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Hydrogenation of Carbonaceous Adsorbed Species on an Iron/Alumina Catalyst

I. Experiments in Isothermal Conditions and Exploitation by a Kinetic Model

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A kinetic model is proposed to interpret the data obtained during the isothermal conversion (into CH_4) of adsorbed species formed during the CO/H_2 reaction on a supported iron/alumina catalyst. The model, based on a sequential hydrogenation of CH_x species, reproduces the experimental observations and reveals parameters influencing the rate of formation of CH_4 such as surface hydrogen concentration, temperature effect, number of steps involved in the process, and activation energy of the reaction. The model allows for the determination of the activation energy of the hydrogenation of adsorbed species. © 1990 Academic Press, Inc.

INTRODUCTION

In the last 5 years the technique of transient experiments for the characterization of surface species formed during a catalytic reaction has been extensively developed. By use of a mass spectrometer and a microreactor system, nonsteady-state conditions may be followed where the concentration in the gas phase, or the temperature of the catalyst, may change even at a fast rate. In addition to the classical temperature-programmed desorption (TPD) technique, well studied in the past from experimental and theoretical points of view (*1, 2*), other methods have been developed, such as temperature-programmed reaction (TPR) and temperature-programmed surface reaction (TPSR) (*3*). Isothermal reaction of the adsorbed species, as in hydrogenation (*4–7*) or isotopic steady-state tracing reactions (*8, 9*) is also useful for characterizing the reactivity of the surface species.

Experimental studies with these new techniques are numerous (*10–12*), but theoretical treatment is rare, except in the case of TPD. In the present paper experimental data on isothermal hydrogenation of carbonaceous species formed during CO/H_2 reaction on an alumina-supported iron catalyst are provided and a kinetic model is proposed. In Part II of this work (succeeding paper), the kinetic model is applied to the temperature-programmed hydrogenation.

EXPERIMENTAL

The catalyst used is 10 wt.% Fe/Al_2O_3 obtained by a precipitation from iron nitrate in the presence of alumina (*6*). This is the same type of preparation as that used in the previous study. The characterization of the catalyst by different techniques has already been published (*13, 14*).

The analytical system has been described previously (*15, 16*). It is a new version of that used in the previous studies (*14, 15*). It consists of a microreactor (1 cm^3 volume) for a mass of catalyst in the 50- to 250-mg range, with an adapted gas-flow control system designed to perform switches between different controlled gas flows, under 1 atm total pressure. The temperature of the reactor is controlled by a home-made

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system designed to create a linear increase in the temperature in the range 1 to 400 K/min. Other programs can be used. Any change in the gas composition, by variation of the temperature (recorded by a capillary thermocouple immersed into the catalyst) or by introduction of a new gas in the reactor, is recorded by a quadrupole mass spectrometer (MIQ-200 of Leybold–Heraeus). The whole system is driven by a microcomputer (*15, 16*). The data resulting are the concentration of every compound in the gas phase and the rate of either the formation or the disappearance of various compounds with time on stream.

The powdered catalyst, which is too finely divided for use as such with the analytical system, is lightly compressed into a disk. This is fragmented and screened to obtain particles. Variations in size for particles smaller than 0.9 mm in diameter have no effect on the kinetic data, and we have selected the range 0.59–0.84 mm with a standard flow rate of gas of 60 cm^3/min for 50 mg of catalyst. These experimental conditions are analogous in those used in previous studies (*6, 17, 18*).

In this study, the pretreatment consists of a reduction of the catalyst by H_2 at 440°C for 14 h. After decreasing the reaction temperature to 285°C, helium gas is introduced for 5 min. The reactant mixture of 10% CO/H_2 is then admitted during a prefixed time, *t*, followed by a treatment in helium for 40 s. In the case of the isothermal experiment at 285°C, H_2 is introduced immediately onto the catalyst and the products evolved are detected.

RESULTS

PRELIMINARY EXPERIMENTAL RESULTS

The experimental results reported here are the basis for the model proposed later in this section. In the discussion other experiments are cited as providing evidence in favor of the proposals.

Some results have been described in detail in previous papers (*6, 17*) for different on-stream reaction times. For the present treatment, we report (Fig. 1) the curve of the rate of the formation of CH_4 at 285°C after different times on stream in the reaction of 10% CO/H_2.

The main observations are as follows:

—For a short reaction period, less than 30 s, only one peak of CH_4 is detected.

—For a longer reaction time with CO/H_2, a second peak appears, first as a shoulder on the first peak, and then as a more and more distinct peak as the reaction time increases. The quantity of CH_4 formed in the first peak remains almost constant (50 μmol/g) and stays independent of the reaction time, while the second peak increases during the first 20 min of the CO/H_2 reaction (*6*).

—A broad peak is also detected after a reaction time of a few minutes (Fig. 1). The quantity of CH_4 formed in this peak increases with time on stream (*6*).

—When the time on stream of the CO/H_2 reaction increases, the time related to the maximum of the two first peaks also increases. It is also noted that the maximum rate decreases during this change. This is immediately observed for the first peak and occurs later (after 10 min) for the second peak. The same results have been observed with a 33% CO/H_2 mixture (*17*).

