JOURNAL OF CATALYSIS 112, 21–33 (1988)

Platinum Single Crystals: The Effect of Surface Structure and the Influence of K and Na on the Activity and the Selectivity for 1,3-Butadiene Hydrogenation

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Received May 11, 1987; revised December 23, 1987

Hydrogenation of 1,3-butadiene has been performed on Pt(100) and Pt(100). The kinetics results may be explained by a consecutive scheme where the butenes are the primary products as has been generally proposed on more conventional supported metal catalysts. The Pt(110) is the most active and the most selective of the low-index faces of platinum. On Pt(100), the influence of K and Na additives on the activity and the selectivity for 1,3-butadiene hydrogenation has been determined. About the same effect has been observed for potassium and sodium. Up to a coverage of less than 0.4 monolayer, alkali additives improve both the activity and the selectivity. This may be understood in terms of changes in electron donation or backdonation induced by the alkali adsorbate on the chemisorbed species leading to a lowering of the bond strength of the unsaturated hydrocarbons with the metal surface atoms. For higher coverages, the geometrical blocking effect dominates.

INTRODUCTION

The different processes for the production of unsaturated hydrocarbons (steam cracking, catalytic cracking or coking) lead to a mixture of hydrocarbons, and further hydrogenation are often necessary to obtain the valuable products commonly used in the chemical industry. For example, acetylene must be selectively hydrogenated to ethylene and diene to olefinic compounds in order to satisfy the drastic specifications needed for further chemical transformations.

For this reason, the selective hydrogenation of dienes has become an important industrial reaction. In order to obtain information on the structural influence of the metal catalyst on the kinetic parameters, 1,3-butadiene hydrogenation has been performed on Pt single crystals. The adsorption strengths of reactants and products are generally dependent on the adsorption sites which are well defined on single crystals.

After Pt(111), which has been previously studied (*1*), the selective hydrogenation of 1,3-butadiene has now been carried out on Pt(100) and Pt(110). The present results will be compared to those already obtained in order to evaluate the overall influence of the geometric arrangement in the surface of Pt.

Moreover, it is interesting to test the influence of alkali additives (K and Na), which by modification of the electronic properties of the metal may improve the selectivity toward unsaturated compounds. Indeed, it is known that in the presence of alkali additives on transition metals, the adsorption strengths of unsaturated hydrocarbons are decreased (*2*) and changes in the competitive adsorption between reactants and products are expected. Therefore the activity and the selectivity for diene hydrogenation can be modified.

On Ni (*3*), it has been found that the butene distribution, characteristic of the metal, was explicable in terms of electronic

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0021-9517/88 $3.00

density and it was even suggested that there were critical electron densities for which the catalytic properties change significantly. In the same way, on supported Pd, activity decreases with the metal crystallite size (*4, 5*) whereas the addition of an electron donor (piperidine) increases both the activity and the selectivity (*6*).

The purpose of this work was to determine the influence of the geometric structure and that of the addition of well-controlled quantities of K (or Na) on the activity and selectivity of Pt for 1,3-butadiene hydrogenation.

EXPERIMENTAL

Experiments were performed in a system including an ion-pumped UHV chamber connected to a quartz reactor in which the single crystal could be transferred under vacuum after cleaning and control. A cylindrical mirror analyzer equipped with a coaxial gun (C.M.A. Riber OPC 105) for Auger electron spectroscopy (AES), a four-grid optics for low-energy electron diffraction (LEED), a quadrupole mass spectrometer, and a gun for ion bombardment were available in the UHV chamber.

The platinum single crystals were cut and polished at the desired (100) and (110) orientations (±0.5°). They could be heated with an IR emitter and cleaned by repeated cycles of argon ion bombardment (500 eV), treatments at 1200 K in 5×10^{-8} Torr of oxygen and annealings until the LEED pattern and the AES spectrum characteristic of the clean sample were obtained. On the (100) and (110) faces LEED patterns corresponding to surface reconstruction were observed. These diffraction patterns, (5 × 1) on Pt(100) (*17*) and (1 × 2) on Pt(110), disappear rapidly after adsorption. A typical AES spectrum of a clean surface is presented in Fig. 1a.

In addition, the system was equipped with a "SAES Getters" potassium or sodium source. The alkali deposition was obtained by Joule heating of the alkali metal disperser in front of the single crystal located about 2 cm away. The amount of alkali at the surface sample was determined, after calibration, by AES. For potassium the K coverage, Θ_K, was deduced (after subtraction of the Pt contribution to the 252 eV peak) from the K_{252}/Pt_{64} Auger peak ratio as previously described (*8*). With sodium, the same procedure of calibration as that for K was carried out, but using a 3-

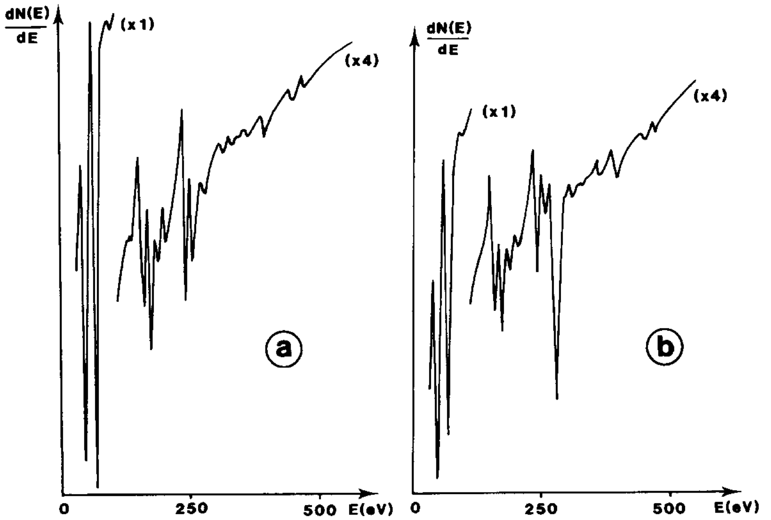


FIG. 1. AES spectra for Pt(100): (a) clean surface, (b) after C_4H_6 hydrogenation.

