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Isothermal Hydrogenation of Carbonaceous Adsorbed Species on an Iron Catalyst.

III. Kinetic Model and Experimental Verification of the Variation of the Surface Hydrogen Concentration

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A kinetic model is studied as an explanation of the results observed during the isothermal hydrogenation (into CH_4) of adsorbed carbonaceous species on Fe/Al_2O_3. On various metal supported catalysts this experiment leads to the observation of peaks in the rate of production of CH_4 as a function of time. In previous studies, we have shown that some results can be explained by the presence of at least two steps with comparable rate constants in the process of CH_4 formation. An alternative qualitative explanation is that the peaks are due to a simultaneous increase of the hydrogen surface concentration. Using a specific situation where this model is fully applicable, a quantitative formulation of these assumptions is presented, supported by various experiments. It is shown that the rate of hydrogen increase is linked to the rate constant of hydrogenation and that a peak can be obtained only if the experimental conditions agree with a specific criterion. Associated with previous studies, this analysis contributes to the interpretation of results obtained from this type of transient experiment. © 1992 Academic Press, Inc.

I. INTRODUCTION

In addition to spectroscopic methods to characterize the adsorbed species on the surface of a powdered catalyst, transient experiments have made an important contribution to this subject over the last 10 years. Those experiments involve the creation of a controlled perturbation of a gas/surface state obtained in dynamic (flow) conditions and the measurement of responses of the gas phase composition. The perturbation is either physical (an augmentation of the temperature) or chemical (a change of the composition of the gas phase). The controlled increase of the temperature leads to temperature-programmed experiments: desorption (TPD) and surface reaction (TPSR) under inert gas or reactions (TPR) under reactive gas. The modification of the composition of the gas phase leads to various isothermal transient experiments, such as the hydrogenation of adsorbed species or the steady state tracing (using isotopic compounds).

Kinetic models have been proposed to interpret the results of some of these experiments and to obtain a better understanding. The TPD can be considered as the transient experiment which has received the most attention. This is partly because the technique is so widely used and also because it has long been possible to relate by a kinetic model parameters of interest such as orders of desorption, activation energy, rate of increasing temperature, and surface coverage (*1*, *2*). Other effects important in specific cases for a given catalyst are: the variation of the activation energy with coverage (*3*), the mass transfer effects in the catalyst (*4*), the effect of readsorption (*5*), and the pseudo-

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equilibrium conditions for which thermodynamic rather than kinetic parameters are obtained (*6*). Thus, at the present time the results of TPD are strongly supported by mathematical analysis which permits the interpretation of the experimental observations (*7, 8*).

Other kinetic models are also available for various temperature-programmed experiments (*8*), but a lack of quantitative analysis of experimental data exists for a number of transient experiments for which the main kinetic parameters have not been characterized. Thus, they appear specific to each catalyst and each adsorbed species. For instance, the isothermal hydrogenation of carbonaceous adsorbed species (*9, 10*), seems strongly dependent of the catalyst (metal, support.) and of the adsorbed species (CO, C_xH_y). In preceding papers (*11, 12*) we have proposed a kinetic interpretation for the hydrogenation to CH_4 (either isothermal or by programming the temperature) of the adsorbed species formed during the CO/H_2 reaction on an Fe/Al_2O_3 catalyst. These studies seem to clarify the main kinetic characteristics of this type of transient experiment. In particular, we have shown (*11*) that for isothermal conditions, the appearance of a peak in the curve of the transient response (rate of CH_4 production vs. the time of hydrogenation) observed on different supported metal catalysts (Ru (*9*), Fe (*13*), Ni (*8, 14*), and Rh (*15*)) is due to a hydrogenation mechanism having at least two steps with a comparable rate constant. For the isothermal hydrogenation of adsorbed species formed during reaction of CO/He with the Fe/Al_2O_3 catalyst, a decreasing production of CH_4 vs. the time of hydrogenation is observed (no CH_4 peak) (*13*). This is explained by the presence of a single rate-limiting step in the process of CH_4 formation (*11*). One of the second-order factors affecting the experimental data is the hydrogen surface concentration. We have shown (*11*) that this parameter affects the time of appearance of each peak; the decrease of the initial hydrogen surface concentration increases the time of appearance of the peaks.

Thus, for the isothermal hydrogenation of adsorbed species on the Fe/Al_2O_3 catalyst the main kinetic parameters affecting the process are (in the order of effect on the results): the number of steps having a comparable rate constant, the activation energy of hydrogenation of the various species, and the coverage of each species. These main features seem to characterize this type of transient experiment independently of the nature of the catalyst. At this point it can be assumed that the presence of some peaks in the response of formation of products vs. the time of isothermal hydrogenation can be explained by the involvement of two or more steps with the same rate constant (equivalent to that for a TPD: an asymmetric peak means a desorption process of first order, and a symmetric one means a desorption process of second order). However, this statement must be proposed with care. In some studies (*13, 16*), the presence of peaks in the rate of CH_4 formation is qualitatively explained by a hydrogenation mechanism associating with one limiting step and a simultaneous increase of the hydrogen concentration on the surface. But since a quantitative analysis has not been performed for this model, it is difficult to know the conditions under which this is true.