From comparative studies by Mössbauer spectroscopy it has been concluded that the third flat peak is due to the hydrogenation of the bulk carbide (*6, 13*). In the present study only the first two peaks are therefore considered to be due to the hydrogenation of carbonaceous adsorbed species. From the experiments, the following questions must be answered:

—How can there be several peaks in the hydrogenation at a constant temperature? Is it correct to assume that two peaks correspond to two adsorbed species?

—Why is there an increase in the time for the appearance of the maxima of those peaks when the time on stream of the CO/

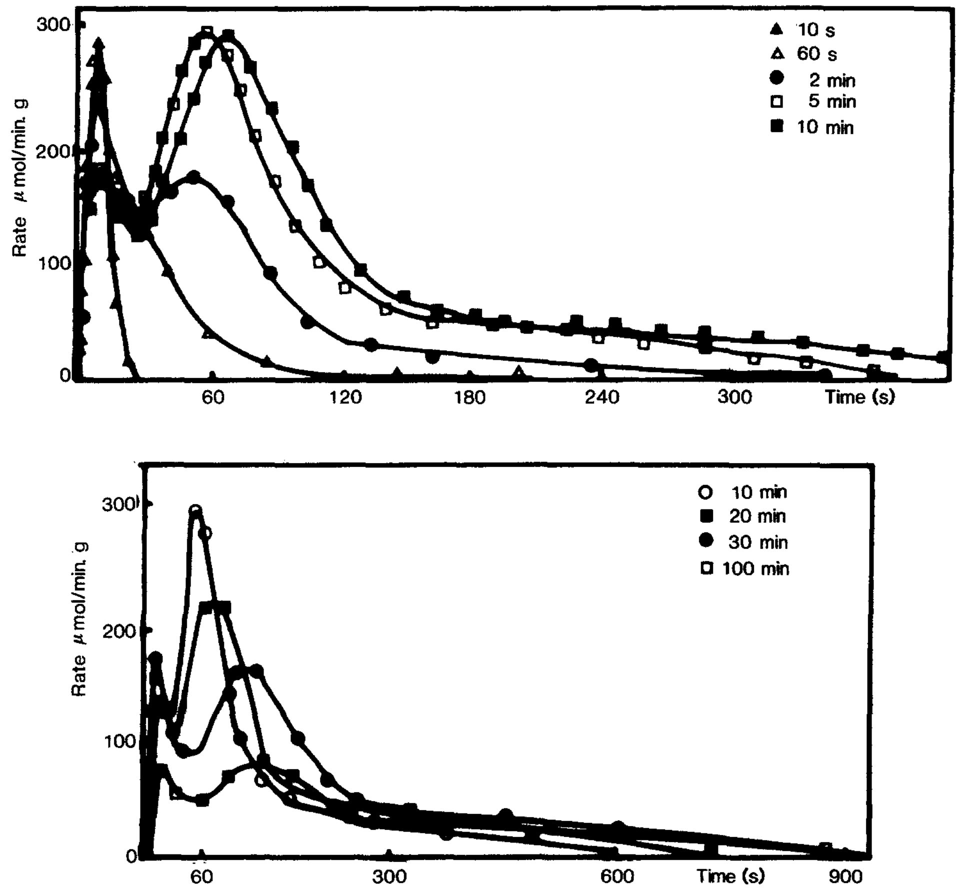

FIG. 1. Isothermal hydrogenation of the adsorbed species at 285°C after different times of CO/H_2 reaction at 285°C.

H_2 reaction increases (well observed for the second peak in Fig. 1)?

The purpose of this paper is to answer these questions with the help of a kinetic model and to present other supporting experiments which also help in the determination of various kinetic parameters.

Kinetic Model for Isothermal Hydrogen of Surface Species

Let us suppose that the original adsorbed species is elementary carbon. The formal mechanism for its hydrogenation is:

$$H_{2_{gas}} \rightleftarrows 2\ H_{ads} \tag{a}$$

$$C_{ads} + H_{ads} \rightarrow CH_{ads} \tag{b}$$

$$CH_{ads} + H_{ads} \rightarrow CH_{2_{ads}} \tag{c}$$

$$CH_{2_{ads}} + H_{ads} \rightarrow CH_{3_{ads}} \tag{d}$$

$$CH_{3_{ads}} + H_{ads} \rightarrow CH_{4_{ads}} \tag{e}$$

$$CH_{4_{ads}} \rightarrow CH_{4_{gas}}. \tag{f}$$

To these reactions can be added

$$CH_{3_{ads}} + CH_{2_{ads}} \rightarrow CH_3 - CH_{2_{ads}} \tag{g}$$

$$CH_3 + CH_{2_{ads}} + H_{ads} \rightarrow CH_3 - CH_{3_{ads}}. \tag{h}$$

If the original adsorbed species is CH_{ads} or other $CH_{x_{ads}}$ species, the corresponding steps, previous to the formation of that species, are deleted.