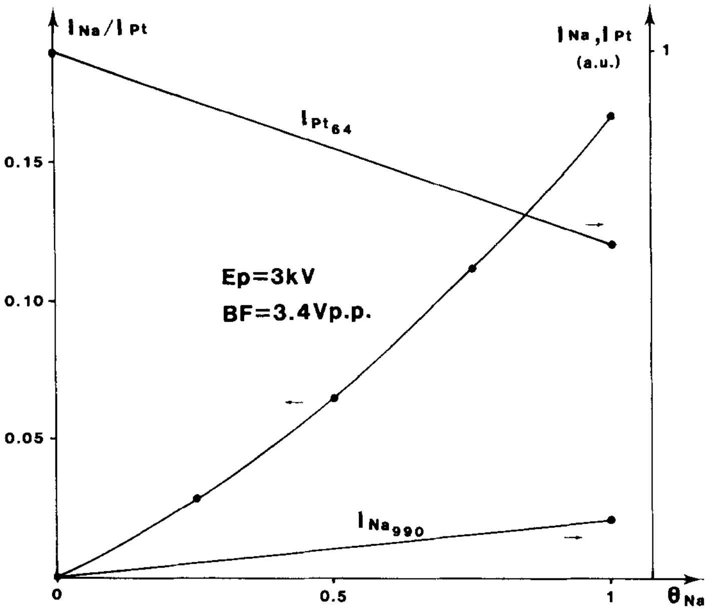


FIG. 2. Variations of the Na_{990} and Pt_{64} Auger peak intensities (peak-to-peak height measured under standard conditions) and of their ratio Na_{990}/Pt_{64} with the Na coverage given in monolayer units.

keV energy for the primary electron beam. The Na coverage, Θ_{Na}, was determined from the Na_{990}/Pt_{64} Auger peak ratio. For a ratio of 0.165, a TDS peak of Na, shifted toward lower temperature, was attributed to the growing of a second Na layer, as for potassium. Figure 2 shows the Na_{990}/Pt_{64} Auger peak ratio, and the associated linear variations of the Pt_{64} and Na_{990} peaks. From this ratio, Θ_{Na} can be easily determined. The Na and K coverages are given as a fraction of a monolayer.

Reactions were performed between 298 and 398 K under static conditions and a simple estimation of gas diffusion in H_2 (5 Torr of hydrocarbon in a near atmospheric pressure of H_2) shows that the kinetic data can be considered free of transport limitations.

Reaction mixtures were analyzed using the mass spectrometer (Riber QM 200) evacuated with a system including an oil diffusion pump and a liquid nitrogen trap in order to avoid the backscattering phenomena.

Hydrogenation of 1,3-butadiene on clean or alkali-promoted Pt single crystals leads to butenes and butane. The selectivity, S_1, is given as the ratio between the total butenes and the total conversion. Butenes are a mixture of 1-butene, *cis*-, and *trans*-2-butenes. The formation of isobutene was not observed. This observation is in line with data obtained with various supported Pt catalysts. Due to the mass spectrometer detection, it has not been possible, under our conditions, to separate *cis*- and *trans*-2-butenes, but nevertheless the selectivity S_2 = 1-butene/Σ butenes can be roughly estimated from

(i) the total amount of butenes which is determined from the $m/e = 41$ peak since about the same sensitivity as that of the parent peak is recorded for the three butenes;

(ii) the $m/e = 15$ peak which allows one to separate the 2-butenes from 1-butene, after subtraction of the *n*-butane contribution. The sensitivity of *cis*- and *trans*-2-butenes with respect to the mass 15 peak is about the same, while it is markedly larger for 1-butene.

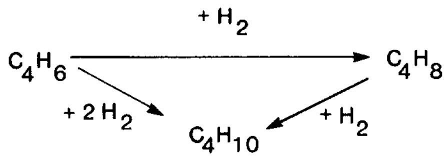
Reactants, 1,3-butadiene (Air Liquide, ≥99.5%, main impurities i-C_4H_8, *n*-C_4H_8, *n*-C_4H_{10}) and H_2 (Air Liquide, ≥99.9995%), were used as supplied.

RESULTS

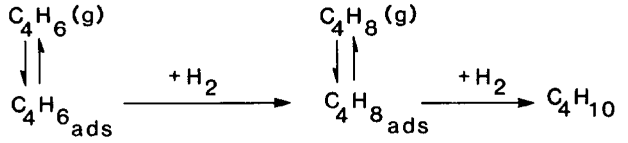
Hydrogenation of 1,3-Butadiene on Pt(100) and Pt(110)

Reactions have been performed under 4–5 Torr of 1,3-butadiene with a H_2 pressure increasing from about 40 Torr up to near atmospheric pressure.

