

# Applicability and Limits of the Ensemble Model in Catalysis by Metals: The Kinetics of Ethane Hydrogenolysis over Pt/SiO<sub>2</sub>

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The rate of ethane hydrogenolysis over the EUROPT 1 (Pt/SiO<sub>2</sub>) catalyst has been studied over a large range of pressure and temperature. At ethane pressures, P<sub>E</sub>, lower than 1.3 kPa the hydrocarbon coverage is shown to be negligible. For T, P conditions which correspond to a degree of hydrogen coverage, θ<sub>H</sub>, below 0.6 ML (monolayer), the rate *r* is found to be related to θ<sub>H</sub> and P<sub>E</sub>, by the equation,  $r = k_0 P_E e^{-E_0/RT} (1 - \beta \theta_H)^X$ , with *k*<sub>0</sub> approximately 4 times smaller than the number of ethane molecules colliding with the Pt surface, E<sub>0</sub> = 55 ± 7 kJ mol<sup>-1</sup>, X = 9 ± 2, and β = 1.3 ± 0.1. This rate equation which models on a quantitative ground the complex variations of *r* with T and P might be considered as describing a two-body process between gaseous ethane and surface ensembles composed of X adjacent platinum atoms free from adsorbed hydrogen, E<sub>0</sub> being the activation energy. The constant β takes into consideration the fact that at saturation the surface stoichiometry H/Pt<sub>s</sub> is larger than unity. In a T, P domain which corresponds to hydrogen coverage above 0.6 ML, a marked change in the evolution of the kinetic parameters is observed: the apparent activation energy starts to decrease and the order versus the hydrogen pressure starts to be less negative by decreasing the temperature. The above purely statistical model does not apply anymore to this kinetic domain, which could be characterised by some H adsorption ordering. This work shows that the ensemble model, successfully applied to describe catalytic reactions occurring over Rh and Ni catalysts, can be extended to the case of Pt, within a domain characterized by a moderate hydrogen coverage and a purely statistical adsorption process. © 1998 Academic Press

**Key Words:** ethane; hydrogenolysis; Pt/SiO<sub>2</sub>; kinetics; ensemble model.

## 1. INTRODUCTION

The idea that adsorbed species and intermediates in catalysis by metals may require ensembles composed of several adjacent free-surface atoms has been first expressed by Balandin (1) who, as early as 1929, suggested that a reacting molecule may be simultaneously adsorbed on several atoms. Since then, this model proves to be versatile: it is frequently invoked to account for various catalytic phe-

nomena such as alloying effects, size sensitivity, poisoning, and compensating effects (2–7). It is also useful in the field of kinetics; in a number of catalytic reactions involving hydrogen and hydrocarbons, such as deuterium–hydrocarbon exchange, hydrogenolysis, and hydro-isomerization, hydrogen demonstrates a strong inhibiting effect which is well accounted for on a quantitative ground assuming that reaction takes place on patches composed of a certain number of metal atoms.

The complex kinetic behaviour of the exchange reaction over Rh films (2) or Ni/SiO<sub>2</sub> catalysts (8) and of hydrocarbon hydrogenolysis over Ni/SiO<sub>2</sub> (9) can be properly described within this framework by using only two parameters: the true activation energy, and the nuclearity of the active site, considered as an ensemble composed of several adjacent free metal atoms. Surprisingly no kinetic treatment of hydrocarbon conversion reaction over platinum, frequently utilised in catalysis by metals, has been achieved using the ensemble model. This paper aims at investigating how far this model can be extended to the case of platinum. Ethane hydrogenolysis was selected as a model reaction owing to its simplicity.

Although this reaction received considerable attention (10–17), the kinetic parameters seem to depend either on the morphology of platinum (13, 15, 16) or on the experimental conditions under which they are measured. As an example, apparent activation energies as different as, e.g., 225 and 84 kJ mole<sup>-1</sup> (10, 11, 16) have been reported. This situation leads us to re-examine these questions by determining apparent kinetic parameters over a large range of experimental conditions including high temperature measurements (above 650 K). This implies a preliminary study of the change of morphological and catalytic properties of the solid undergone by thermal treatments.

The catalyst is the EUROPT 1 Pt/SiO<sub>2</sub> material, extensively described in a series of papers (18–22). Hydrogen adsorption isotherms are available (18, 19). As a first step the influence of the reduction temperature of the catalyst on its morphological and catalytic properties is examined. Then the experimental conditions where the platinum surface is mainly covered with hydrogen (i.e., with a negligible

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hydrocarbon coverage,  $\theta_{\text{HC}}$ ) are determined using isotopic transient kinetic methods. The third stage of this study consists of measuring the variation of the rate  $r$  with temperature  $T$  and partial pressures,  $P_{\text{E}}$  and  $P_{\text{H}}$ , ethane and hydrogen partial pressures, respectively, at conditions where  $\theta_{\text{HC}}$  is small. From these data, a kinetic model based on the above-mentioned statistical approach is tested, which significance and limits are discussed in the last section of this paper.