Confrontation of this scheme with the experimental data shows that reactions (g) and (h) can be eliminated, because only a small quantity of C_2H_6 (1 μmol/g) has been recorded during the isothermal hydrogenation of the first peak. Reaction (f) cannot be the rate-limiting step of the process because it has been observed that CH_4 is desorbed from the iron surface at room temperature (*19*). The adsorption of H_2 is only slightly activated (*20, 21*) and the activation energy of desorption of H_2 has been evaluated (104 kJ/mol) in a TPD experiment (*25*). Reaction (a) is supposed to be in equilibrium at any time, considering the high temperature and pressure of hydrogen (1 atm) employed in this study.

As a result, the rate of formation of CH_4 is controlled by Eqs. (b) to (e). To evaluate this rate in relation to the hydrogenation time, two cases may be explored: either one step controls the process or two, three or, at the most, four steps with the same rate constant act in the process.

Depending on these two main hypotheses, various linear equations can be formulated, and their resolution by classical methods (*22–24*) leads to various expressions for the rate of formation of CH_4. Table 1 gives in the first column the number of steps considered and in the second column the rate of formation of CH_4 as a function of the hydrogenation time. The last column gives the characteristics of the curve: time at maximum, slope at $t = 0$, and inflection points.

In this calculation, all the steps have the same rate constant. The reasons for this restriction are considered in the discussion. Thus we have

$$k = A \exp(-E_r/RT), \qquad \text{(I)}$$

where A is the preexponential factor, E_r is the activation energy of hydrogenation, T is the temperature of reaction, and the coverage in hydrogen chemisorbed (noted as H) is given assuming the Langmuir model for dissociative adsorption of H_2,

$$H = \frac{\sqrt{\lambda p}}{1 + \sqrt{\lambda p}} H_0,$$

where p is the pressure of hydrogen, H_0 is the coverage at saturation, and λ is the adsorption coefficient.

From statistical theory assuming the loss of 3° of translation, the adsorption coefficient is given by

$$\lambda = \frac{h^3}{(2\pi m)^{3/2}} \frac{1}{(kT)^{5/2}} \exp\left(\frac{Q_a}{RT}\right),$$

where h is Planck's constant, k is Boltzmann's constant, $Q_a = E_d - E_a$, the heat of adsorption, E_d is the activation energy of desorption, E_a is the activation energy of

TABLE 1

Characteristics of the Rate of Formation of CH_4 Expected from the Model (C_0 Is the Initial Value of $CH_{x_{ads}}$)

Steps of hydrogenation with same k	Rate ϕ of CH_4 production versus the time of hydrogenation	Characteristics of the maximum	Inflection point	Initial rate and slope of rate at $t = 0$
One limiting step $C_{ads} + H \rightarrow CH_{ads}$	$\phi = C_0 k\mathrm{H}e^{-kHt}$	$t_m = 0, \phi_m = kC_0H$ (no maximum)	None	$\phi_{(0)} = kHC_0$ $d\phi_{(0)}/dt = -C_0(kH)^2$
$C_{ads} + H \rightarrow CH_{ads}$ $CH_{ads} + H \rightarrow CH_{ads}$	$\phi = C_0(kH)^2te^{-kHt}$	$t_m = 1/kH$ $\phi_m = \exp(-1)kC_0H$ $= 0.367kC_0H$	One at: $t_i = 2t_m$	$\phi_{(0)} = 0$ $d\phi_{(0)}/dt = C_0(kH)^2$
$C_{ads} + H \rightarrow CH_{ads}$ $CH_{ads} + H \rightarrow CH_{ads}$ $CH_{2_{ads}} + H \rightarrow CH_{3_{ads}}$	$\phi = (C_0(kH)^3/2)t^2e^{-kHt}$	$t_m = 2/kH$ $\phi_m = 2\exp(-2)C_0kH$ $= 0.270C_0kH$	Two at $t_{i_1} = (2 - \sqrt{2})/kH$ and $t_{i_1} = (2 + \sqrt{2})/kH$	$\phi_{(0)} = 0$ $d\phi_{(0)}/dt = 0$
$C_{ads} + H \rightarrow CH_{ads}$ $CH_{ads} + H \rightarrow CH_{2_{ads}}$ $CH_{ads} + H \rightarrow CH_{3_{ads}}$ $CH_{3_{ads}} + H \rightarrow CH_{4_{ads}}$	$\phi = (C_0(kH)^4/6)t^3e^{-kHt}$	$t_m = 3/kH$ $\phi_m = (27/6)\exp(-3)C_0kH$ $= 0.224C_0kH$	Two at $t_{i_1} = (3 - \sqrt{3})/kH$ and $t_{i_1} = (3 + \sqrt{3})/kH$	$\phi_{(0)} = 0$ $d\phi_{(0)}/dt = 0$

adsorption, and m is the weight of the molecule.

In order to obtain a practical mathematical expression this adsorption coefficient λ can be considered under the form

$$\lambda = \text{constant} \cdot \exp(Q_a/RT).$$

The various cases are successively considered in Table 1. Comparison of these results with the experimental data where maxima are always observed under isothermal conditions of hydrogenation shows that there is more than one step influencing the process. Two, three, or four steps acting with comparable rate constants may therefore be assumed. If there were one rate-limiting step, with a value of k much less than those of the other steps, no maximum would be produced.