A schematic parallel-consecutive diagram may be presented for the hydrogenation of C_4H_6 (*9*)



However, according to Cosyns (*9*), the direct hydrogenation of an alkadiene leading to the alkane would be nil so that a scheme deduced from the rake scheme would be more realistic



This scheme has been previously assumed in the work of Bond and co-workers (*10*). Then the initial selectivity would be to a large extent controlled by the desorption rate of C_4H_8 adsorbed species compared to their hydrogenation rate and (or) by the competitive adsorption between C_4H_6 and C_4H_8.

Assuming such a model, the kinetic behavior of the two consecutive reactions may be determined from the total reaction.

The order with respect to C_4H_6 is found to be equal to zero: the catalytic activity is found to be constant for the same hydrogen pressure, while the C_4H_6 pressure is largely decreased in the course of the run (Fig. 3).

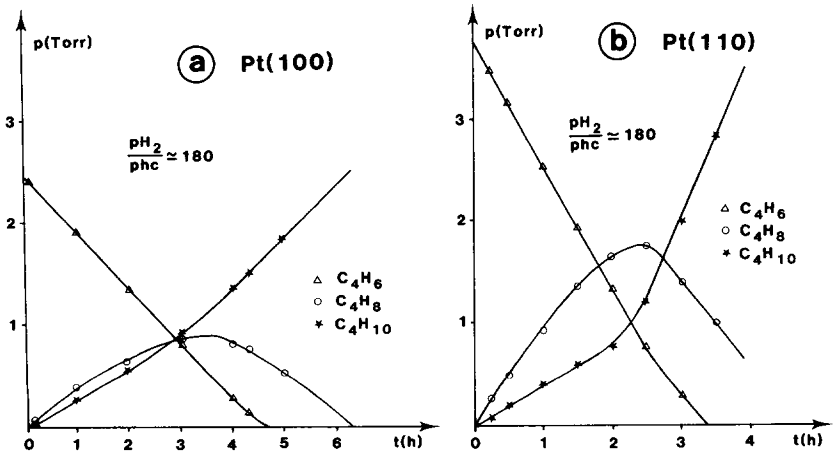


FIG. 3. Catalytic activity of Pt(100) and Pt(110) versus reaction time (T = 298 K).

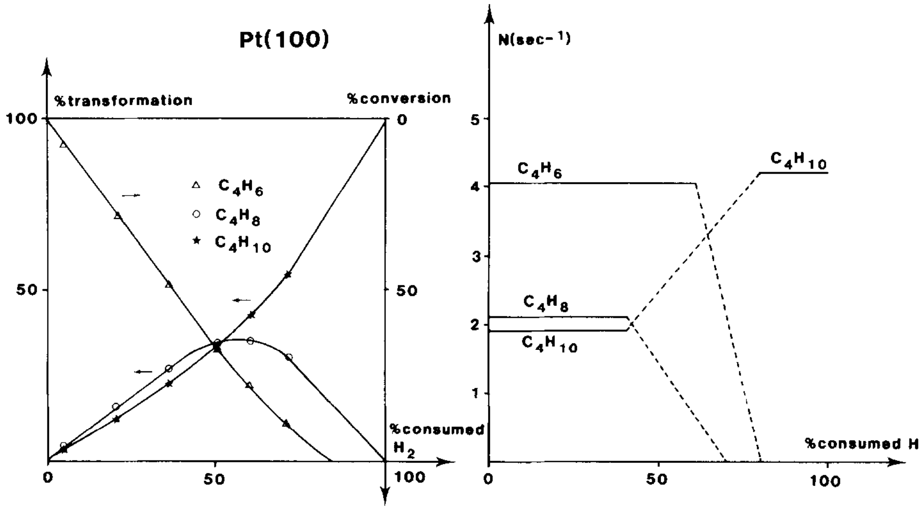


FIG. 4. Catalytic activity of Pt(100) versus H_2 consumption.

With respect to H_2, the kinetic order measured at room temperature is about 1 ± 0.1 for the C_4H_6 and C_4H_8 consecutive hydrogenations.

The apparent activation energy has been measured between 298 and 398 K. A lower value has been found for the C_4H_8 consecutive hydrogenation, 7 ± 1 kcal mol^{-1}, as compared with about 10 ± 1 kcal mol^{-1} for the first hydrogenation. Typical results concerning both the activity and the selectivity with respect to the consumed H_2 are shown in Figs. 4 and 5. The activity (turnover number N) for butadiene hydrogenation on Pt(100) is about twice that observed on Pt(111) (4 s^{-1} as compared with 2 s^{-1}) but the S_1 selectivity relative to the selective hydrogenation is slightly weaker. A higher activity for C_4H_6 hydrogenation and a better S_1 selectivity are observed on Pt(110) (Table 1).

Hydrogenation of 1,3-Butadiene on K-Promoted Pt(100)

The selective hydrogenation of C_4H_6 has been performed on samples for which the K coverage is varied from 0.1 to 0.7 monolayer. Only two measurements have been carried out with Na, for 0.38 and 0.43 monolayer Na coverage.

Typical Auger spectra of two K-promoted samples are presented in Figs. 6a and 7a.