In this paper we present a case where the analysis based on the variation of the surface hydrogen concentration is fully applicable. Experimental evidence shows that the basic assumptions of the model are valid. In association with previous parts (*11, 12*), the present study helps to select between possible interpretations of the isothermal hydrogenation of adsorbed species.

II. EXPERIMENTAL

The experimental conditions used have been described in detail in Part I (*11*). The catalyst, a reduced (H_2, 713 K) precipitated 10 wt% Fe/Al_2O_3 has been characterized by various techniques (*17, 18*). The analytical system enables one to perform several transient experiments on the same catalyst sample either under isothermal conditions (catalytic reaction, adsorption, hydrogenation of adsorbed species) or under programming the temperature (TPD, TPR) (*19*). The apparatus consists of a quartz microreactor of 1 cm^3 nominal volume with a gas-flow control system under 1 atm. Three controlled gas flows, in the range 30–200 cm^3/min, can be selected to be introduced to the catalyst bed. A saturator permits also the feeding of liquid compounds (in this study, water). The gases are purified using a copper catalyst (B.A.S.F R-3.11) in order to remove O_2 and a zeolite to remove H_2O. When experimental conditions are suitable a small liquid nitrogen trap is used just before the reactor. The gas phase at the outlet of the reactor is continuously monitored by a quadrupole mass spectrometer (MIQ-200 Leybold-Heraeus) by use of a capillary inlet system and a Faraday cup detector. The whole system is driven by a microcomputer, which allows the recording of 10 preselected mass numbers and the temperature of the catalyst (via a microthermocouple immersed into the catalyst bed). The analyzed data are expressed as concentration (for every compound in the gas phase) and rate of disappearance or formation with time on stream.

The powdered catalyst is lightly compressed into a disk, fragmented, and screened to obtain particles in the range 0.59–0.84 mm. This assures that the reaction is kinetically controlled. The mass of catalyst used is in the range 50–300 mg.

III. RESULTS

A presentation of the kinetic model is first made before we expose the experimental results.

As discussed in the introduction, the main problem in the experiments of isothermal hydrogenation of adsorbed carbonaceous species is to explain the appearance of a peak in the response of the rate of formation of the product gas (mainly CH_4). One of the explanations which has been described in Part I (*11*) was the presence of at least two steps with the same rate constant in the mechanism of sequence of elementary steps. A second explanation presented in the discussion of Part I (*11*) was to assume that during the initial formation of CH_4 by a mechanism with one limiting step, the surface hydrogen concentration increases (*13, 16*). To quantify the second assumption we assume a limiting step such as: $CH_x + H \rightarrow CH_4$ ($x = 0, 1, 2$, or 3) with a rate constant k and a linear increase of the hydrogen concentration with time of hydrogenation, t,

$$H = H^O(1 + \gamma t), \tag{1}$$

where H^O is the concentration at time 0 according to a Langmuir model (dissociative chemisorption of H_2):

$$H^O = (\lambda P)^{1/2}/(1 + (\lambda P)^{1/2})H_{SO} = \vartheta H_{SO}. \tag{2}$$

Here, P is the pressure of adsorption (in this study 1 atm), λ is the adsorption coefficient (temperature dependent given by statistical theory assuming fixed species), H_{SO} is the number of sites able to chemisorb H (measured by chemisorption at low temperature), and ϑ is the coverage of sites.

The Langmuir model used seems to agree with results observed on crystal faces, polycrystal, and supported catalyst, which all give an activation energy of desorption in the range 88–108 kJ/mole (*20*). The linear relationship between H and t, which includes all the surface reactions able to generate hydrogen sites, permits an analytical solution for the rate of production of CH_4 which reveals the effects of the main kinetic parameters. This law must be fitted during the first period of hydrogenation, but we will examine the limits in the discussion section. The solution for the rate of formation of CH_4 is

$$\Phi = kC_OH^O(1 + \gamma t) \exp(-kH^O(t + \gamma t^2/2)), \tag{3}$$

where C_O is the initial surface concentration of the carbonaceous species.

The maximum of this rate is given by

$$\Phi_{\mathrm{m}} = kC_{\mathrm{O}}H^{\mathrm{O}}(\gamma/kH^{\mathrm{O}})^{1/2} \exp\{-(\tfrac{1}{2})(1 - kH^{\mathrm{O}}/\gamma)\} \quad (4)$$

$$t_{\mathrm{m}} = (1/\gamma)((\gamma/kH^{\mathrm{O}})^{1/2} - 1). \quad (5)$$

To observe a peak in the curve of the rate of CH_4 production ($t_{\mathrm{m}} > 0$) the value of γ must fulfill the condition $\gamma > kH^{\mathrm{O}}$. According to this model, the presence of a CH_4 peak is a function of (a) the initial hydrogen concentration H^{O}, (b) the rate constant of hydrogenation k, and (c) the value of γ. This shows that a qualitative use of the model to interpret experimental data is insufficient, because the surface hydrogen concentration must increase according to $\gamma > kH^{\mathrm{O}}$ in order to create a peak in the rate of CH_4 formation.

