

## Hydrogenation of Carbonaceous Adsorbed Species on an Iron/Alumina Catalyst

### II. Experiments and Interpretation of the Temperature-Programmed Hydrogenation by a Kinetic Model

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A kinetic model for the hydrogenation (into CH<sub>4</sub>) of adsorbed carbonaceous species formed on an iron catalyst during the CO/H<sub>2</sub> reaction has been previously proposed to interpret the isothermal hydrogenation. The same model is now shown to fit the experimental data obtained in the temperature-programmed hydrogenation (nonisothermal). The effect of various kinetic parameters acting during the temperature-programmed hydrogenation is included in the kinetic equation, and the main experimental observations are explained. The values of the activation energy of hydrogenation of the various adsorbed species are obtained from the kinetic equation and are compared with those found under isothermal conditions. © 1990 Academic Press, Inc.

#### INTRODUCTION

The recent development of transient experiments in catalysis is mainly due to the possibility provided by quadrupole mass spectrometers of fast analysis of the perturbations in the gas phase in contact with a solid catalyst. The modifications of the gas–solid system concern either a physical parameter such as the temperature or the chemical composition of the reactive gas. This causes differences between the various transient experiments. The change in temperature gives the well-known temperature-programmed desorption techniques (TPD) (1, 2) or the more recent temperature-programmed reaction (TPR) (2). The controlled change in gas-phase composition leads to different types of experiments, in particular isotopic steady-state tracing (3–5) and the isothermal reaction of the adsorbed species with a gas, for example hydrogenation (6–8). Although many ex-

perimental studies are available, theoretical treatments are rare, except for TPD (1, 2, 10–12). Some theoretical treatments of other transient experiments have recently been developed, such as wavefront analysis (13) and temperature-programmed reduction of solids (14).

In Part I (15) we proposed a kinetic model for the interpretation of the results obtained in the isothermal hydrogenation of the adsorbed species formed during the CO/H<sub>2</sub> reaction on an iron/alumina catalyst. This model is based on a sequential hydrogenation of CH<sub>x</sub> species by consecutive reactions, with the same rate constant. It fits the main experimental observations and allows for the determination of the hydrogenation activation energy of various adsorbed species. In the present paper we apply the same model for the temperature-programmed (nonisothermal) hydrogenation of CH<sub>x</sub> species. These transient experiments have been used in various studies (7, 16, 17) but only a few have been aimed at the kinetic interpretation (17).

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## EXPERIMENTAL

The experimental conditions have been described in detail in Part I (15). The catalyst, a reduced precipitated 10 wt% Fe/Al<sub>2</sub>O<sub>3</sub>, has been characterized by various techniques (8, 9). The analytical system consists of a quartz microreactor with an adapted gas-flow control system under atmospheric pressure. The gas phase at the outlet of the reactor is continuously analyzed by a quadrupole mass spectrometer (MIQ-200 Leybold-Heraeus) by use of a capillary inlet system and a Faraday cup as detector. The temperature of the reactor is controlled by a system giving a linear increase in temperature in the range 1 to 400 K/min.

The experimental procedure consists of reduction of the catalyst (in the mass range 50–200 mg) by H<sub>2</sub> at 440°C for 14 h. After a decrease to the reaction temperature, helium gas is introduced for 5 min. The reactant mixture, 10% CO/H<sub>2</sub>, is then admitted during a prefixed time *t* followed by a treatment in helium for 40 s. The catalyst is

quickly cooled to room temperature in helium and hydrogen is introduced. The temperature of the catalyst is increased using a linear rate of 5 K/s (compatible with the sensitivity of the detector).

## RESULTS

*Experimental Data*

Figures 1 and 2 give the rate of formation of CH<sub>4</sub> (no other hydrocarbon compound has been detected) during the increase in temperature as a function of the time of the CO/H<sub>2</sub> reaction. It is observed in Fig. 1 that for a short reaction time (less than 30 s) only one peak is recorded, but when this time increases a second peak appears. As the second peak intensifies with increasing time of the CO/H<sub>2</sub> reaction, the first peak becomes a shoulder on the second peak and after 8 min it is no longer distinct. Also, after a reaction time of 8 min, a third peak is detected at higher temperatures.

The presence of three peaks in the TPR spectrum after a period of CO/H<sub>2</sub> reaction is in agreement with the result observed by

