temperature-controlled resistance furnace.

After studying the reactions, the reactants and products were pumped off and the sample was transferred to the UHV chamber. The surface was then analyzed with the CMA Auger facilities.

### Reactants

$\text{H}_2$  of purity  $>99.9995\%$  (Air Liquide) was used without further purification. The organic reactants were obtained from Aldrich-Chemie (CROALD +99%, BUTALD 99%, CROALC 97%, MeBUTALD 99%, MeCROALC 99%) and from Merck (MeCROALD +96%). When used as supplied, large amounts of sulfur were observed on the samples after reaction. These sulfur polluting agents were eliminated by bringing the liquid reactants into contact with neutral alumina activated for chromatography. The reaction mixture was prepared separately in a 6-liter glass tank. The catalytic hydrogenation reactions were performed under static conditions. We made each catalytic test first at room temperature and then after a certain time interval (chosen to obtain and record a noticeable variation in composition of the

reaction mixture) the temperature was raised to a temperature around 330 K and stabilized as rapidly as possible, with the mixture *in situ*. Similarly, we studied the reactions at other constant temperatures. The reaction mixture, introduced through a leak valve, was analyzed by mass spectrometry. It was checked that the analysis did not change the reaction conditions appreciably.

The *m/e* peak distribution and the sensitivity factors were determined by recording separately the spectra of all the reactants and the products at a given partial pressure. From the calculations of the peak heights of the 31, 56, 70, and 72 *m/e* ratios the respective concentrations of CROALD, CROALC, BUTALD, and butanol contained in mixtures were determined. Similarly the composition of mixtures of the methylated compounds were obtained from the peak heights of the 58, 70, 71, and 84 *m/e* peaks.

#### RESULTS AND DISCUSSION

The hydrogenations of CROALD and MeCROALD were carried out on Pt(111) and Pt<sub>80</sub>Fe<sub>20</sub>(111) at different temperatures. They were restricted to low or medium conversions. Figure 2 shows the variations of the reaction products as a function of time. Note that the Pt<sub>80</sub>Fe<sub>20</sub> sample has a higher activity than the Pt(111). The selectivity toward the unsaturated alcohol formation is very low for the CROALD reaction on both the Pt and Pt-Fe samples. However, it is higher than 0.5 for the hydrogenation of the MeCROALD where one hydrogen of the CROALD is substituted by a methyl group.

The turnover frequencies (TOF) for these reactions are reported in Table 1. They have been calculated for 330 K and for a hydrogen pressure  $P_H$  of 3 Pa, assuming the reaction orders to be one and zero with respect to the pressures of hydrogen and the organic reactants, respectively. This is quite reasonable if one considers the linear decrease of the CROALD (and MeCROALD) partial pressure during the course of the reaction.

TABLE I

Turnover Frequencies (TOF) in  $10^{-2} \text{s}^{-1}$  per Surface Metal Atom and Apparent Activation Energies ( $E_a$ ) in  $\text{kJ mol}^{-1}$  for the CROALD and MeCROALD Hydrogenation Reactions

Reaction	Pt(111)			Pt <sub>80</sub> Fe <sub>20</sub> (111)		
	TOF	$E_a$	<i>S</i>	TOF	$E_a$	<i>S</i>
CROALD	BUTALD	5.6	48	20	33	
	CROALC	0.6	46	0.1	2.9	25
MeCROALD	MeBUTALD	1.8	46	5.5	50	
	MeCROALC	2.3	23	0.56	13	34

Note. Values are given for 330 K, and 3 Pa for the hydrogen pressure. Selectivity, *S*, is defined as the rate of unsaturated alcohol formation to the overall reaction rate.

Moreover, it has been experimentally verified that the CROALD hydrogenation occurs at the same rate at 0.03 and 0.005 Pa for the unsaturated organic reactant pressures.

The apparent activation energy for the formation of the MeCROALC is lower than that for the formation of the MeBUTALD. Consequently, the selectivity into unsaturated alcohols decreases (while the selectivity into saturated aldehydes increases) with increase of the reaction temperature. Such a phenomenon can be directly inferred from a rough observation of the curves in Fig. 2.

In Fig. 3 we present the CMA Auger spectra of the Pt and Pt-Fe samples before and after the reactions. A noticeable increase of carbon in the surface is evident.