The reaction rate as measured from the C_4H_6 conversion is constant along the run in agreement with a zero order for C_4H_6 (Fig. 8). The H_2 order for the partial and for the total hydrogenation has been determined and found to be about the same (1 ± 0.1) for both reactions, nearly independent of the alkali coverage.

The apparent energy of activation has been determined between room tempera-

TABLE 1

Catalytic Behavior of Low-Index Faces of Pt

Catalysts	N at 298 K[a] (s^{-1})	S_1		S_2
		[b]	[c]	
Pt(100)	4	0.54	0.5	0.55
Pt(110)	7	0.64	0.6	0.55
Pd(111)[d]	2	0.58	0.55	0.5
Pd(100) + K[e]	4	0.6	0.54	0.8

[a] $p_{H_2} \simeq 755$ Torr, $p_{C_4H_6} \simeq 5$ Torr.
[b] Up to 50% conversion (298 K).
[c] At 80% conversion.
[d] From Ref. (1).
[e] $\Theta_K \leq 0.43$.

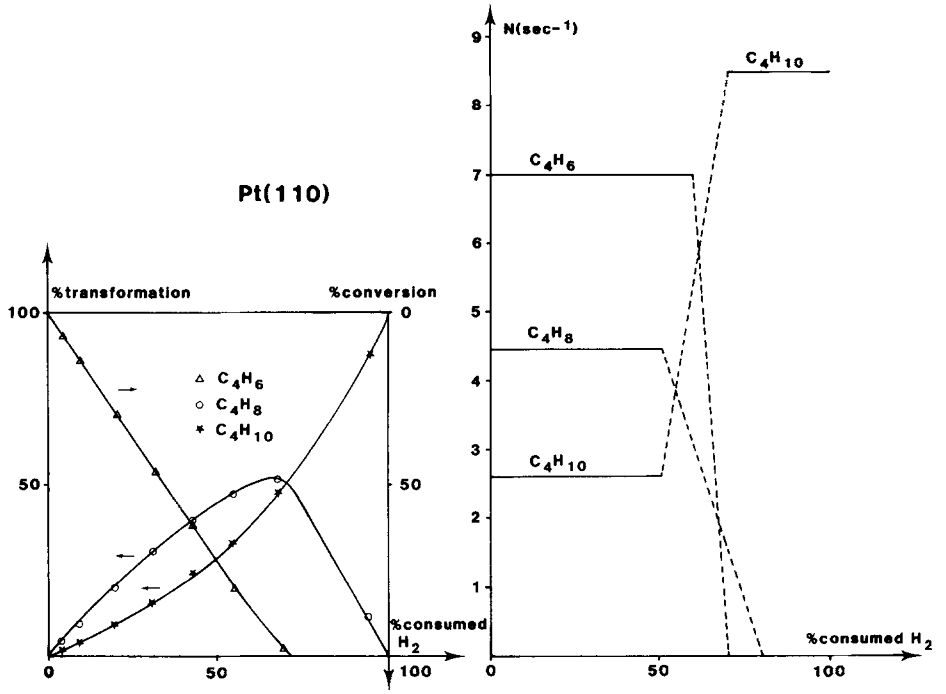


FIG. 5. Catalytic activity of Pt(110) versus H_2 consumption.

ture and 373 K for three Θ_K values: 0.1, 0.19, and 0.43. The value for C_4H_8 formation is 11 ± 1 kcal mol^{-1} and that for C_4H_{10} formation 8 ± 1 kcal mol^{-1}. No significant difference has been recorded with the different Θ_K values and with the results gained on pure Pt(100). However, as on the pure metal, the selectivity S_1 = 1-butene/Σ prod-

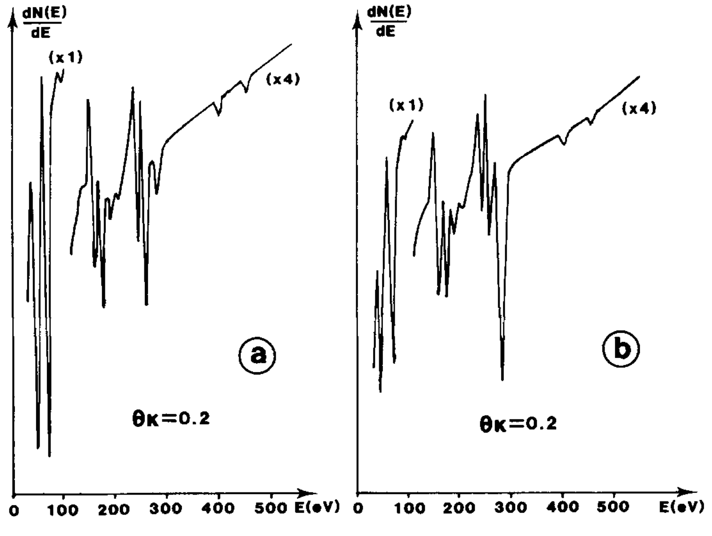


FIG. 6. AES spectra for Pt(100) + K: (a) before reaction, (b) after C_4H_6 hydrogenation (Θ_K = 0.2 monolayer).