This statement can be verified using a specific case for the hydrogenation of adsorbed species. It has been observed (*13*) that the hydrogenation of the adsorbed carbonaceous species at 558 K, formed after passing a 10% CO/He mixture over a reduced 10% Fe/Al_2O_3 catalyst, leads upon the switch to H_2 to a rate of CH_4 formation decreasing exponentially from time 0 of hydrogenation. This result has been explained by a process with one limiting step. Thus, the first condition relative to the application of the kinetic model is fulfilled. Supposedly, if the hydrogen concentration increases during the titration, γ is less than kH^{O}. However, by deactivating part of the hydrogen sites by a reversible poisoning, it may be possible to alter H^{O} and γ without altering k so that $\gamma > kH^{\mathrm{O}}$. This will result in a profile with a peak for the production of CH_4. The value of γ and H^{O} can be measured by suitable experiments and therefore, the criterion and the kinetic model can be verified. Three further remarks must be made.

Remark 1. The criterion γ is obtained assuming a linear increase of the hydrogen sites, Eq. (1). This assumption can be compared to the result obtained assuming that this increase arises from the removal of one adsorbed carbonaceous species. On the Fe/Al_2O_3 catalyst this assumption may not be completely valid since the removal of several adsorbed species (C, O) may occur during the recovering of sites. However, it is of interest to confront the linear assumption to a more accurate kinetic model. Considering that one hydrogen site is created by the elimination of xC from the surface ($x \geq 1$),

$$dH_{\mathrm{s}}/dt = -(1/x)dC/dt \quad \text{or} \quad (C_{\mathrm{O}}/x) + H_{\mathrm{SO}} = (C/x) + H_{\mathrm{S}} = n_{\mathrm{O}}, \quad (6)$$

where H_{S} and H_{SO} are surface sites for hydrogen chemisorption at time t of hydrogenation and at $t = 0$, respectively (to be compared with the preceding notation: $H = \vartheta H_{\mathrm{S}}$, Eq. (2)), and n_{O} is the number of sites available for hydrogen chemisorption after all carbonaceous species have been removed. If the rate of CH_4 formation versus the time of hydrogenation is $\Phi' = dCH_4/dt = -dC/dt = k\vartheta CH_{\mathrm{S}}$, then the rate of increase of hydrogen sites is $dH_{\mathrm{S}}/dt = k\vartheta H_{\mathrm{S}}C/x$. Using the relation between H_{S} and C (Eq. (6)) and after integration,

$$H_{\mathrm{S}} = (n_{\mathrm{O}}H_{\mathrm{SO}}/(n_{\mathrm{O}} - H_{\mathrm{SO}}))(1/(H_{\mathrm{SO}}/(n_{\mathrm{O}} - H_{\mathrm{SO}}) + \exp\text{-}(n_{\mathrm{O}}\vartheta kt))). \quad (7)$$

The rate for CH_4 production is $\Phi' = k\vartheta x(n_{\mathrm{O}} - H_{\mathrm{S}})H_{\mathrm{S}}$, with maximum when $n_0 - 2H_{\mathrm{S}} = 0$ at

$$t'_{\mathrm{m}} = (1/\vartheta n_{\mathrm{O}}k) \ln ((n_{\mathrm{O}} - H_{\mathrm{SO}})/H_{\mathrm{SO}}). \quad (8)$$

Experimentally, a peak will be observed only if $H_{\mathrm{SO}} < n_{\mathrm{O}}/2$ (i.e., only if the number of initial sites for hydrogen chemisorption is less than $\frac{1}{2}$ of the available sites obtained after the removal of carbonaceous species). Using $n_{\mathrm{O}}\vartheta kt < 1$, valid at the beginning of hydrogenation, for a relatively low reaction temperature, and after some series approximations, Eq. (7) gives

$$H_{\mathrm{S}} = H_{\mathrm{SO}}(1 + k\vartheta(n_{\mathrm{O}} - H_{\mathrm{SO}})t). \quad (9)$$

Multiplying Eq. (9) by ϑ, the linear expression of Eq. (1) for H is obtained, which gives $\gamma = k\vartheta(n_{\mathrm{O}} - H_{\mathrm{SO}})$. The condition $\gamma > kH^{\mathrm{O}} = k\vartheta H_{\mathrm{SO}}$ is equivalent to the condition $H_{\mathrm{SO}} < n_{\mathrm{O}}/2$. Thus, the two conditions are identical and the assumption of a linear increase appears as a good approximation to the more accurate kinetic model. The advantage of the simplest expression of Eq. (1) for H is that it is more general because it includes all surface reactions (even if not known) able to generate hydrogen sites during hydrogenation.