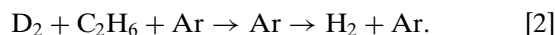
## 2. EXPERIMENTAL

The reference catalyst EUROPT 1 (6.3 wt% Pt/SiO<sub>2</sub>) was prepared by impregnation of SiO<sub>2</sub> (Sorbisil AQ U 30 from Crossfield Chemical, surface area equal to 185 m<sup>2</sup> g<sup>-1</sup>) with Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> in alkaline solution. It was reduced for 15 h at different temperatures in flowing hydrogen (3 liters h<sup>-1</sup>). Some complementary morphological characterisations were carried out using volumetric hydrogen chemisorption and electronic microscopy. The amount of adsorbed gas at room temperature under 5.2 kPa was measured in a classical volumetric apparatus equipped with a Texas Instruments gauge, after outgassing the catalyst at 573 K for 1 h. The electron microscopy investigation was carried out in a JEOL, JEM 100 CX microscope.

Kinetic studies were carried out in a flow system using quartz fixed-bed microreactors at atmospheric pressure. The total gas flow was 7 liters h<sup>-1</sup> and partial pressures of hydrogen and ethane were varied over the ranges 6.6–80 and 0.03–5 kPa, respectively, helium being used as a diluent.

Several pressure and temperature cycles were carried out to check that aging did not lead to excessive uncertainties. The catalyst weight was changed from 30 to 1000 mg to span a large range of temperature and pressure, while keeping conversion smaller than a few percentages.

Experiments aimed at comparing the adsorption of hydrogen in the presence (under hydrogenolysis conditions) and in the absence of ethane were carried out using the isotopic transient kinetic technique described elsewhere (23). They consisted in titrating the adsorbed hydrogen (deuterium) in steady-state regime under given  $T$  and  $P$  conditions either in the presence or in the absence of ethane. The two following sequences were used at constant flow rate and pressures: (total flow rate, 30 ml min<sup>-1</sup>; H<sub>2</sub> and D<sub>2</sub> partial pressure = 13 kPa, C<sub>2</sub>H<sub>6</sub> partial pressure = 1.3 kPa in sequence [2]):



Argon was used to flush the initial gaseous phase. The flushing time was minimised in order to limit the desorption of the D species adsorbed during the initial adsorption step. The total amount of titrated deuterium was calculated by

summing the area of the D<sub>2</sub> peak and half the area of the HD peak. It was checked by increasing rapidly the temperature after having obtained the HD and D<sub>2</sub> peaks under isothermal conditions that no significant further exchange (production of D<sub>2</sub> and HD) occurred, whatever the titration temperature. This allowed us to discard the possibility of an exchange of hydroxyl groups from the silica via proton spillover occurring simultaneously with the H/D exchange on the Pt particles.

## 3. RESULTS AND DISCUSSION

### 3.1. Particle Size and Hydrogen Chemisorption

The results are summarized in Table 1. The surface average diameter,  $D_{\text{s}}$ , of Pt particles in EUROPT 1 reduced at 676 K is found to be 1.85 nm by electron microscopy, in good agreement with data of other laboratories (18–22). As the reduction temperature,  $T_{\text{r}}$ , increases,  $D_{\text{s}}$  increases moderately confirming that this catalyst is particularly thermostable.

The amount of adsorbed hydrogen over the sample reduced at 673 K is found to be nearly equal to that reported by other groups. Hydrogen uptake decreases more rapidly than expected from the increase of particle diameter determined from electron microscopy as the reduction temperature increases. This is illustrated in Table 1 by comparing  $D_{\text{s}}$  and  $D_{\text{H}}$ , the diameter calculated from hydrogen chemisorption, assuming that both diameters coincide at  $T_{\text{r}} = 673$  K. It has been shown elsewhere (24) that this behaviour is very similar to that observed for Pt/TiO<sub>2</sub> catalysts; as a matter of fact, an oxygen treatment of Pt/SiO<sub>2</sub> reduced at high temperature, followed by a reduction at moderate temperature, restores the chemisorption properties. This behaviour is typical of the so-called strong metal–support interaction (SMSI).

TABLE 1  
Dependence of Morphological Characteristics of EUROPT 1 on Reduction Temperature,  $T_{\text{r}}$

$T_{\text{r}}$ (K)	$D_{\text{s}}^a$ (nm)	$q_{\text{H}}^b$ ( $\mu\text{mol} \cdot \text{g}^{-1}\text{cat}$ )	$D_{\text{H}}^c$ (nm)
553		167	
673	1.85	167	1.85
773		138	2.24
968		54	5.7
1045	2.5		
1103	2.9	19	16.2
1273	5.0		

<sup>a</sup> Surface average diameter calculated from the examination of ca 400 particles by electron microscopy ( $D_{\text{s}}: \sum_i n_i D_i^3 / \sum_i n_i D_i^2$ ).

<sup>b</sup> Amount of adsorbed hydrogen at room temperature under 5.3 kPa.