This first conclusion (that there is no single rate-determining step) already answers some questions raised before. Equations for t_m and ϕ_m can be written in the form

$$t_m = \frac{\alpha - 1}{AH \exp\left(-\frac{E_r}{RT}\right)}, \qquad (II_1)$$

where α is the number of steps of equal k (*1–4*) (all other steps have rate constants $\gg k$).

H is the assumed constant during the hydrogenation:

$$\phi_m = \beta_\alpha k C_0 H. \qquad (II_2)$$

The values of β_α are: $\beta_1 = 1.0$ ($t_m = 0$), $\beta_2 = 0.367$, $\beta_3 = 0.270$, $\beta_4 = 0.224$.

These equations have the advantage of showing the main kinetic parameters acting on t_m and ϕ_m independently of the number of steps involved.

From the expressions (II_1) and (II_2) the following can be concluded (with $\alpha \neq 1$):

—If two species are present on the surface with different activation energies of hydrogenation and the same preexponential factor, two peaks should occur in the rate of formation of CH_4. The species with the smaller activation energy gives the first peak. The maximum rate is a function of both the initial adsorbed quantity C_0 and the concentration of H adsorbed. This explains the results observed in Fig. 1. The first two peaks in Fig. 1 are due to the presence of two species with different hydrogenation activation energies and in different quantities.

On ruthenium Winslow and Bell (*26*) have also observed two peaks in the rate of formation of CH_4 during the hydrogenation of the adsorbed species, formed after various reaction times of CO/H_2. On a Fe/TiO_2 catalyst, two peaks were also observed during isothermal hydrogenation (*7*).

—If the number of sites chemisorbing H_2 decreases, for example by poisoning during the reaction, the time required for the appearance of the maximum increases and, simultaneously, the maximum rate decreases. This explains the shift in the maxima of the peaks in relation to the time on stream of the CO/H_2 reaction. During this reaction the number of sites for H_2 chemisorption decreases because of surface graphite formation (*6*). For comparison, on ruthenium, no shift is observed in the maxima of the peaks in relation to the time on stream of the CO/H_2 reaction (Figs. 6 and 8 of Ref. (*26*)). More likely, the number of sites for H_2 chemisorption remains constant on this metal and t_m remains constant, but ϕ_m increases because C_0 increases.

EXPLOITATION OF THE MODEL FOR THE ISOTHERMAL EXPERIMENTS

From the equations for t_m and ϕ_m, some measurements can be made concerning the energetic factors involved during the hydrogenation.

(*a*) *Direct Measurement of the Activation Energy of the Hydrogenation of a Given Species*

From Eq. II_1 (with $\alpha \neq 1$) for t_m one writes

$$\ln t_m = \ln(\alpha - 1) + \frac{E_r}{RT} - \ln(AH).$$

Let us assume in this first approach that the adsorption of H_2 is controlled at a temperature T by the Langmuir equation. Two cases of practical interest can be studied:

(1) $\sqrt{\lambda p} \geqslant 1$, $H = H_0$, and $\ln t_m = \ln[(\alpha - 1)/AH_0] - E_r/RT$

(2) $\sqrt{\lambda p} \leqslant 1$, $H = \sqrt{\lambda p}\, H_0$ with $\lambda = B_1 \exp(Q_a/RT)$, and $\ln t_m = \ln B_2/AH_0 + (E_r/RT - Q_a/2RT)$, where B_1 and B_2 are constants.

For both of these cases, the plotting of ln (t_m) versus ($1/T$), where T is the temperature of the isothermal hydrogenation, gives a straight line, whose slope is related to the activation energy of hydrogenation. This requires the study of the change in the value of t_m with the temperature of the isothermal hydrogenation for a given CO/H_2 reaction time and at a constant temperature (285°C).

Figures 2 and 7 give the results obtained after 30 s of CO/H_2 reaction when only the first species is present on the surface. These results are obtained through the following procedure: after 30 s of the CO/H_2 reaction at 285°C, the reactor is cooled in He to the desired hydrogenation temperature and H_2 is introduced. Given the values for t_m and T, the curve $\ln t_m$ against $1/T$ can be drawn (Fig. 3). In the temperature range studied, a straight line is well observed, in agreement with the previous equation. Two experimental points are outside the line. This is because the hydrogenation temperatures used here are too high and therefore the corresponding t_m values are too short (probably 1–2 s) compared to the response time of the analytical system, and this leads to an error in the value of t_m. It can be noted (not reported in the figure) that the hydrogenation of the species has been observed even at 134°C.

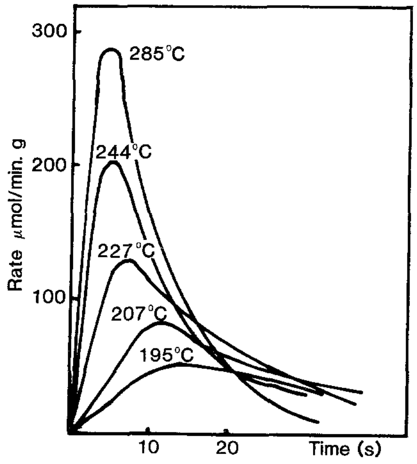

FIG. 2. Isothermal hydrogenation at different temperatures of the adsorbed species formed after 30 s of CO/H_2 reaction at 285°C.