Remark 2. The kinetic model developed for one adsorbed carbonaceous species can be used when two or more species are present on the surface. Each species, characterized by its initial coverage C_0 and a rate constant of hydrogenation k, will give a CH_4 production rate according to the value of γ. Thus, for given values of γ and H^0 some species will produce a peak and some others (more reactive) will produce a decreasing exponential profile for the CH_4 rate. The recorded response will be an overlap of these profiles, each one given by Eq. (3) with appropriate value of C_0 and k. Thus, three kinds of curves can be observed: a decreasing exponential profile (all the species follow the condition $\gamma < kH^0$), a succession of broad peaks (all the species follow the condition $\gamma > kH^0$), or a decreasing profile followed by one or several broad peaks. For the experimental conditions selected in this study, only one adsorbed carbonaceous species is present on the surface, as will be shown later. An extension of the model for more complex surfaces will also be discussed.

Remark 3. In what follows, we shall refer to three expressions for time of treatment of the catalyst: the time t_1 under 10% CO/He, the time t_2 under the reversible poison, and the time t for the hydrogenation of the adsorbed species. For a given value of t_1, the effect of different values of t_2 on the response of CH_4 production vs. t can be studied.

(*a*) *Selection of the Reversible Poison*

The measurement of the decrease in the number of sites able to chemisorb H_2 is made by chemisorption of H_2 according to the following procedure (see Ref. (*20*) for details): hydrogen is first adsorbed on the catalyst at 383 K and 1 atm for 10 min. Then the catalyst is cooled to room temperature in H_2 flow. After a switch to helium, the adsorbed quantity is measured by integrating the TPD response (5 K/s, T_m = 480 K). On a catalyst reduced at 713 K for 14 h and purged with He for 3 min, the quantity of atomic hydrogen chemisorbed is found to be 45 μmol H/g of cat., in agreement with literature for the same type of catalyst (*20*).

The reversible poisoning of the surface must be studied with the simplest experiment, which will give a slow decrease in the number of sites able to chemisorb H_2. This in order to have enough data to study the kinetic model and to prevent a drastic change in the state of the bulk iron. Two compounds have been tested as poison: oxygen and water present in low concentration in He carrier gas. In each case the experimental procedure is the following: after reduction at 713 K for 14 h, the catalyst is cooled in He to 558 K (the temperature used for the CO/He reaction). The mixture with the poison is introduced over the catalyst during a time t_2. Then, the catalyst is cooled in helium to 383 K, where chemisorption of H_2 occurs for 10 min according to the procedure previously mentioned.

A contact time t_2 = 30 s with a 2% oxygen/He mixture (60 cc/min) is found to be enough to decrease the zero the quantity of atomic hydrogen chemisorbed (initially 45 μmol H/g). This short time is inadequate to test the model. Oxygen present in even lower concentration (0.2%) leads also to an increase of the temperature of the catalyst and the appearance of a coloration (initially on the top of the catalytic bed), which indicates the formation of iron oxide. For these reasons the oxygen has not been used as a poison.

A mixture of H_2O/He has been found more suitable for the purpose of this work. Helium (60 cm^3/min) passes through a saturator containing pure water at 278 K. At the reaction temperature, 558 K, some of the water is decomposed on the reduced iron and leads to the production of H_2 (i.e., 50

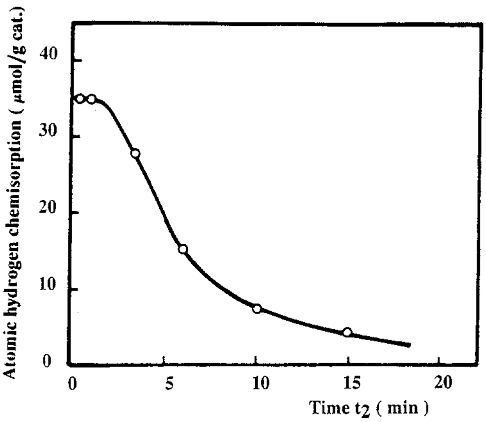

FIG. 1. Evolution of the hydrogen chemisorption on the 10% Fe/Al_2O_3 catalyst as a function of time t_2 in H_2O/He steam at 558 K.

μmol H_2/g of cat. are produced during the first 5 min). Part of the oxygen produced from this decomposition is adsorbed on the metallic iron surface and another part diffuses in the particles. Figure 1 gives the evolution of hydrogen chemisorption as a function of time t_2. It can be observed that the decrease of the H_2 chemisorption is low for $t_2 < 1$ min. This occurs because H_2O is adsorbed on the alumina support which is partially dehydrated by the treatment at 713 K. Rehydration of Al_2O_3 acts as a screen for the metallic iron during this period. For $t_2 >$ 1 min, a regular decrease in the hydrogen sites is recorded for 15 min. As shown in the next part, this poisoning is reversible.