The carbon left on the surface was determined from the  $I_{\text{Pt}}(237)/I_{\text{C}}(275)$  Auger peak ratio. This was done by the method of calibration proposed by Biberian and Somorjai (8) with some corrections taking into account the CMA (cylindrical mirror analyzer) versus RFA (retarding field analyzer) transmission differences with kinetic energy. The amount of carbon left on the surface ranges between 0.4 and 0.6 of a monolayer (one monolayer corresponds to  $4 \times 10^{15}$  C atoms per  $\text{cm}^2$ ).

For the Pt-Fe alloy sample no significant changes in the Fe to Pt characteristic Auger peak intensity ratios were observed after the

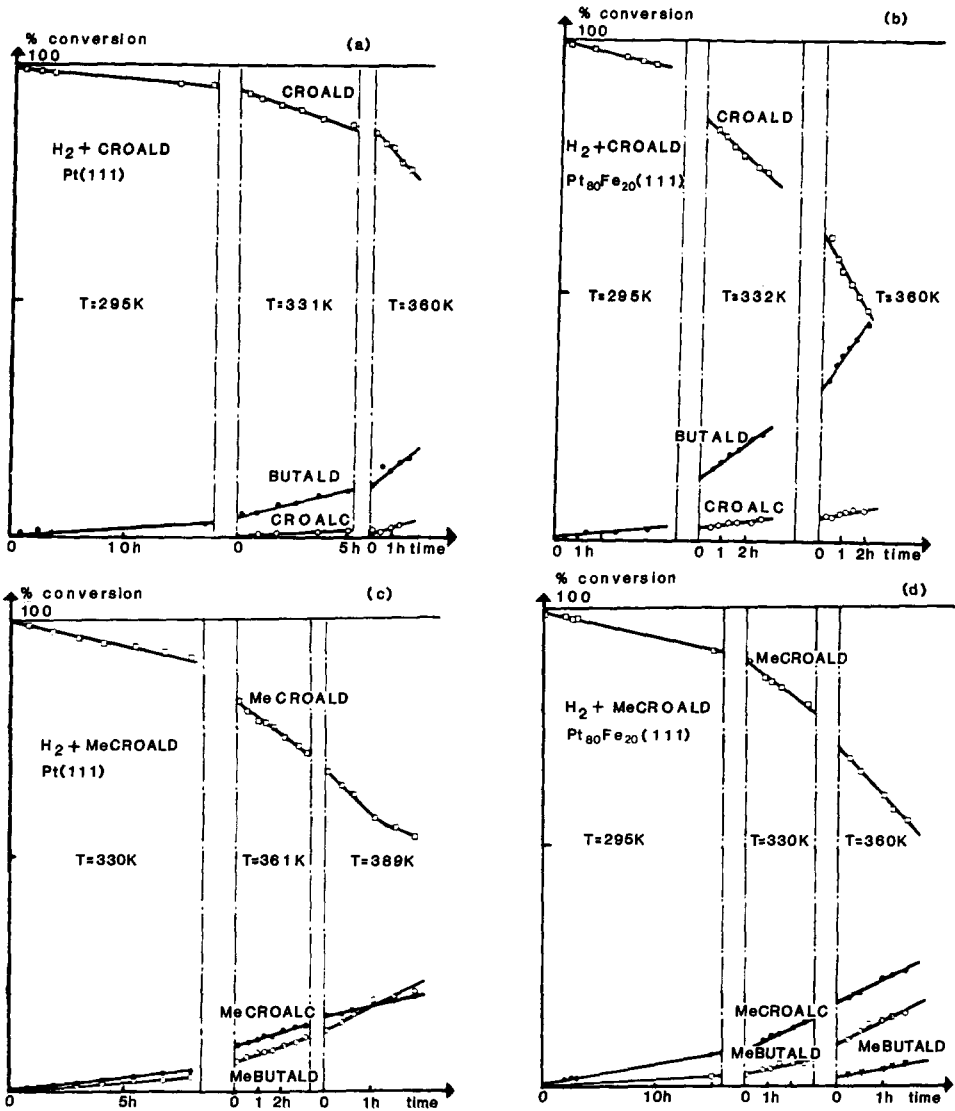


FIG. 2. Conversion versus time for the hydrogenation reaction of (a) crotonaldehyde on Pt(111) ( $P_{\text{H}_2} = 2.8 \text{ Pa}$ ;  $P_{\text{CROALD}} = 5.6 \times 10^{-3} \text{ Pa}$ ; sample area =  $0.52 \text{ cm}^2$ ); (b) crotonaldehyde on  $\text{Pt}_{80}\text{Fe}_{20}(111)$  ( $P_{\text{H}_2} = 2.65 \text{ Pa}$ ;  $P_{\text{CROALD}} = 5.3 \times 10^{-3} \text{ Pa}$ ; sample area =  $0.3 \text{ cm}^2$ ); (c) methylcrotonaldehyde on Pt(111) ( $P_{\text{H}_2} = 2.67 \text{ Pa}$ ;  $P_{\text{MeCROALD}} = 5 \times 10^{-3} \text{ Pa}$ ); (d) methylcrotonaldehyde on  $\text{Pt}_{80}\text{Fe}_{20}(111)$  ( $P_{\text{H}_2} = 2.83 \text{ Pa}$ ;  $P_{\text{MeCROALD}} = 5.3 \times 10^{-3} \text{ Pa}$ ).