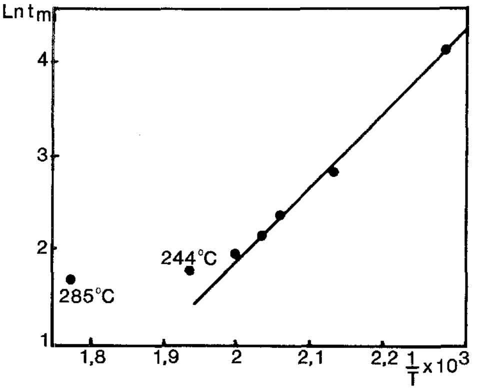

FIG. 3. Plot of $\ln t_m = f(1/T)$ for the isothermal hydrogenation of the first species (from Fig. 2).

The same type of experiment has been done after 5 min of CO/H_2 reaction at 285°C, when the second species is also present. Figure 4 gives the rate of formation of CH_4 for various temperatures of hydrogenation. Figure 5 represents $\ln t_m$ versus $1/T$, from the t_m values measured in Fig. 4 at the corresponding value of T. For this species a straight line is observed (Fig. 5) for the whole temperature range studied. Lower temperatures cannot be studied because of the lack of precision in the determination of t_m.

In these two previous cases, the curve predicted by the model (straight line) agrees well with the experimental data.

Winslow and Bell (*26*) used the isothermal hydrogenation to study the adsorbed carbonaceous species formed on their ruthenium catalyst after various times on

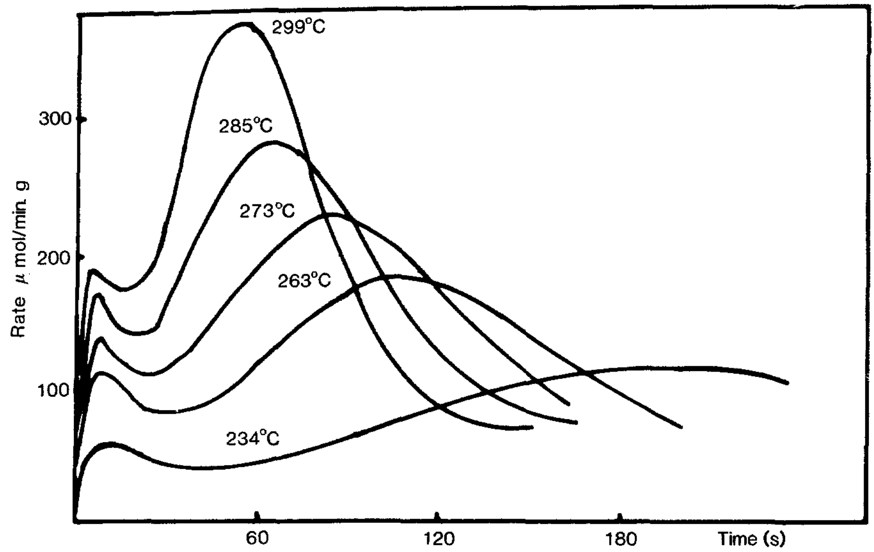

FIG. 4. Isothermal hydrogenation at different temperatures of the adsorbed species formed after 5 min of CO/H_2 reaction at 285°C.

stream for the CO/H_2 reaction. By use of their data from Fig. 13 of Ref. (*26*), the curve in Fig. 6 can be drawn for this catalyst. Here also a straight line is obtained in agreement with our model.

The hydrogenation activation energy can be evaluated with the help of two hypotheses concerning the adsorption of hydrogen. The adsorption heat of hydrogen, Q_a, in the adsorption coefficient is taken as equal to 83 kJ/mol when a value for the activation energy of 104 kJ/mol, found by TPD experiments, is used and an activation energy of adsorption of only 21 kJ/mol is used (hydrogen chemisorption is only slightly acti-

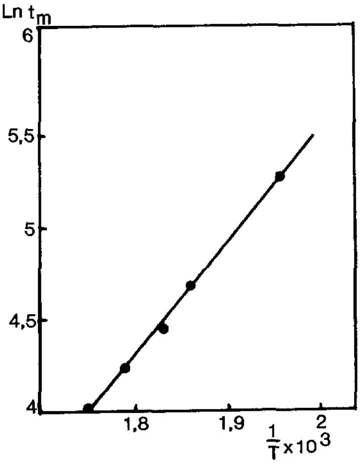

FIG. 5. Plot of ln $t_m = f(1/T)$ for the isothermal hydrogenation of the second species (from Fig. 4).

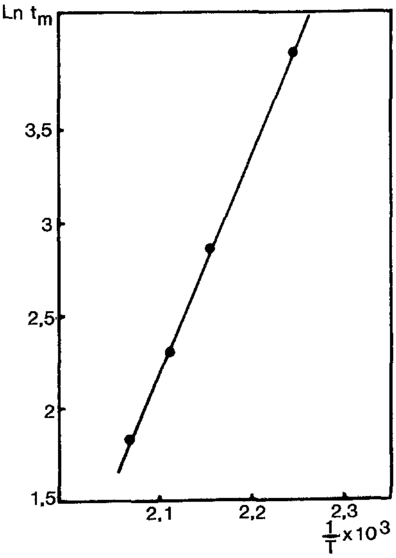

FIG. 6. Plot of ln $t_m = f(1/T)$ from the results of Winslow and Bell (*26*) on Ru catalysts.