<sup>c</sup> Diameter calculated from H<sub>2</sub> chemisorption assuming that  $D_{\text{s}} = D_{\text{H}}$  at  $T_{\text{r}} = 673$  K.

### 3.2. Hydrocarbon Coverage in the Course of Reaction

Figure 1 compares the amount of adsorbed deuterium (hydrogen) in the presence or in the absence of ethane as determined from the isotopic transient kinetic titration. In the absence of ethane (sequence D<sub>2</sub> + Ar/Ar/H<sub>2</sub> + Ar), the amount of adsorbed hydrogen thus obtained is in agreement with data obtained from volumetric technique by Crucq *et al.* (18) for EUROPT 1 reduced at 573 K. As an example, under 0.13 kPa the extent of the hydrogen adsorption at 500 and 550 K is found to be 88 and 75  $\mu\text{mol g}_{\text{cat}}^{-1}$  by the latter authors, and 94 and 67  $\mu\text{mol g}_{\text{cat}}^{-1}$  by the present transient method, respectively. This observation confirms that this technique is a valuable tool for evaluating the hydrogen coverage of a catalytic surface (23). The main feature revealed in Fig. 1 is that the amounts of adsorbed hydrogen are very close either in the absence or in the presence of ethane (1.3 kPa) over the wide T range studied. This means that the adsorption of hydrogen onto a platinum surface is not significantly altered by the simultaneous presence of ethane. This is also consistent with the idea that the hydrocarbon coverage is probably small and that the surface is mainly covered with hydrogen for this low hydrocarbon partial pressure. As a matter of fact, the accumulation of adsorbed hydrocarbon on the surface would have increased the amount of exchangeable H (or D) species under hydrogenolysis conditions.

A similar hypothesis has been put forward for the case of ethane hydrogenolysis over Ni/SiO<sub>2</sub> (9). This was based on the fact that the order with respect to the ethane partial pressure was found to be unity, arguing that significant hydrocarbon coverages would lead to orders smaller than unity (5). For the case of Ni/SiO<sub>2</sub> catalysts, however, no ad-

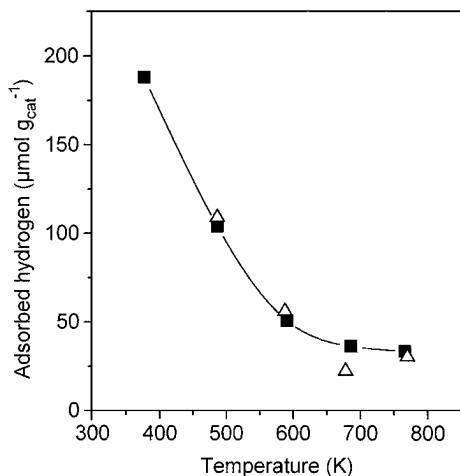


FIG. 1. Amounts of adsorbed hydrogen measured by isotopic transient kinetic titration over 5.3 mg of EUROPT 1 reduced at 773 K in the absence of ethane (squares) or under hydrogenolysis conditions (triangles).

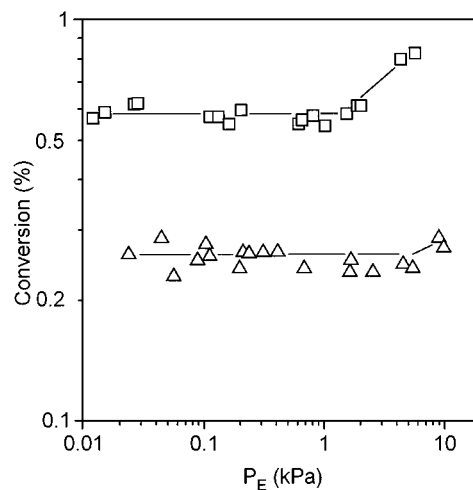


FIG. 2. Ethane conversion as a function of partial pressure of ethane over EUROPT 1 reduced at 773 K. Hydrogen pressure, 50.4 kPa, catalyst weight 29 mg, temperature of measurement 674 K (squares); hydrogen pressure 13.1 kPa, catalyst weight 526 mg, temperature of measurement 554 K (triangles).

ditional evidence from the isotopic transient technique was provided.

As expected, the order with respect to ethane,  $n_E$ , is also found to be unity on Pt/SiO<sub>2</sub> at moderate ethane pressure as illustrated by Fig. 2. The conversion of ethane is plotted against the partial pressure of ethane at 674 and 554 K over Pt/SiO<sub>2</sub> reduced at 773 K. Observed conversions are unchanged when varying  $P_E$  from low to high pressures and vice versa over two orders of magnitude. At ethane pressure in excess of 1.6 kPa at 674 K, the order is larger than unity (1.3). A similar behaviour was already reported for ethane hydrogenolysis over Ni/SiO<sub>2</sub> for which no clear explanation was provided (9). It could be speculated that at high ethane pressure, new catalytic sites would arise from mobile carbonaceous adspecies, as proposed by Somorjai *et al.* (29). A precise *in situ* evaluation of the surface coverage of such adspecies (e.g., by isotopic transient kinetics) is required for any further kinetic treatment.