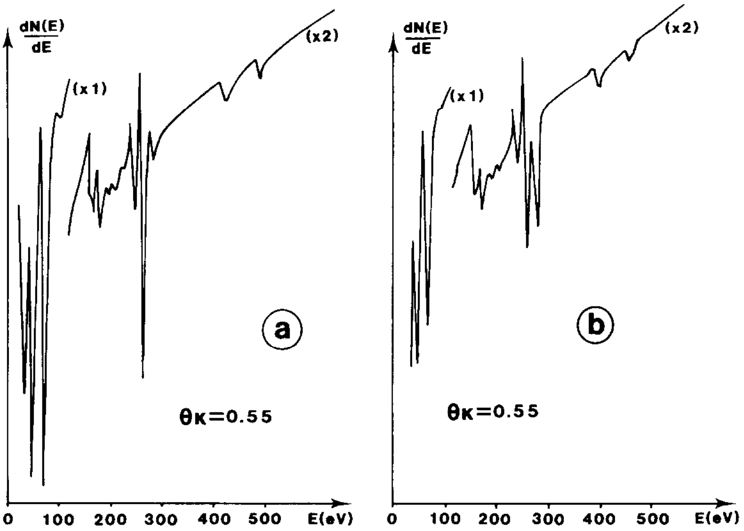


FIG. 7. AES spectra for Pt(100) + K: (a) before reaction, (b) after C_4H_6 hydrogenation ($\Theta_K = 0.55$ monolayer).

ucts is increased when increasing the reaction temperature, at least between 298 and 373 K.

The diagrams of activity and selectivity expressed as a function of the total amount of consumed H_2 are shown in Figs. 9–12 for different Θ_K values. The activity, expressed as the turnover number in second^{-1} is determined *by taking into account the same total number of Pt surface atoms* on the sample whatever the alkali coverage, i.e., the number of unpromoted Pt atoms on the clean surface.

Up to $\Theta_K \leq 0.43$, the activity is quite comparable to or slightly higher than that of pure Pt(100) ($\simeq 4\ s^{-1} \pm 0.2\ s^{-1}$). As the number of Pt atoms uncovered by K is decreasing with Θ_K, the activity of unblocked Pt atoms must be considered as higher, while the S_1 selectivity in total butenes is slightly enhanced. With respect to the total butene amounts, a higher 1-butene content in the

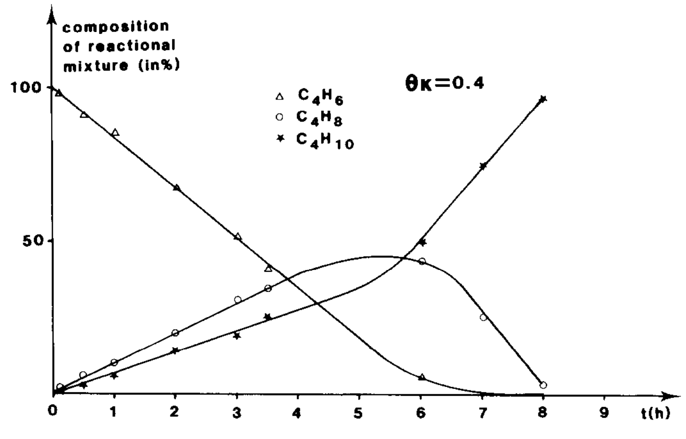


FIG. 8. C_4H_6 hydrogenation on Pt(100) + K: $\Theta_K = 0.4$ monolayer). Activity versus the reaction time.

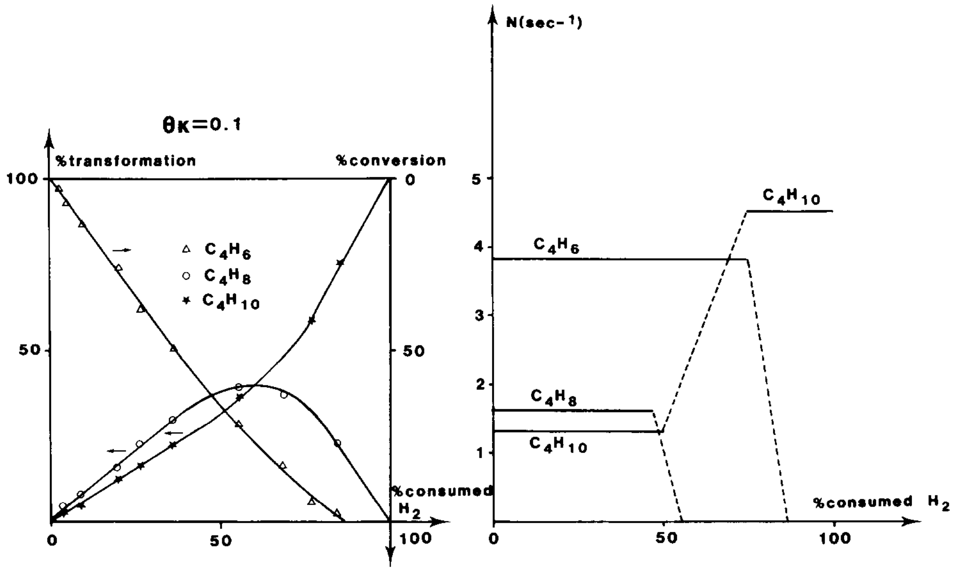


FIG. 9. C_4H_6 hydrogenation on Pt(100) + K (Θ_K = 0.1 monolayer): conversion and respective rates for C_4H_6, C_4H_8, and C_4H_{10} versus the H_2 consumption.

reactive mixtures is measured: 82 ± 5% for Θ_K = 0.19, 86 ± 5% for Θ_K = 0.4 instead of ≃60% on pure Pt.