Figure 1 shows that the initial hydrogen quantity (37 μmol H/g of cat.) is less than the 45 μmol H/g previously mentioned. This is due to the fact that for these experiments the liquid nitrogen trap placed close to the reactor must be removed in order to avoid condensation of water used as poison. Residual water in the feed gas during reduction process may affect the reduction of metallic iron surface.

(*b*) *Isothermal Hydrogenation of Adsorbed Species after Poisoning of the Hydrogen Sites*

The procedure is the following: after reduction of the catalyst in H_2 for 14 h at 713 K, the temperature is decreased in He at 558 K. Then the mixture of 10% CO/He is introduced for $t_1 = 6$ min, followed by a switch to He for 40 s. Next, water is passed over the catalyst for time t_2 followed by a switch to He for 40 s, followed by a hydrogen switch. The appearance of CH_4 during the latter switch is recorded as a function of time *t*. After H_2 reduction at 713 K for 14 h, a new value of t_2 is studied. Figure 2 gives the rate of CH_4 formation for various values of t_2. For short times of water contact ($t_2 < 1$ min) the initial rate decreases, but the response decreases exponentially. For $t_2 = 60$ s, an initial flat maximum is observed, followed by a decrease in the rate of CH_4; for $t_2 > 1$ min, a peak is observed.

Remark. The experimental conditions for the formation of the adsorbed carbonaceous species (6 min in 10% CO/He at 558 K, followed by desorption in He for 40 s) have been selected because they lead to a surface with only one adsorbed species. This can be emphasized by considering the CH_4 response during a TPR under H_2 as a function of time on stream (using the same procedure previously described for the CO/H_2 reaction (*12*)). For times on stream less than 6 min

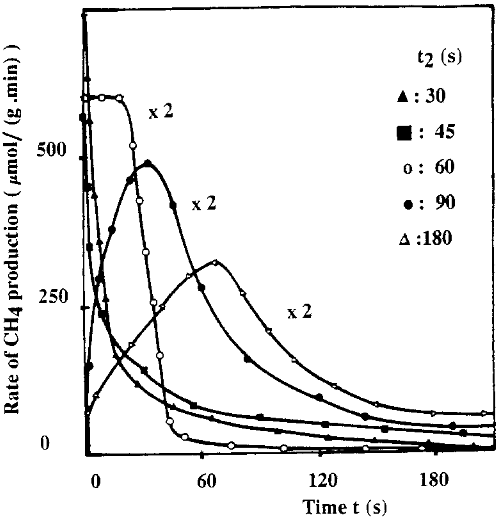

FIG. 2. Evolution of the CH_4 production rate by isothermal hydrogenation at 558 K after $t_1 = 6$ min in CO/He as a function of time t_2 in H_2O/He.

only one peak is observed. This means that only one main adsorbed species is present. The quantity of CH_4 increases with time on stream in agreement with the isothermal experiment (*13*). For the same time on stream but with CO/H_2, two distinct peaks had been observed (*12*). For longer times (i.e., 12 min) on stream in CO/He this surface state is not the same. A shoulder appears at the high temperatures followed by a second shoulder. The first shoulder may be attributed to the hydrogenation of iron carbide according to the rate of carburization measured in a previous study (*17*). The second shoulder may be due to the hydrogenation of graphitic-like carbon formed by a slow process. This process is not yet clearly understood on iron and may be similar to the one proposed on Ru (*21*). This species is responsible for the low decrease of the hydrogen chemisorption measured when the time in CO/He increases (*20*) and cannot be hydrogenated with a significant rate at 558 K. Thus, 6 min on stream leads to only one adsorbed species, with such initial quantity to follow the decrease of the rate of hydrogenation by the poisoning of the hydrogen sites. The He treatment after the 6 min in CO/He at 558 K leads to the desorption of all the molecularly adsorbed CO. This has been shown by different studies on various Fe crystal faces such as [100] (*22*) or [111] (*23*). Three forms of molecularly adsorbed CO observed at low temperatures desorb successively before 500 K. At 500 K only one form of dissociated CO is detected (*22, 23*). As was reported (*23*), the various Fe planes do not differ very much in their reactivity towards CO. This observation is also valid for H_2 (*20*).

The results presented in Fig. 2 are in good agreement with the present kinetic model. In particular, the change from a decreasing response to one containing a peak when the number of hydrogen sites decreases (increasing time t_2 in H_2O) is well observed. These results support the view that a linear increase of sites vs. the time of hydrogenation occurs. The curve for $t_2 = 60$ s shows a characteristic flat maximum at $t = 0$ which corresponds to the condition of $\gamma = kH^0$. This allows one to estimate the activation energy of hydrogenation by measuring the values of γ and H^0. Then, the validity of the criterion γ can be verified by comparing the experimental value of γ and the values of kH^0 for different values of t_2.