Very similar data not shown here are obtained at intermediate reaction temperatures (609 K) and over Pt/SiO<sub>2</sub> reduced at 1045 and 573 K. These results show that irrespective of the reduction and measurement temperatures the order with respect to ethane is equal to unity over a large range of pressure as long as the ethane pressure does not exceed 1.3 kPa; this compares well with previous results reported for Pt/SiO<sub>2</sub> (10) and Pt/Al<sub>2</sub>O<sub>3</sub> (11).

### 3.3. Kinetic Study

The results reported below have been obtained in conditions where  $n_E = 1$ . Figure 3 illustrates the variation of the intrinsic activity (per unit area deduced from hydrogen chemisorption) with the reduction temperature. Catalytic

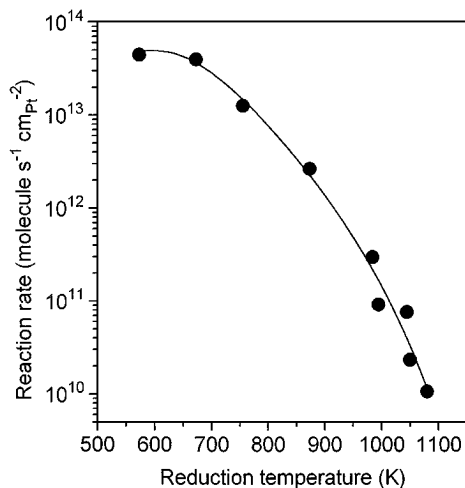


FIG. 3. Reaction rate measured at 673 K,  $P_H = 29$  kPa,  $P_E = 0.83$  kPa, as a function of the temperature of catalyst reduction.

activity is not much altered at reduction temperatures lower than 723 K; it decreases by more than three orders of magnitude when the reduction temperature is increased to 1080 K, confirming qualitatively preliminary results from our group (24) and results from Xu and Bond for the case of butane hydrogenolysis (25) which indicate that Pt/SiO<sub>2</sub> catalysts demonstrate a SMSI behaviour.

Orders with respect to hydrogen partial pressure were determined by varying the pressure in the range 8.3–80 kPa. They were found to be pressure dependent over this range. Average differential orders determined at 13, 26, and 53 kPa are shown in Figs. 4a, b, c, respectively. These data show that, as a first approximation, these orders do not depend on the reduction temperature for the case of Ni/SiO<sub>2</sub> catalysts (26). In contrast, orders in hydrogen vary with temperature and hydrogen pressure. Two domains can be distinguished: (i) at low temperatures (below 650 K),  $-n_H$  increases as T increases or  $P_H$  decreases; (ii) at high temperatures (above 650 K),  $-n_H$  decreases when T increases or  $P_H$  decreases. In contrast with the former trend, the latter trend can be compared to that observed over Ni/SiO<sub>2</sub> (24).

These data reveal a complex kinetic behaviour which can hardly be accounted for by a simple power law. Figure 5 shows the variation of apparent activation energy,  $E_a$ , for a given hydrogen partial pressure ( $P_H = 26$  kPa), with temperature measured at intervals of 40 K. Our results confirm previous results of the literature, indicating that this coefficient might be temperature dependent; Bond and Lou Hui (17) have observed a decrease of  $E_a$  when the temperature decreases from 610 to 550 K. Gao and Schmidt (16) have reported activation energies as low as 117 and 84 kJ mol<sup>-1</sup> at 525 and 550 K which are in line with our observations.

The volcano shape of the  $E_a$  vs T curve is quite remarkable and parallels the  $-n_H$  vs T curves of Fig. 4. This sit-

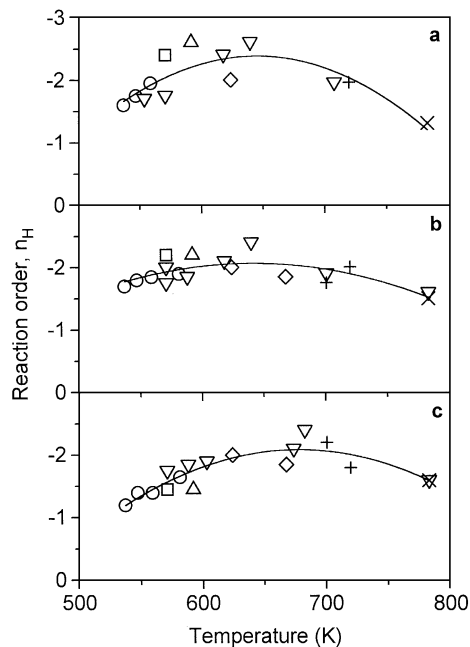


FIG. 4. Orders in hydrogen as a function of temperature of measurement at three hydrogen pressures, 13, 26, and 53 kPa (curves a, b, and c, respectively). The reduction temperatures are 573 (circle), 581 (square), 671 (up triangle), 773 (down triangle), 873 (diamond), 980 (+-cross), and 1076 K (x-cross).