The same behavior has been observed with Na additives. For the two Θ_{Na} values considered, a slight increase in both butenes and 1-butene selectivities are measured. The activity for the total reaction stays about the same as that of the clean surface, as for the K-promoted Pt surface.

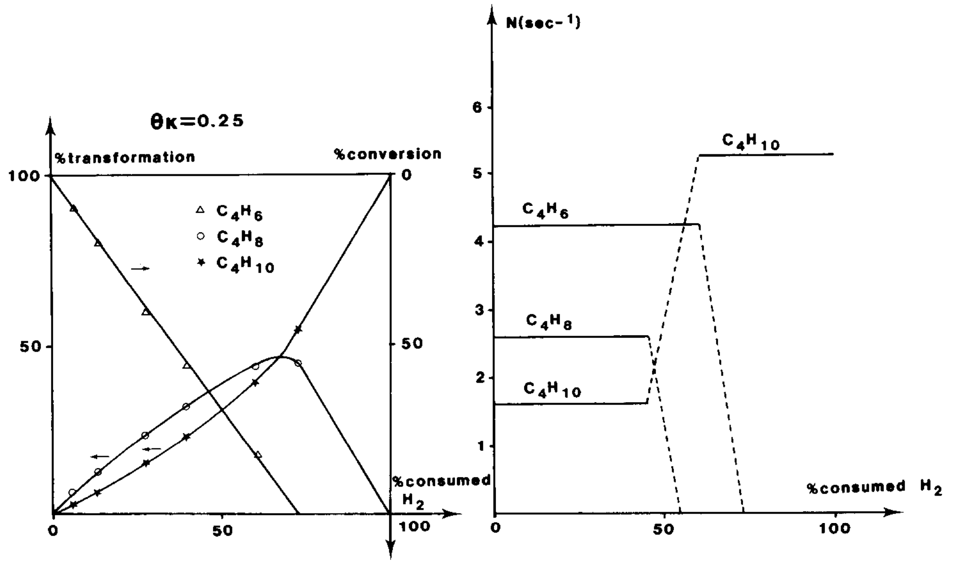


FIG. 10. C_4H_6 hydrogenation on Pt(100) + K (Θ_K = 0.25 monolayer): conversion and respective rates for reactant and products versus the H_2 consumption.

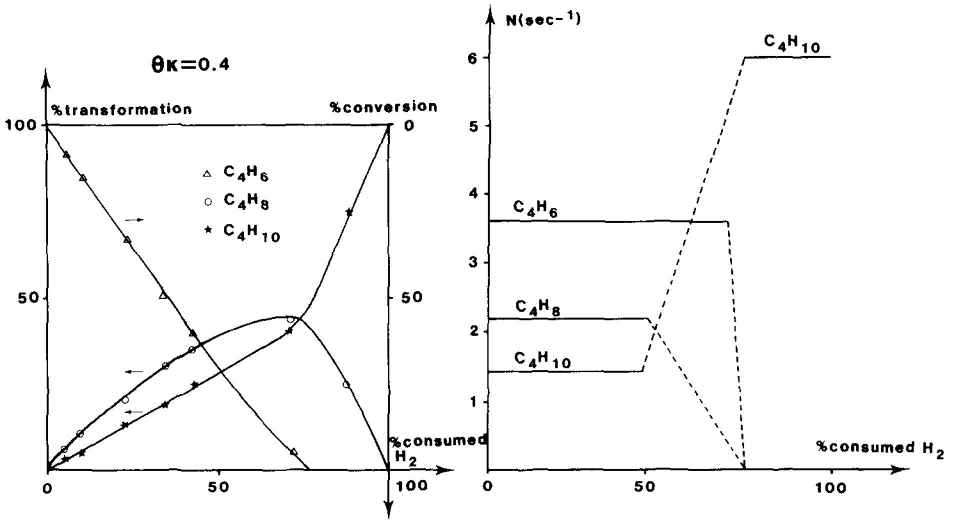


FIG. 11. C_4H_6 hydrogenation on Pt(100) + K (Θ_K = 0.4 monolayer): conversion and respective rates versus the H_2 consumption.

DISCUSSION

On pure Pt(100) and Pt(110) samples the respective orders for the hydrocarbon (zero) or H_2 (near unity) and the apparent energies of activation are in good agreement with those reported for the Group VIII metals (*10, 11*) and consistent with the butadiene species being more strongly adsorbed than hydrogen under the experimental conditions on both Pt(100) and Pt(110). The 1-butene is 55 ± 5% of the total amount of the butenes. This proportion is only poorly dependent on the H_2 pressure (300