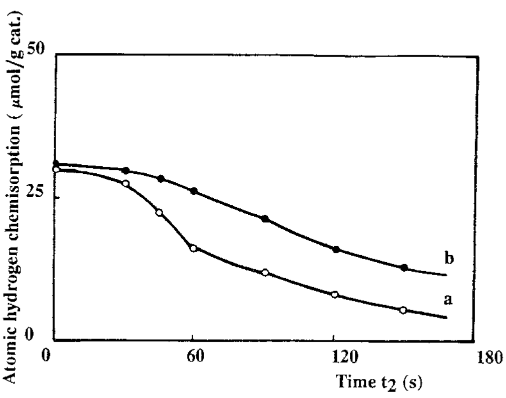

FIG. 3. Evolution of hydrogen chemisorption after $t_1 = 6$ min in CO/He at 558 K as a function of time t_2 in H_2O/He. Curve (a) at $t = 0$; curve (b) after $t = 30$ s of isothermal hydrogenation.

(*c*) *Determination of the Value of* γ

To measure γ, assuming a linear increase of the hydrogen sites, only two experimental data are needed: first, the value of the number of sites able to chemisorb H_2 on the iron surface in the presence of adsorbed carbonaceous species (after the contact of H_2O during time t_2), and second this value after a short time t of hydrogenation.

The first value is obtained according to the following procedure: after passing 10% CO/He over the catalyst for $t_1 = 6$ min, followed by a switch in He for 40 s, followed by introduction of H_2O for t_2, the catalyst is then cooled in He at 383 K where chemisorption of H_2 is made. Curve (a) of Fig. 3 gives the change of the hydrogen sites as a function of time t_2. This response is similar to that of Fig. 1 for the fresh reduced catalyst, but the initial quantity is less due to the presence of carbonaceous species.

The second value needed to measure γ is obtained according to the following proce-

TABLE 1

Isothermal Hydrogenation of Adsorbed Carbon Species Formed after $t_1 = 6$ min in CO/He, and Different Times t_2 in H_2O/He. Comparison of the Experimental Value of γ to the Value of kH^O

Time in H_2O (s)	30	45	60	90	120	150
$H^O/10^{13}$ (H/cm^2)	11.1	9.1	6.6	4.8	3.3	2.2
$\gamma/10^{-2}$ (s^{-1})	0.3	0.9	2	2.7	3.1	4.6
$kH^O/10^{-2}$ (s^{-1})	3.7	3.1	2	1.6	1.1	0.74

dure: 10% CO/He (558 K, $t_1 = 6$ min) → He (558 K, 40 s) → H_2O (558 K, t_2) → He (558 K, 40 s) → H_2 (558 K, t) → He (558 K, 40 s) → He (383 K) → H_2 (383 K, 10 min) → H_2 (300 K) → He (TPD). Note that between two experiments the catalyst is reduced at 713 K for 14 h in H_2.

Curve (b) in Fig. 3 corresponds to t = 30 s. It can be seen that when $t_2 < 40$ s, regeneration of sites is almost complete after t = 30 s; for higher values of t_2 the sites are not completely regenerated. For the case t_2 = 90 s we have studied the effect of a higher value of t. For t = 2 min, the number of sites is 26 μmol/g, so after the first 30 s of hydrogenation (21 μmol/g) the sites are still being regenerated but with a lower rate. In fact, we need to measure γ when the peaks of CH_4 are measured during the first minute of hydrogenation in accordance with Fig. 2. Even for $t_2 = 0$, some sites are regenerated and this will be discussed later.

Table 1 gives the value of H^O (first line) and the value of γ (second line) for various values of time t_2 according to the following. For the case of γ, which is independent of the units used to measure H and the coverage at the temperature of reaction, it is considered that between the two curves of Fig. 3 the variation of H is linear. H^O (atom H/cm^2) is obtained using the Langmuir equation (2): $H^O = \vartheta H_{SO}$. Curve (a) in Fig. 3 gives the number of sites available per gram of catalyst. The Fe particle size of a fresh reduced catalyst is in the range 13–20 nm (*18*), so the Fe surface area is 3–4 m^2/g of cat. Note that during the 6 min treatment in CO/He some fragmentation of Fe particles occurs (*20, 24*) probably due to the carburization of the iron (*21*). Thus, the Fe surface area must increase. According to Bussiere *et al.* (*24*), we assume here a value of 15 m^2/g of cat. (particle size of 5 nm) to convert the unit of H from μmol/g of cat. to atom/cm^2 of iron (Table 1, line 2). The coverage ϑ (Eq. (2)) at the reaction temperature is obtained using an activation energy for desorption of H_2 of 105 kJ/mol (from TPD data, (*20*)) and as the chemisorption of H_2 is slightly activated a value of 21 kJ/mol is used for the activation energy of adsorption (*25*). These values give a coverage of ϑ = 0.9 at 558 K.