uation is not unexpected, since, as discussed below, both parameters are related by the Temkin's equation (27)

$$E_a = E_0 - n_H Q, \quad [3]$$

where  $E_0$  is the true activation energy and  $Q$  is the isosteric heat of hydrogen adsorption. It can also be noticed that the high temperature variation of  $E_a$  with T is qualitatively

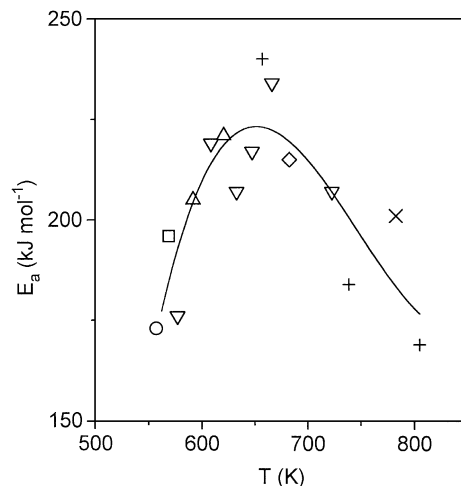


FIG. 5. Apparent activation energy at  $P_H = 26$  kPa as a function of temperature; symbols have the same significance as in Fig. 4.

similar to that observed over Ni/SiO<sub>2</sub> catalysts, suggesting comparable kinetic law.

In order to analyse and model these kinetic data, a precise knowledge of the hydrogen coverage is first required, over the large T, P conditions investigated in the present study.

### 3.4. Hydrogen Coverage Data

Crucq *et al.* (18) have measured the hydrogen coverage over EUROPT 1 reduced at 573 K over a large range of pressure (0.06 Pa–20 kPa) and temperature (77–562 K). Unfortunately, their data cannot be utilised directly for the substitution of  $\theta_H(T, P_H)$  in  $r(T, P_H)$  since our kinetic measurements were carried out in the 8.3–80 kPa and 538–800 K ranges. They can easily be extrapolated, however, since isotherms have been shown to obey the Temkin's law (they yield straight lines in a semilogarithm transform  $\theta_H$  vs  $\log P_H$ ). This extrapolation can be achieved using a Clapeyron transform,  $\log P_H$  vs  $1/T$  at isocoverage which yields the points (black symbols, curves 5–7) of the isobar network shown in Fig. 6. Experimental data of Crucq *et al.* (18) (open symbols, curves 1–5) were also successfully modelled using an empirical sigmoid-like function,  $\theta_H = ((T/b)^a + 1)^{-1}$ , where  $a$  and  $b$  depend upon the hydrogen pressure according to  $a = 4.13 P_H^{-0.035}$  and  $\log b = 2.56 + 4.1 \times 10^{-2} \log P_H + 5.2 \times 10^{-3} (\log P_H)^2$ , where  $P_H$  is expressed in Pa,  $b$ , and  $T$  in K. The isobars thus calculated can be compared to experimental and extrapolated points (curves 1–5 and 5–7, respectively) in Fig. 6 (solid lines). The  $\alpha$  coefficient of the Temkin's law,  $\theta_H \sim \alpha \log P_H$ , calculated according to data of Ref. (18) is found to be nearly constant over the range 500–800 K ( $\alpha = 0.12 \pm 0.01$ ); it decreases to 0.07 at 300 K.

From these data, an analysis of the two kinetic domains revealed in Figs. 4 and 5 can now be undertaken.

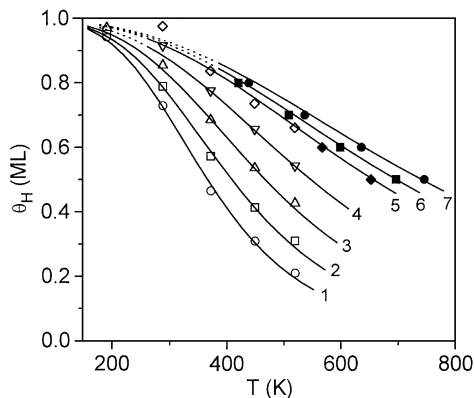


FIG. 6. Hydrogen coverage (monolayer) as a function of temperature at 1.3, 13, 131 Pa, 1.3, 13, 26.3, 53 kPa (data points in curves 1–7, respectively); solid symbols of curves 5–7 (black symbols) are obtained by extrapolation of data in Ref. (18) using the Clapeyron transform. Lines correspond to the sigmoid function (see text).