reactions. This suggests that surface composition remained unaltered during the reactions.

Taking into account the consecutive and parallel schemes, generally considered for this selective hydrogenation, we have

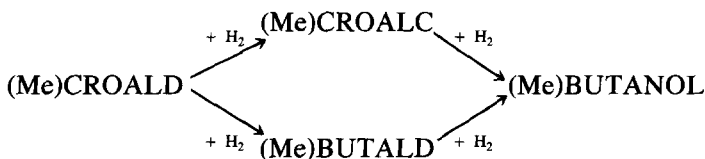


TABLE 2

Turnover Frequencies (TOF) in  $10^{-2} \text{s}^{-1}$  per Surface Metal Atom and Apparent Activation Energies ( $E_a$ ) in  $\text{kJ mol}^{-1}$  for the BUTALD, CROALC, MeBUTALD, and MeCROALC Hydrogenation Reactions

Reaction	Pt(111)		Pt <sub>80</sub> Fe <sub>20</sub> (111)	
	TOF	$E_a$	TOF	$E_a$
BUTALD → BUTANOL	0.2	54	3.1	42
CROALC → BUTANOL	27	29	67	35
MeBUTALD → MeBUTANOL	0.35	50	5.3	52
MeCROALC → MeBUTANOL	(1.6)	(44)	(7)	(44)

Note. Values are given for 330 K, and 3 Pa for the hydrogen pressure.

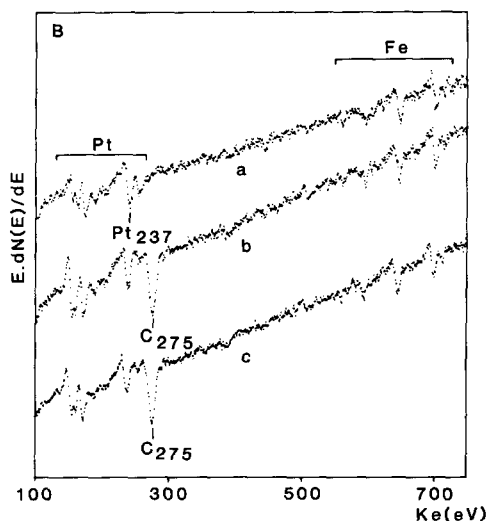
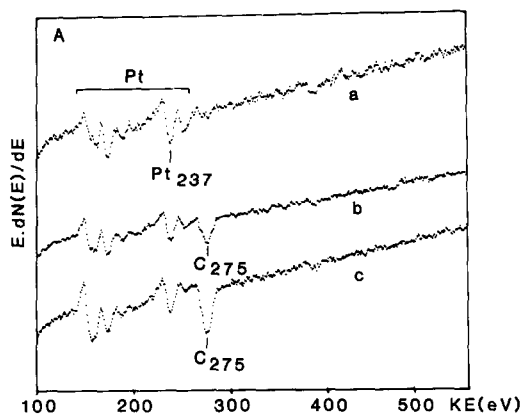


FIG. 3. CMA Auger spectra of (A) Pt(111) (B) Pt<sub>80</sub>Fe<sub>20</sub>(111): (a) clean; (b) after CROALD hydrogenation reaction; (c) after MeCROALD hydrogenation reaction (primary energy  $E_p = 1.5 \text{ keV}$ ; modulation amplitude  $V_{p,p} = 3.4 \text{ V}$ ).

Knowledge of the kinetic parameters associated with the hydrogenation of the half-hydrogenated intermediate products allows us to obtain complementary information on the intrinsic properties of both the pure Pt and the Pt-Fe alloy in the hydrogenation of C=C and C=O chemical functions.