IV. DISCUSSION

The good qualitative agreement between the experimental data of Fig. 2 and the projections of the kinetic model imply that the basic assumptions made are reasonable (in particular the linear increase of the hydrogen sites during the first minute of hydrogenation). This agreement is also consistent to the fact that only one adsorbed carbonaceous species is present on the surface. One of the consequences of the kinetic model to observe a peak in the rate of CH_4 formation is that the hydrogen sites must increase according to the criterion $\gamma > kH^O$; for values lower than kH^O a peak cannot be observed.

This criterion can be checked using the values of Table 1. First, the activation energy of hydrogenation can be estimated considering t_2 = 60 s, which gives a CH_4 peak with a flat maximum (Fig. 2). According to the kinetic model, this corresponds to $\gamma = kH^O$ for which the activation energy of hy-

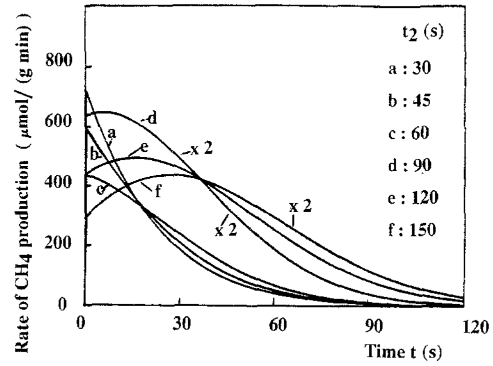

FIG. 4. Simulation results according to the kinetic model for the production of CH_4 by isothermal hydrogenation after 6 min in CO/He and various times t_2 in H_2O/He.

drogenation is $Er = RT \ln (H^O A/\gamma)$. Using the values of H^O and γ of Table 1, and assuming a preexponential factor of 10^{-2} cm^2/(site *xs*), a value of the activation energy for hydrogenation Er = 144 kJ/mol is obtained (assuming no fragmentation of the Fe particles, Er = 149 kJ/mol). If we consider that the real coverage of H is smaller than 0.9 (obtained from the assumption of immobile species) Er will be smaller; i.e., for $\vartheta = 0.1$ Er = 134 kJ/mol. These values are in the range (70–150 kJ/mol) reported in the literature for the hydrogenation of common adsorbed carbonaceous species (*26*). Using the value of Er = 144 kJ/mol, it is possible to compare kH^O (Table 1, line 3) to the measured value of γ (line 2). This comparison shows that for $t_2 < 60$ s γ is less than kH^O, and this agrees with the fact that no CH_4 peak is detected (Fig. 2, t_2 = 30 s and 45 s). For $t_2 > 60$ s, γ is greater than kH^O, and this agrees also with the fact that a peak of CH_4 is detected (Fig. 2, t_2 = 90 s and 180 s).

The assumption of a linear variation of H with t presents the advantage of resulting in a simple relation between the time at which the maximum of the peak of CH_4 appears, t_m, and the kinetic parameters affecting the results. In real conditions this linearity may not be followed during a long period of time (see Eq. (7)) and, therefore, some differences will exist between the kinetic model and the results. For example, the value of Er and the exact shape of the peaks may be affected. The results of Fig. 4 compared to those of Fig. 2 give some indications on this. In Fig. 4 the production of CH_4 according to Eq. [3] is given using an activation energy of Er = 144 kJ/mol and values for H^O and γ from Table 1. The value of C_O is 9.3×10^{14} C/cm^2 considering that the production of CH_4 is 230 μmol/g of cat. based on the hydrogenation of surface carbon species as recorded after t_1 = 6 min in CO/He. The comparison between the results of Fig. 4 and Fig. 2 shows an agreement between the two responses. But, when the peaks appear ($\gamma > kH^O$) for a given value of H^O and γ, the time required to reach the maximum t_m is larger for the experimental conditions (for t_2 = 90 s, t_m = 32 s) than the simulation (t_m = 8 s). This arises mainly because of the experimental error on the activation energy which affects strongly the value of t_m (i.e., using 147 kJ/mol instead of 144 kJ/mol the simulated t_m become 29 s). Note also that the shapes of experimental peaks are slightly different from those of the simulation (less symmetric). This arises mainly because the linearity between H and t is not followed exactly, and that the value of $\gamma = dH/dt$ diminishes with time of hydrogenation. Thus, at time t the real rate of CH_4 production is smaller than the simulated one. This parameter affects the sharpness of the peak, but has very little effect on the time t_m, which is very sensitive to the value of the activation energy. A curve fitting of the whole experimental curve associated with other experimental information might improve the values of Er and γ, but this was out of the scope of the present study.