TABLE 2

Activation Energy (in kJ/mol) of Hydrogenation of Various Adsorbed Species from the Plot $\ln t_m = f(1/T)$ as a Function of the Expression for Hydrogen Coverage

	$H = H_0$	$H = \sqrt{\lambda p} H_0$
First species	64	114
Second species	51	101
Winslow and Bell (*26*) data on Ru	102	

vated (*20*, *21*)). Table 2 gives the value obtained from Figs. 3, 6, and 7 using the two previous relationships between $\ln t_m$ and T depending on the approximation for the factor $\sqrt{\lambda p}$.

In these two cases of approximation, the best hypothesis for this direct measure of the activation energy is discussed below.

(*b*) *Measurement of the Difference between the Hydrogenation Activation Energies of Two Species*

Two peaks in the rate of the formation of CH_4 under isothermal conditions may reveal two adsorbed species with different hydrogenation activation energies. It then follows that

—first species $t_m = (\alpha - 1)/AH \exp(-E_r/RT)$, $\alpha \neq 1$

—second species $t'_m = (\alpha' - 1)/AH \exp(-E'_r/RT)$, $\alpha' \neq 1$,

assuming that H, which is the quantity of H_2 adsorbed dissociatively at the temperature T, is constant during the hydrogenation experiment (irreversible poisoning of the sites during the CO/H_2 reaction). The difference between the activation energies for the two species is

$$E_r - E'_r = RT\left(\ln\frac{t_m}{t'_m} - \ln\left(\frac{\alpha - 1}{\alpha' - 1}\right)\right).$$

Taking the values of two maxima of Fig. 4 after 5 min of CO/H_2 reaction for two temperatures of hydrogenation it follows that

T = 263°C: $t_m = 7.8$ s and $t'_m = 106$ s

T = 234°C: $t_m = 9$ s and $t'_m = 192$ s.

The difference between the activation energies of the two species is in the range 16.7–8.4 kJ/mol, depending on the number of steps involved in the hydrogenation (value of α and α').

(*c*) *Discussion on the Evaluation of the Activation Energy*

The calculated values proposed in Table 2 depend on the approximation in the Langmuir model. For the second species

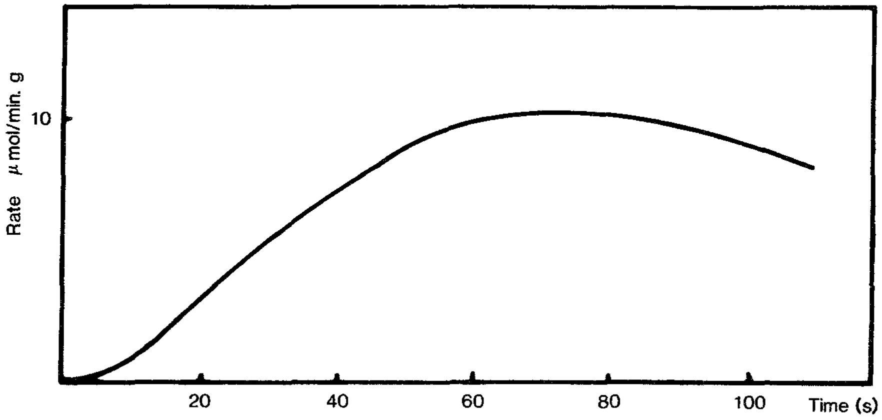

FIG. 7. Isothermal hydrogenation at 164°C of the adsorbed species formed after 30 s of CO/H_2 reaction at 285°C.

arising at higher temperatures of hydrogenation, the second hypothesis ($\sqrt{\lambda p} \ll 1$) is the most probable one; also the value of 101 kJ/mol appears to be correct and in agreement with the value proposed in the literature (*27, 28*). For example, for the hydrogenation of carbon species a range of values (70 to 130 kJ/mol) has been proposed for the most active form of carbon (C_α) and the least active (C_β), respectively (*29*).

For the first species the data are observed at low hydrogenation temperatures; therefore the first hypothesis ($\sqrt{\lambda p} \gg 1$) seems the most probable. The value found, 64 kJ/mol, is of the same order as that found for the hydrogenation of the most active form, C_α, of carbon (*29*). The second hypothesis leads to an excessive value, 114 kJ/mol, if compared to the value for the second species because, as shown in (b), the activation energy for the first species must be smaller than that for the second species. It is not excluded that for this first species we are in the range of temperatures where the two hypotheses (on the value of $\sqrt{\lambda p}$ compared to 1) are not applicable. From this discussion concerning the direct calculation of the activation energy, it is concluded that the activation energy of the first species is in the range 114–64 kJ/mol. However, assuming that the value of the activation energy of the second species is equal to 101 kJ/mol and that the difference between the two energies is in the range 16.7–8.4 kJ/mol, a value of 84 kJ/mol (in the range mentioned above) (*27–29*) for the activation energy of the most active carbon species can be proposed.