### 3.5. Kinetic Analysis of the High Temperature Domain (above 650 K)

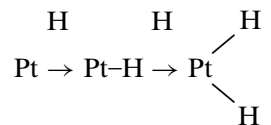
The data obtained at temperatures above ca 650 K in Figs. 4 and 5 parallel those obtained over Ni (9). For the latter metal the rate was shown to vary as  $(1 - \theta_H)^X$ . Let us investigate a similar law for Pt. Writing that the order in hydrogen pressure is equal to:

$$n_H = \left( \frac{\partial \log r}{\partial \log P_H} \right)_T = \left( \frac{\partial \log r}{\partial \theta_H} \right)_T \left( \frac{\partial \theta_H}{\partial \log P_H} \right)_T,$$

then differentiating  $r = k(1 - \theta)^X$  and considering that the Temkin's law is verified for  $P_H > 1$  kPa, i.e., for the hydrogenolysis conditions, ( $\theta_H \sim \alpha \log P_H$ ), Eq. [2] is obtained:

$$n_H = -\alpha \frac{X}{(1 - \theta_H)} \log e. \quad [4]$$

When plotting  $n_H$  versus  $1/(1 - \theta_H)$  the line thus obtained (not shown in this paper) does not go through the origin, indicating that Eq. [4] does not describe the kinetic data satisfactorily. The model can be improved by considering that over platinum two types of sites capable of accepting hydrogen atoms may coexist. This idea is based on the fact that the surface stoichiometry at saturation,  $H/Pt_s$ , where  $Pt_s$  denotes a surface platinum atom, is larger than unity. For the case of EUROPT 1 the experimental value of the  $H/Pt_t$  ratio, where  $Pt_t$  is the total number of platinum atoms, is found to be 1.1 (19). This shows that the mean stoichiometric ratio  $H/Pt_s = \beta$  is a fortiori larger than the latter value. Thus, it can be postulated that the concentration of Pt atoms free from adsorbed hydrogen atoms varies as  $(1 - \beta\theta)$  and that it goes to zero at  $\theta = \beta^{-1}$ . At coverage in excess of  $\beta^{-1}$ , some Pt–H sites are capable of accepting a second hydrogen atom and are therefore transformed into sites denoted Pt (–H)<sub>2</sub> according to the following steps:



The concentration of ensembles composed of adjacent free platinum atoms is now given by  $(1 - \beta\theta_H)^X$  and the relationship between  $n_H$  and  $\theta_H$  can be written as:

$$n_H = -\alpha \frac{\beta X}{1 - \beta\theta_H} \log e \quad [5]$$

or

$$\frac{\alpha}{n_H} = \frac{\theta_H}{X \log e} - \frac{1}{\beta X \log e}. \quad [6]$$

Thus, by plotting  $\alpha/n_H$  against  $\theta_H$ , a straight line should be obtained with a slope equal to  $(X \log e)^{-1}$  and the ordinate at  $\theta_H = 0$  equal to  $-(\beta X \log e)^{-1}$ . As can be seen in Fig. 7,

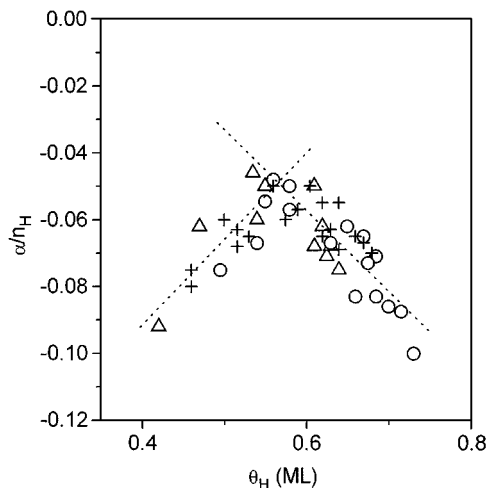


FIG. 7. Variation of  $\alpha/n_H$  with hydrogen coverage,  $\theta_H$  (ML). The order with respect to hydrogen,  $n_H$ , is measured at 13, 26, and 53 kPa (triangles, crosses, circles, respectively).

our kinetic data are reasonably well represented by such a model in the domain of  $\theta_H$  values below ca 0.6, which corresponds actually to the high T hydrogenolysis conditions. It can be stressed at that point that the two kinetic domains revealed by the volcano shape curves in Figs. 4, and 5 could therefore be related directly to the hydrogen coverage, as indicated in Fig. 7. A linear regression analysis of low  $\theta_H$  data shows that  $X = 9.0 \pm 0.2$  (as calculated from the slope). However, accounting for the uncertainty on  $\alpha$  and  $n_H$  values, the actual uncertainty on X is evaluated to  $\pm 2$ . Introducing this X value in the ordinate at  $\theta_H = 0$ , the mean surface stoichiometry,  $\beta = H/Pt_s$ , is found to be  $1.3 \pm 0.1$ , which is a plausible value arising from a combination of PtH and PtH<sub>2</sub> species. In other words, within the domain of low H coverage, the complex variations of the order in hydrogen with T and P which have been observed are fully accounted for from a quantitative point of view assuming that the reaction rate varies as

$$r = k(1 - \beta\theta_H)^X P_E, \quad [7]$$

where k is the rate constant,  $P_E$  is the pressure of ethane which accounts for the order one observed experimentally (Fig. 1),  $\beta$  is the surface stoichiometry for hydrogen adsorption; the active site is an ensemble composed of X adjacent platinum atoms free from hydrogen atoms with  $X \approx 9$ .