We note that γ can be experimentally determined and compared to kH^O. This has been done for the hydrogenation of carbonaceous adsorbed species formed under 10% CO/He treatment. It is known (*13*) that the quantity of carbonaceous species increases with time t_1 on stream, and whatever this time is the hydrogenation of the various ad-

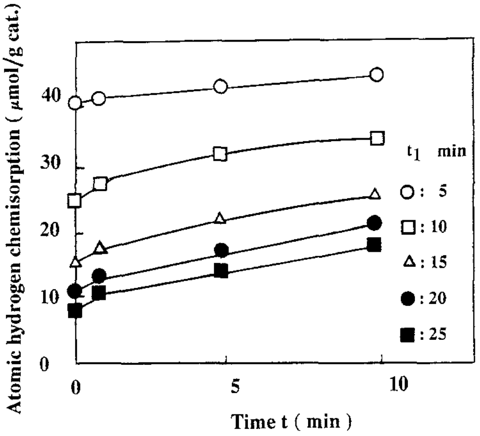

FIG. 5. Evolution of the hydrogen chemisorption at 558 K as a function of time t of the isothermal hydrogenation for various times t_1 in CO/He.

sorbed species leads to a CH_4 production with a decreasing exponential response (a CH_4 peak is never detected). This means that there is a limiting step in the process of hydrogenation and that the hydrogen sites either do not increase or increase with a value of $\gamma < kH^O$. These hypotheses should be checked by further experiments.

According to a previous study (*20*), during a CO/He treatment of the catalyst the number of hydrogen sites follows an evolution with t_1 in three steps; a fast decrease in the first minute due to the adsorption of elementary carbon, followed by an increase during a 5-min period attributed to fragmentation of iron particles during their carburization, followed by a slow decrease due to the formation of graphitic- like carbon. In this work we have studied the recovery of the sites during hydrogenation of carbonaceous species. Figure 5 gives the hydrogen sites as a function of the time t of hydrogenation for different contact times t_1 under 10% CO/He. Table 2 gives for various times t_1 the measured value of γ and H^O assuming a linear increase in the hydrogen sites during the first minute. The corresponding values of kH^O using an activation energy of Er = 144 kJ/mol are also reported. It can be observed that in each case $\gamma < kH^O$, with kH^O/γ in the range 5–10. This explains why no peak is detected even though the hydrogen sites are increasing. The decrease in the number of hydrogen sites with t_1 (Fig. 5) is responsible for the decrease of the initial rate of CH_4 production previously observed (Fig. 2 in Ref. (*13*)) in agreement with the expression for Φ (Eq. (3)).

The experimental conditions used in this study were appropriate to produce only one adsorbed carbonaceous species on the iron surface. This cannot be, of course, the case on all metal surfaces. For example, on Rh/Al_2O_3, dissociated CO as well as molecularly adsorbed CO species are present even after a short contact time in CO/He (*27*). These species are hydrogenated simultaneously under isothermal conditions. The observed CH_4 production response consists of an initial fast decrease followed by a broad peak (Fig. 8 in Ref. (*27*)). Assuming that these species are hydrogenated following the mechanism described in this study (i.e., assuming an increase of the hydrogen chemisorption during titration) and considering Remark 2 of the model, the observed curves (*27*) seem to correspond to the case of a hydrogenation of one reactive species obeying the condition $\gamma < kH^O$ (decreasing

TABLE 2

Isothermal Hydrogenation of Adsorbed Carbon Species after Various Times in CO/He. Comparison of the Experimental Value of γ to the Values of kH^O

Time in CO/He (s)	300	600	900	1200	1500
$H^O/10^{13}$ (H/cm^2)	12.6	10.1	6.7	4.1	3.4
$\gamma/10^{-2}$ (s^{-1})	0.06	0.13	0.17	0.33	0.27
$kH^O/10^{-2}$ (s^{-1})	4.2	3.4	2.0	1.35	1.15

exponential profile) and another less reactive species obeying the condition $\gamma < kH^{O}$ (broad peak). This result shows that the present kinetic model can be useful to understand complex CH_4 responses obtained during isothermal hydrogenation of several carbonaceous adsorbed species. Of course, as can be seen from the simulation using Eq. (3), the resolution of this method of characterizing adsorbed species depends on the relative value of the rate constant and the coverage of the various species.

V. CONCLUSIONS

The kinetic model described here, and the results presented show that the hydrogenation of adsorbed carbon species by a mechanism with one limiting step linked to an increase in the hydrogen surface concentration with hydrogenation time can explain the presence of a peak in the response of isothermal production of CH_4. On the other hand, a qualitative analysis is not enough and the criterion $\gamma > kH^{O}$ must be checked by experimental data. The present work contributes to a better understanding of transient isothermal data. The appearance of peaks is explained either by a mechanism with one limiting step linked to an increase in the surface hydrogen concentration ($\gamma > kH^{O}$ must be valid) or by a mechanism with at least two steps with comparable rate constants (*11, 12*). These kinetic models could be applied in other isothermal transient experiments such as oxidation.

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