(*d*) *Other Applications of the Model*

Two other applications of this model are suggested.

(*i*) *Determination of the number of steps involved in the hydrogenation of the first species.* From the equation giving the rate of formation of CH_4, considering the hydrogenation by successive steps with the same rate constant k, the slope of the curve at time 0 gives Table 1:

$$\text{two steps} \quad \frac{d\phi_{(0)}}{dt} = C_0(kH)^2$$

$$\text{three or four steps} \quad \frac{d\phi_{(0)}}{dt} = 0.$$

In the case of three or four steps, the slope is zero. Figure 2 shows that, in the case of the first species (after 30 s of the CO/H_2 reaction at 285°C), the slope is not zero for the temperature studied. However, in Fig. 7, which gives the data for hydrogenation at the lowest temperature, 164°C, a doubt exists because the slope is close to zero, probably because the temperature used gives a small value for the rate constant k. It seems, therefore, that the hydrogenation process for this species runs through two steps with comparable rate constants.

(*ii*) *Determination of the initial quantities of adsorbed species.* From the equations for t_m and ϕ_m it can be observed that their product gives C_0. The various values of C_0 for the second species obtained (Table 3), depending on the number of steps involved in the hydrogenation, can be compared with the values calculated by integration under the experimental curve for CH_4 for-

TABLE 3

Comparison between the Values of C_0 (Initial Coverage of Adsorbed Species) Found Experimentally and Those Found by the Model for the Second Species at T = 285°C

	Second species		
Time of CO/H_2 reaction (min)	2	10	20
t_m (s)	50	65	129
ϕ_m (μmol/min · g)	136	227	104
C_0 from 4 steps (μmol/g)	169	366	333
C_0 from 3 steps (μmol/g)	210	455	414
C_0 from 2 steps (μmol/g)	309	670	610
C_0 from experimental value (μmol/g) (Ref. (*6*))	150	309	290

TABLE 4

Value of the Product $t_m\phi_m$ for the First Species (from Figs. 3 and 7) versus the Temperature of Hydrogenation

Temperature hydrogenation (°C)	t_m (s)	ϕ_m (μmol/min g)	$t_m\phi_m$ (μmol/g)	$C_0 = t_m\phi_m/0.367$ (μmol/g)
227	7	128	14.9	41
207	11.5	82	15.7	43
195	16	51	13.6	37
164	68	10	11.3	31

mation. The experimental results are those previously published (*6, 17*) at the isothermal temperature of 285°C. The maximum rate for the second species is obtained by subtraction of the rate of hydrogenation of the carbide from the experimental value of the maximum. The rate of the carbide hydrogenation corresponds to the value of the third flat peak (Fig. 1), which is in the range 25–50 μmol/(g min) depending on the time on stream of the CO/H_2 reaction. Table 3 gives this comparison between experimental and predicted values of C_0 in the case of the second species. It can be observed that in the case of three or four steps a fair agreement is found between the calculated predictions and the experimental value.

Another comment can be made as follows. If for a given species there are no changes in the hydrogenation mechanism in the temperature range explored, the product $t_m\phi_m$ must be constant for the whole hydrogenation temperature range. Using the result of Fig. 3 for the first species, Table 4 is obtained, and this shows a good agreement between experimental result and the model. Column 5 gives the values of C_0 in the case of two steps. They are very similar and are in agreement with the experimental data (50 μmol/g) (*6*).

DISCUSSION

The kinetic model for the isothermal hydrogenation of the adsorbed species, following sequential steps proceeding with comparable rate constants, leads to the interpretation of the main experimental observations. The mathematical equations derived from the kinetic treatment lead to a valuable exploitation of the experimental data described here.

As observed previously, the results on ruthenium obtained by Winslow and Bell (*26*) are also in good agreement with the present model. However, some data in the literature give only a continuously decreasing peak of CH_4 (*4*) with the time of hydrogenation. In the previous study (*17*), using CO/He as a reactive mixture on the same catalyst as that used in the present work, a decreasing peak for the formation of CH_4 has also been observed. The explanation might be that in this case one limiting step controls the process and therefore no maximum is obtained (Eq. II_1, $\alpha = 1$). However, the equation for t_m shows that this may be also due, for a given rate constant, to a higher number of sites for hydrogen chemisorption after a CO/He reaction than after a CO/H_2 reaction. Thus, even in the case of the CO/He mixture, hydrogenation of C species might proceed with a sequence of two, three, or four steps with comparable rate constants. Some data on the hydrogen chemisorption changes during the reaction with CO/H_2 and CO/He would help to select the best hypothesis.

Other comments can be made. In order to obtain some exploitable mathematical expressions from the kinetic model, all the steps must have exactly the same rate constant. However, a mathematical solution exists if it is considered that two steps exhibit slightly different rate constants k_1, k_2 but the final mathematical equation for t_m is less useful. Of course, if k_1 and k_2 are very different, the case of one limiting step is found.