The TOF and  $E_a$  values deduced from the experimental curves are reported in Table 2. It may be noted here that the values for MeCROALC hydrogenation (within brackets in Table 2) must be regarded cautiously since they have been obtained in the pres-

ence of some MeCROALD (about 10%) produced during the desulfurization process.

From the values presented in Table 2 one can conclude the following:

(i) The hydrogenation rate of the C=C chemical function is decreased roughly by an order of magnitude with the substitution of one H atom by a CH<sub>3</sub> group. Furthermore, the hydrogenation rate increases 3–4 times on the Pt<sub>80</sub>Fe<sub>20</sub> alloy surface.

(ii) The hydrogenation rate of the C=O aldehyde function, on the other hand, is slightly higher for the methylated aldehyde and the rate increases by a factor of about 15 for the alloy surface. We can compare these results with the results given in Table 1 for the hydrogenation of C=C and C=O chemical functions in conjugation. We find that (a) the hydrogenation rate of the conjugated C=C bond decreases by a factor of about 4 (instead of about 10 for the double bond alone) in the presence of a methyl group, but increases with alloying, and (b) the hydrogenation rate of the conjugated C=O aldehyde function increases about 4 times in the presence of the CH<sub>3</sub> group (instead of about 1.5 times in the case of a C=O bond alone). This hydrogenation rate also increases with alloying, but less than that for a nonconjugated C=O bond.

The increase in both the activity and the selectivity for unsaturated alcohols in the hydrogenation of methylcrotonaldehyde due to alloying Pt with Fe can be closely compared with the results obtained in the

case of cinnamaldehyde hydrogenation of Pt<sub>80</sub>Fe<sub>20</sub> alloy particles supported on carbon (3, 9). The overall CROALD hydrogenation rate over the Pt(111) single crystal is comparable to that measured by Vannice and Sen (10) for the same reaction on Pt/SiO<sub>2</sub> supported catalysts. For both catalysts the selectivity for unsaturated alcohol is very poor. However, when the hydrogenation of half-hydrogenated intermediate compounds was performed separately, a higher activity for BUTALD hydrogenation to butanol was observed on Pt/SiO<sub>2</sub> (10) as compared to that on Pt(111). This may be related to the presence of the oxide support that plays an important role in the activation of the C=O group. The hydrogenation rate of CROALC (and to a lesser extent MeCROALC) into butanol (and methylbutanol) is very high on Pt(111) single crystals as well as on Pt/SiO<sub>2</sub> (10). Therefore, the very low amount of saturated alcohols in the reaction products cannot be explained by kinetic considerations. This may be due to the higher adsorption energies of the  $\alpha,\beta$ -unsaturated carbonyl compounds compared with those of the half-hydrogenated intermediates.

The selectivity for unsaturated alcohols depends mainly on the kinetic parameters. Indeed, the selectivity is substantially increased in the presence of the methyl group which causes the C=C bond hydrogenation rate to decrease and the corresponding rate for the aldehyde function to increase.

The main influence of alloying Pt with Fe is to increase the hydrogenation rate of the whole set of reactions considered, with a slightly higher increase for the C=O bond hydrogenation rate than the corresponding C=C rate. The alloying, therefore, induces a favorable effect on the selectivity.

Further work must be done for a better understanding of all these phenomena. First, we must consider the geometric and the electronic effect of the CH<sub>3</sub> group in the  $\alpha,\beta$ -unsaturated aldehyde. Second, comparative chemisorption studies of various substituted compounds must be carried out. Moreover, the commonly proposed bifunctional effect, in which iron in a Fe <sup>$\delta$ +</sup> state

preferentially activates the C=O group, cannot be retained as the outermost surface is a quasi-complete Pt layer (7). Therefore, one must consider the effect of Fe atoms on the electronic properties of the Pt catalyst surface and the composition of the Pt-Fe alloy surface. Further experiments are necessary to check these assumptions.

In conclusion, the presence of an additional terminal methyl group is found to be responsible for a large enhancement of the selective hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds to unsaturated alcohols. The major influence of alloying Pt with Fe results in a noticeable increase in the hydrogenation rates for all the considered C=C and C=O chemical functions. This influence cannot be related to the presence of Fe atoms in the surface which would favor the chemisorption of the  $\alpha,\beta$ -unsaturated aldehyde by the C=O group, as has previously been invoked (1), but rather by a modification of the geometric and electronic properties of some Pt atoms in the first layer (7).

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