As discussed elsewhere (9), the apparent activation energy,  $E_a$ , is a coefficient of temperature originating from the variations of k and  $(1 - \beta\theta)^X$  with T. It can be written as

$$E_a = E_0 + E_\theta, \quad [8]$$

where  $E_\theta$  is the energy related to the hydrogen adsorption,  $E_0$  is the true activation energy related to the rate constant

k as

$$k = k_0 e^{-E_0/RT}. \quad [9]$$

The true activation energy  $E_0$  can be calculated using the Temkin's equation [3], relating  $E_a$ ,  $E_0$  and  $n_H$ . Figure 8 shows the variations of  $E_a$  with  $n_H$ . Our experimental points are in agreement with data of the literature (10, 11, 13, 28). An extrapolation at zero order of our data obtained at high temperature over the 648–805 K range (circles, Fig. 8) is very uncertain. The data of Crucq *et al.* (18) show that the slope of the extrapolation line, Q, which is the isosteric heat of hydrogen adsorption, can be considered to a first approximation, nearly constant; it varies from 88 to 79 kJ mol<sup>-1</sup> for the extreme conditions of temperature used in Fig. 8 (650–800 K), which corresponds to small variations of hydrogen coverages (0.55–0.45 ML). Using the average value,  $Q = 84$  kJ mol<sup>-1</sup>, the following true activation energy,  $55 \pm 7$  kJ mol<sup>-1</sup> is calculated from a linear regression. The true activation  $E_0$  being known,  $k_0$  can be directly calculated from Eqs. [7] and [9].

Thus, the rate measured at 673 K,  $P_H = 29$  kPa,  $P_E = 0.83$  kPa is found to be  $4 \times 10^{-13}$  molecule s<sup>-1</sup> cm<sup>-2</sup> Pt (Fig. 3). The corresponding  $\theta_H$  is 0.54 (Fig. 6). The constant  $k_0$  is found to be  $0.6 \times 10^{20}$  molecule cm<sup>-2</sup> Pt s<sup>-1</sup> kPa<sup>-1</sup> ethane with an estimated uncertainty of 250% originating mainly from  $E_0$  and  $\beta$  uncertainties. This constant can be compared with the number of ethane molecules colliding with a unit surface area of platinum per second and per kPa of ethane at 673 K. The  $\nu$  value, deduced from the kinetic theory of gases ( $\nu = 27 * 10^{22}$  P (MT)<sup>-1/2</sup>; M, molecular

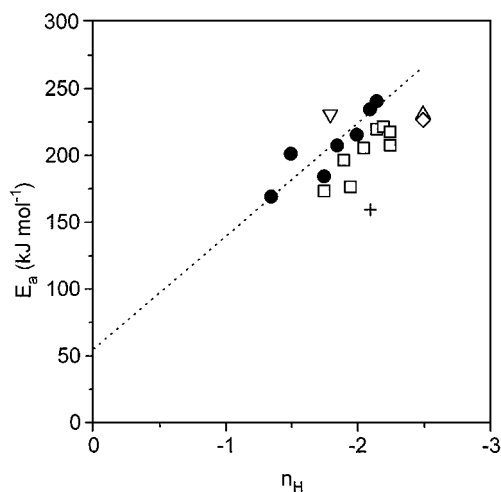


FIG. 8. Apparent activation energy of ethane hydrogenolysis over Pt/SiO<sub>2</sub> as a function of the order in hydrogen,  $n_H$ , measured at  $T > 650$  K (circles) and  $T < 650$  K (squares). Data from the literature: Refs. (10, 11, 13, 28) (diamond, down triangle, cross, up triangle, respectively). The straight line is the best fit of data obtained at  $T > 650$  K (circles), using a slope  $Q = 84$  kJ mol<sup>-1</sup> (Ref. (18)), for which an ordinate at  $n_H = 0$ ,  $E_0 = 55 \pm 7$  kJ mol<sup>-1</sup> is deduced.

weight) is found to be  $2.5 \times 10^{20}$  molecule  $\text{cm}^{-2} \text{s}^{-1} \text{kPa}^{-1}$ , four times larger than  $k_0$ .

The rate expression in Eq. [6] which accounts for the complex variations of  $r$  with the reactant partial pressure and the temperature in excess of 650 K is now completed as

$$r = k_0 e^{-E_0/RT} (1 - \beta \theta_H)^X P_E, \quad [10]$$

where  $k_0 = 0.6 \times 10^{20}$  molecule  $\text{cm}^{-2} \text{Pt s}^{-1} \text{kPa}^{-1}$  ethane,  $E_0 = 55 \text{ kJ mol}^{-1}$ ,  $\beta = 1.3$ , and  $X = 9$ .