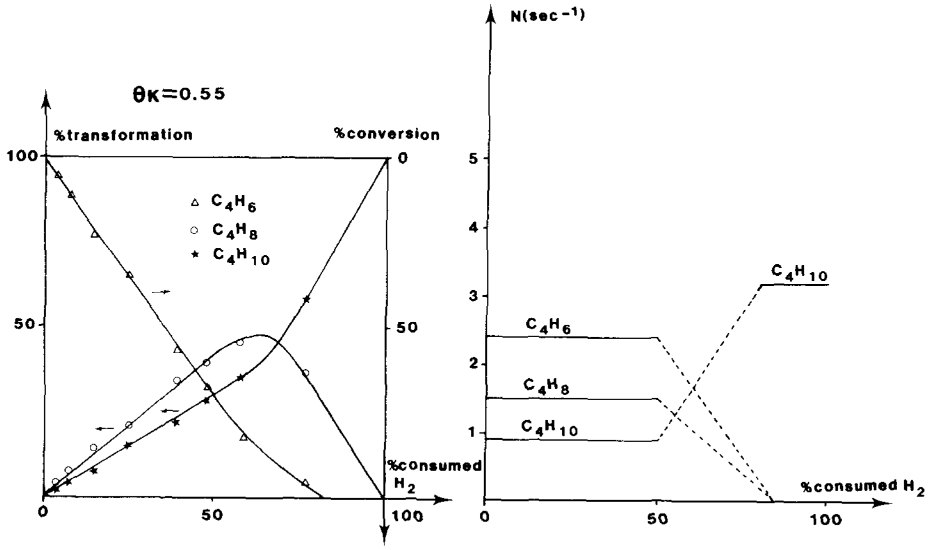


FIG. 12. C_4H_6 hydrogenation on Pt(100) + K (Θ_K = 0.55 monolayer): conversion and respective rates versus the H_2 consumption.

or 760 Torr) and on the temperature up to 398 K.

Such an invariance of product composition with the temperature and the reactant pressures has already been observed on other Group VIII metals including Co and Ni (*11*), Re (*12*), Rh and Pt (*10, 13*). It may be assumed, therefore, as has been established for the other metals, that all the isomeric butenes are formed as primary products and that butene isomerization before desorption is negligible (*13*). Thus, Pt(100) and Pt(110) single crystals behave in the same way as the more conventional supported Pt catalysts.

Concerning the butane yield, three main points must be discussed (*12*):

(i) the relative activities of platinum for butadiene and butene hydrogenation and the ratio between the C_4H_8 desorption rate and that for the C_4H_8 hydrogenation which has been estimated ≈0.05 on Pt(10) (this ratio is therefore not in favor of an enhancement of the S_1 selectivity);

(ii) the difference between the adsorption coefficient of butadiene and butene; and

(iii) the existence of regions in the metal in which H_2 occlusion occurs.

This third point has been invoked in order to differentiate two different reaction sites, a site where no occluded hydrogen would be present (which would then be responsible for the selective hydrogenation) and a second type of site keeping hydrogen occluded in some disorders generated during the reduction process (*14*). These disorders would consist of vacancies or cavities in the structure. The surface having hydrogen in it would be able to supply the hydrogen available to convert butadiene into butane (*12*). The presence of occluded hydrogen has been evidenced on supported catalysts where, according to Wells and coworkers, 20% of the hydrogen available is titrated very rapidly and about 80% is exchanged over a long period. However, such an occlusion in well-annealed single-crystal platinum samples must be very weak (*15*).

The butane yield is therefore mainly dependent on the two first points. In order to appreciate the importance of the relative rates for the hydrogenation of diene and that of olefin, hydrogenation of 1-butene alone on Pt(100) has been undertaken at about 4 Torr for butene and near atmospheric pressure for H_2. A constant rate ($\approx 8\ s^{-1}$, 298 K) is observed in the course of the run which indicates a zero order for C_4H_8. This rate is higher than that observed for C_4H_6 hydrogenation and therefore would lead to a significant decrease in selectivity S_1. Indeed, the rate of the disappearance of C_4H_8 is higher than the corresponding rate for its formation. An S_1 selectivity weaker than 0.5 is expected even at the beginning of the reaction. Nevertheless, the hydrogenation of butene consecutive to the C_4H_6 hydrogenation on Pt(100) is about 3–4 s^{-1} (Fig. 4). This lower value results from the partial poisoning of the surface sample. Indeed, as shown in Fig. 1b, carbon is left after reaction. From the I_{Pt237}/I_{C272} Auger peak ratio, the carbon coverage Θ_C, determined from the calibration proposed by Somorjai and co-workers (*16*) (a correction has been made since measurements are performed with a CMA spectrometer), equals about 0.6 monolayer after the reaction.

In addition to these differences in the relative hydrogenation rates for the diene and the olefin, the competition of adsorption between C_4H_6 and C_4H_8 must be considered to explain the S_1 selectivity increase, the 1,3-butadiene being the more strongly bonded species. The decrease in S_1 when the conversion increases results from the increase in the surface coverage by butenes, since their partial pressure increases, whereas that of C_4H_6 decreases.

On Pt(110), the higher activity results from a less strong interaction with C_4H_6 or (and) an increase in the H–metal bond strength and consequently a higher hydrogen coverage. The adsorption energy of H_2 is higher for the more open surfaces, increasing from 16 kcal mol^{-1} on Pt(111) (*17*) to 22–25 kcal mol^{-1} on polycrystalline samples (*18, 19*).

The S_1 selectivity changes are the consequence of modifications in the relative hydrogenation rates and (or) in the adsorption strengths between the 1,3-butadiene and the butenes. Different adsorption modes have been invoked for C_4H_6 (*10*) depending on the surface structure (*20*). In addition, a different behavior for C_4H_6 hydrogenation has been reported on Pt(100) or Pt(110) with respect to their sulfur resistance (*21*).