For example, in the case of two steps,

$$C_{ads} + H_{ads} \xrightarrow{k_1} CH_{ads}$$

$$CH_{ads} + H_{ads} \xrightarrow{k_2} CH_{2_{ads}},$$

the CH_4 formation rate is given by

$$\phi = \frac{k_1}{\left(1 - \frac{k_1}{k_2}\right)} C_0 H e^{-k_1 H t}(1 - e^{(k_1 - k_2)Ht}). \qquad (\mathrm{III}_1)$$

By considering k_2 to be higher than k_1, i.e., $k_2 = xk_1$ with $x > 1$, the rate of production of CH_4 will be equivalent to the case of one limiting step if x is large. By considering that $x = 10$ and that the preexponential factor for k_1 and k_2 is the same, the difference in the activation energies of the two steps is $\Delta E = 7.4$ kJ/mol. Higher values of ΔE lead to the case of a limiting step. Values of ΔE lower than 7.4 kJ/mol are not significant compared to the measured value of activation energy (70–100 kJ/mol) and the experimental precision. The assumption that the rate constants for all the steps (two or more steps) are equal is thus reasonable.

A last comment on the proposed kinetic model is that another theoretical explanation is possible to interpret the presence of peaks in the isothermal hydrogenation experiments. The proposal is based on the increase in the amount of hydrogen chemisorbed during the isothermal hydrogenation experiment. For example, a site for chemisorption of H_2 can be created by the removal, by H_2, of some poisoning carbonaceous species or other species, such as oxygen adsorbed during the isothermal hydrogenation of the carbonaceous species. We have not detected water during these experiments but this compound is quantitatively analyzed with great difficulty by mass spectrometry. The sequential hydrogenation model for CH_x species with the same rate constant remains valid in the case of this last hypothesis. However, the point of interest is that, depending on conditions discussed later, even with one limiting step in the hydrogenation process, a peak of CH_4 formation may be observed during the isothermal hydrogenation.

By assumption of a linear increase in the hydrogen chemisorption versus the time of hydrogenation $H = H^0(1 + \gamma t)$ (with H^0 hydrogen chemisorption at time zero according to the Langmuir model) and by consideration only of the case of one limiting step, the solution for the rate of formation of CH_4 is

$$\phi = kC_0H^0(1 + \gamma t)e^{-kH^0(t + \gamma t^2/2)}. \qquad (\mathrm{IV}_1)$$

This equation leads to the determination of the time of the maximum t_m as a function of not only the rate constant and the hydrogen coverage but also of γ (rate of increase of hydrogen chemisorption):

$$t_m = \frac{1}{\gamma}\left(\sqrt{\frac{\gamma}{kH^0}} - 1\right)$$

and

$$\phi_m = kH^0C_0\sqrt{\frac{\gamma}{kH^0}}\, e^{-(1/2)(1 - kH^0/\gamma)}.$$

Therefore, a maximum peak can be observed only if the value of γ obeys some conditions. If $\gamma < kH^0$ there is no peak in the rate of CH_4 formation (the rate is maximum at $t = 0$). If $\gamma > kH^0$ a maximum might be observed. Since t_m is a function of γ for a given value of k and H^0, t_m has a maximum value in $\gamma = 4\ kH^0$, where $t_m = \frac{1}{4}\ kH^0$ and $\phi_m = 1.37\ C_0kH^0$. A higher value of γ makes t_m decrease and ϕ_m increase. It can be observed that the equation for t_m is close to that found with the kinetic model without limiting steps. However, the equation for the rate of CH_4 formation (IV_1) shows that the initial rate is $\phi_{(0)} = kC_0H^0$, while the experimental value for the initial rate is almost zero (Figs. 2 and 7) for the first species. This means that for a given value of k and C_0 the chemisorption of hydrogen should be small at the beginning of the hydrogenation, even for the first species after 30 s of CO/H_2 reaction. This behavior has not been experimentally observed. Thus, the model with one limiting step associated with an increase in the hydrogen chemisorption during the hydrogenation of CH_x does not fit the experimental results. Nevertheless, it is not excluded that hydrogen chemisorption actually increases and this point should be introduced in the kinetic model without limiting steps. However, this hypothesis requires experimental data concerning the change in the hydrogen chemisorption, first, during the CO/H_2 reaction and, second, during the hydrogenation of the adsorbed species. Thus will be discussed in a forthcoming paper.

CONCLUSION

The present study aims at showing the interest of a kinetic interpretation of the data obtained by transient experiments for the case of isothermal hydrogenation.

The model, based on sequential hydrogenation of CH_x species, where two, three, or four steps have comparable rate constants (with a highest probability for three or four steps for the second species and two for the first species) is in good agreement with various experimental observations. The effects of the kinetic parameters, such as temperature, hydrogenation activation energy, initial quantity of adsorbed species, and hydrogen chemisorption, are explained and compared with the experimental data. This leads to the determination of the hydrogenation activation energy by isothermal experiments using the experimental value of t_m, the time of appearance of the peak maximum in the CH_4 formation.

For a further development of the kinetic model and the confirmation of its validity, effort must be concentrated on the evaluation of the chemisorption of H_2 in relation to different parameters such as the time of the CO/H_2 reaction and the isothermal hydrogenation time.

In Part II of this work, the present model is extended to the temperature-programmed hydrogenation of the adsorbed species.

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