This equation allows us to further speculate on the hydrogenolysis mechanism. As a matter of fact, it has been shown that the rate constant,  $k_0$ , is smaller by a factor of 4 than the constant of the kinetic theory of gases,  $\nu$ , and that the order in ethane is equal to unity in a large range of pressure. Then, Eq. [10] can be considered as describing a two-body process between gaseous ethane and surface ensembles composed of ca nine adjacent platinum atoms free from adsorbed hydrogen, considered as active sites as a whole. Only a fraction of ethane molecules colliding with the active site would be transformed into reaction products. This two-body process of the Eley–Rideal type would be activated with  $E_0 = 55 \text{ kJ mol}^{-1}$ . These conclusions are very similar to those drawn from the study of ethane hydrogenolysis over Ni/SiO<sub>2</sub> for which the  $E_0$  and  $X$  values were found to be comparable, viz.  $58 \text{ kJ mol}^{-1}$  and 15, respectively. The difference between the  $X$  values found for Pt and Ni (9 and 15, respectively) could arise from a weaker cracking character of platinum as compared to nickel, which would require a smaller ensemble of free surface atoms for the ethane activation process and its hydrogenolysis into methane. It should also be stressed that this model differs from the classical mechanism involving a dehydrogenating step of ethane adsorption, where the inhibiting effect in hydrogen pressure is related to the degree of dehydrogenation of the most abundant adsorbed species  $\text{C}_2\text{H}_y$  (5). Furthermore, as shown by Frennet (5), the latter model is unable to account for the variations of  $n_H$  with  $T$  and  $P$ , whilst the ensemble model, which considers that the inhibition arises from the  $(1 - \beta \theta_H)^X$  term, explains such variations. Finally, it can be questioned how far the model is sensitive to the definition of hydrogen saturation, which remains a controversial question. If the hydrogen coverage is multiplied by a  $\delta$ -factor arising from a new definition of saturation, it suffices to adjust the parameter  $\beta$  by dividing it by  $\delta$  to obtain the same  $(1 - \beta \theta)$  values, irrespective of  $T$  and  $P_H$ . It results that  $X$  is not altered by such a new definition. The slope of the extrapolation curve of Fig. 8 related to the heat of hydrogen adsorption is obviously unchanged, so that  $E_0$  has the same value. The constant,  $k_0$ , calculated from  $E_0$  and  $(1 - \beta \theta_H)^X$  is not changed, either. This shows that the values of the intrinsic kinetic parameters,  $k_0$ ,  $E_0$ , and  $X$  are insensitive to the definition of  $\theta_H = 1$ .

### 3.6. Kinetic Analysis of the Low Temperature (below 650 K) or High H Coverage (above 0.6 ML) Domain

A similar kinetic treatment of the data obtained in the low temperature domain corresponding to  $\theta_H > 0.6$  in Fig. 7 leads to a rate expression such as

$$r = k(1 - \gamma \theta_H)^Y, \quad [11]$$

where  $Y = -7.3$  and  $\gamma = 2.5$ .

Indeed these parameters do not present any direct physical significance, which indicates that the kinetic domain corresponding to high hydrogen coverage cannot be represented by a simple statistical model as developed above for the low  $\theta_H$  domain. A possible explanation would be that for these experimental conditions where  $\theta_H$  is in excess of 0.6, a reconstruction of the platinum surface atoms might occur, such as observed in single crystal studies as a function of the hydrogen coverage (30, 31). It would bring about an ordering of the hydrogen atoms leading to the preferential formation of H adatom islands. Such a positive order would result in a less inhibiting effect of the hydrogen pressure, in a qualitative agreement with the observations reported in this work at temperatures below 650 K. Other close phenomena such as the evidence of at least two distinct states of adsorbed hydrogen as a function of coverage on (110 Pt) surface (32, 33) could also be considered. Further investigations such as *in situ* AFM/STM on single crystals and mathematical simulation of a surface ordering via a Monte Carlo surface representation could provide new insights to explore this kinetic domain where the statistical ensemble model does not apply anymore.

## 4. CONCLUSION

From this work, it can be concluded that the kinetic features of ethane hydrogenolysis under conditions where the hydrogen coverage remains below ca 0.6 ML can be modelled using the ensemble model: the complex variations of the rate with temperature and pressure are quantitatively accounted for assuming that the active site is an ensemble composed of ca nine adjacent metal atoms free from adsorbed hydrogen and that ethane hydrogenolysis occurs via a two-body process between gaseous ethane and surface ensembles with a true activation energy  $E_0 = 55 \text{ kJ mol}^{-1}$ .

This behaviour is very similar to that previously observed for the same reaction over Ni-based catalysts and for the  $\text{D}_2\text{-CH}_4$  exchange reaction over Rh films, suggesting that this model is of general applicability.

This study has also shown that for high hydrogen coverage (above 0.6 ML, i.e., at temperatures lower than 650 K under the hydrogenolysis conditions), the kinetic regime is different from the previous one; the apparent activation

energy, as well as  $-n_H$ , increases with temperature. This behaviour which cannot be accounted for by the statistical ensemble model is the matter of further works.

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