After alkali (Na or K) addition on Pt(100), the kinetic parameters are not markedly varied with respect to pure platinum; therefore it may be reasonably assumed that the same reactive scheme is still relevant.

Depending on the relative bond strengths between the adsorbed species, the selectivity and activity may vary, as already observed on other metals (*3, 5, 6, 12*). Thus, in order to appreciate more accurately the alkali effect on the selective hydrogenation of 1,3-butadiene, the modification of chemisorptive properties induced by alkali additive effect must be discussed.

Indeed, alkali-promoted Pt is showing modified chemical properties. From a previous study (*8*), it has been concluded that for low K coverage, $\Theta_K \leq 0.35$, a large charge donation occurs generating a so-called "via the metal interaction" from the alkali through the underlying platinum crystal. As a consequence, a CO bond-strengthening has been observed at low alkali coverage on Pt(100) (*8*) and also on Pt(111) (*22*). For an adsorbed hydrocarbon such as benzene or acetylene for which the chemisorption involves generally a transfer from the hydrocarbon to the metal, a weakening of the hydrocarbon–metal interaction is expected, the metal acting as a Lewis acid toward these hydrocarbons (*2*) as observed on K + Pt(111) (*22*). An alternative explanation is proposed based on a theoretical study developed from the HOMO-LUMO concept of molecular orbital theory which concludes that the alkali adsorption changes the relative position of the adsorbate levels with respect to the Fermi level of the metal due to the positive charge of the adsorbed alkali (*23*). This would modify the donating and (or) back-donating contributions to the adsorption energy of adsorbed species.

Therefore, up to $\Theta_K = 0.4$ monolayer, where K^+ ions are supposed to be statistically distributed on the surface (*8*), the influence of the alkali promoter must be compared to that obtained by the ligand effect of piperidine on Pd (*6*), inducing an increase in the activity and in the S_1 selectivity. The alkali would act as a decomplexing ligand. Also, from the "volcano curve" (rate constant, *k*, versus adsorption coefficient, *b*) (*9*) a decrease in *b* for C_4H_6 would induce an increase in *k*. The reverse behavior is occurring for C_4H_8. In addition, an enhancement of activity can also be expected if H_2 is more strongly bonded on K-promoted Pt, as has been indicated for K + Ni (100) (*24*).

In the same way, an increase in the selectivities of butene-1/Σ butenes and of *cis*-2-butene/*trans*-2-butene has been evidenced on Ni promoted by an electron donor (boron) (*3*) and related to an increase in the electron density on the nickel particles (evidenced by a negative shift of the binding energy measured by XPS) (*25*).

For higher alkali content, K or Na would have a metallic rather than ionic character, as shown for example, from the effective constancy of the work function (*8*). Results can be explained in terms of a pure geometric blocking effect by the alkali deposits. As a matter of fact, the activity decreases with Θ_K: for $\Theta_K = 0.55$ the activity is 2.40 s^{-1} and only 0.95 s^{-1} for $\Theta_K = 0.7$.

It is noteworthy to add that the butene hydrogenation rate after the total conversion of C_4H_6 is not very much changed and is even increased ($\simeq 6$ s^{-1} for $\Theta_K = 0.4$) with respect to pure Pt when Θ_K is increased up to 0.4; this corresponds to a higher activity if related only to uncovered Pt atoms. The same behavior is also observed for the simple C_4H_8 hydrogenation (without 1,3-C_4H_6); the rate, $\simeq 8$ s^{-1} up to $\Theta_K \simeq 0.4$, is only decreasing markedly for $\Theta_K = 0.7$ (3 s^{-1}). Moreover, the carbon deposit after the run determined by AES spectroscopy (*16*) corresponds to about $\Theta_C = 0.6$. Therefore, the reaction would occur on a surface nearly covered by the alkali metal and the carbon unless the arrangements in the surface of K and C are growing by islands of several layers: this cannot be ruled out, at least for large values of the K coverage, although on Pt(111), for $\Theta_K \simeq 0.9$–1, a LEED pattern has been observed corresponding to K hexagonally ordered on the surface (*26*).

In conclusion, the whole set of results for the selective hydrogenation of 1,3-butadiene on Pt(100) may be explained by a consecutive scheme, in which the totality of butenes would be the primary products, since the S_2 selectivity is independent of the reactant pressures and the reaction temperature. The S_1 selectivity and its diminishing value in the course of the run results mainly from the competitive adsorption between C_4H_6 and C_4H_8. Nevertheless, the existence of two types of site on Pt(100), one for selective hydrogenation and the other for the complete hydrogenation, is quite improbable. This could be a difference with respect to conventional catalysts since on platinum single-crystal samples the presence of occluded hydrogen is highly improbable, but not so on supported Pt samples. Therefore, the selectivity on Pt would be closely dependent on the relative hydrogenation rates between C_4H_6 and C_4H_8 and on their respective adsorption coefficients.

Alkali additives improve the activity and the selectivity for the 1,3-C_4H_6 hydrogenation up to a Θ_K of 0.4. Up to this value, the alkali acts as an electron donor and changes the relative energies of adsorbate and metal orbitals. Its effect may be compared to that of the piperidine ligand. For higher Θ_K values, a pure blocking effect may be invoked.

The increase in activity observed both on the more open structures and on K-promoted platinum may be related to a weakening of the hydrocarbon adsorption bond strength and (or) an increase in the H–metal bond strength.

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