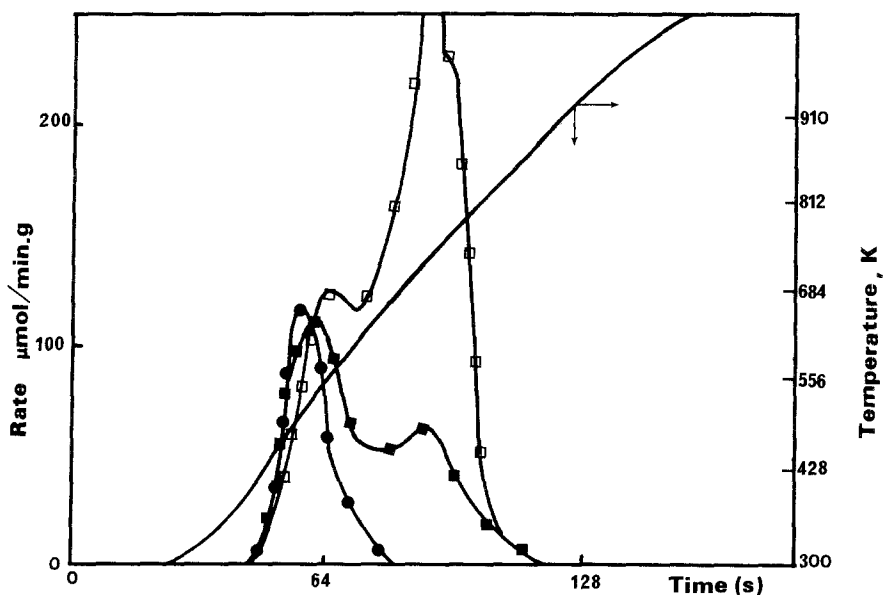


FIG. 1. Temperature-programmed hydrogenation of the adsorbed species formed during the first 3 min of the 10% CO/H<sub>2</sub> reaction; (●) 0.5 min of CO/H<sub>2</sub> reaction, (■) 1.5 min of CO/H<sub>2</sub> reaction, (□) 3 min of CO/H<sub>2</sub> reaction.

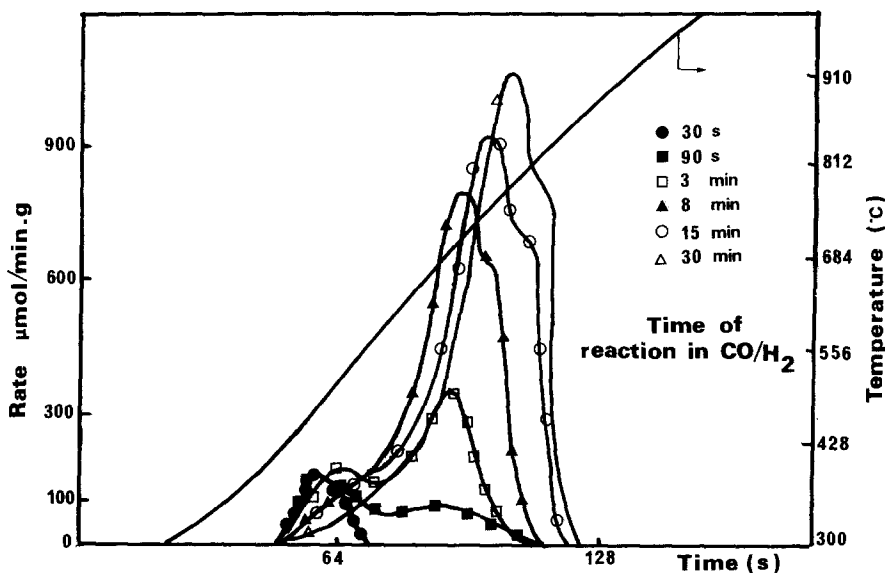


FIG. 2. Temperature-programmed hydrogenation of the adsorbed species formed during the first 30 min of the 10% CO/H<sub>2</sub> reaction.

isothermal hydrogenation of the adsorbed species, where three peaks have also been detected (8, 15).

It can be observed in Fig. 2 that the temperature of the maximum of the peaks increases when the CO/H<sub>2</sub> reaction time in-

creases. This is clearly seen for the second and third peaks between 3 and 30 min.

The amounts of CH<sub>4</sub> produced in the different peaks are given in Table 1. Since deconvolution of these peaks is not easy after a period of reaction higher than 3 min, the

TABLE 1

Quantity of CH<sub>4</sub> Produced in Various Temperature-Programmed Reaction Peaks as a Function of the Time of the CO/H<sub>2</sub> Reaction; Comparison with Isothermal Results

| Time of CO/H <sub>2</sub> reaction (min) | Temperature-programmed reaction results |                      |                              | Isothermal results at 285°C (Refs. (8, 9)) |                              |
|--|---|----------------------|------------------------------|--|------------------------------|
|  | First peak (μmol/g)                     | Second peak (μmol/g) | Second + third peak (μmol/g) | Time of CO/H <sub>2</sub> reaction (min)   | Second + third peak (μmol/g) |
| 0.5                                      | 44 <sup>a</sup>                         | 0                    |                              | 0.5  | 68 (58.4) <sup>d</sup>       |
| 1.5                                      | 51 <sup>a</sup>                         | 27                   |                              | 2  | 245 (150)                    |
| 3  | 47.8 <sup>a</sup>                       | 154.1                |                              | 5  | 456 (251)                    |
| 8  | <sup>b</sup>                            | <sup>c</sup>         | 393.9                        | 10   | 618 (309)                    |
| 15                                       | <sup>b</sup>                            | <sup>c</sup>         | 461.7                        | 20   | 716 (290)                    |
| 30                                       | <sup>b</sup>                            | <sup>c</sup>         | 525.2                        | 30   | 679 (226)                    |

<sup>a</sup> For comparison the value given by the isothermal experiment is 50 μmol/g.

<sup>b</sup> Quantity-assumed constant.

<sup>c</sup> Difficulty of deconvolution.

<sup>d</sup> The numbers in parentheses refer to the second species.

data of Table 1 have been obtained with the help of the previous isothermal results. From these results it is considered that the first peak is constant with the time of reaction. This is essentially confirmed in the TPR results up to the first 3 min of CO/H<sub>2</sub> reaction when the deconvolution of two first peaks is possible (Table 1; data for 0.5, 1.5, and 3 min). Hence, the quantity of CH<sub>4</sub> detected in the first peak after 0.5 min of reaction can be subtracted from the second peak. When the third peak is detected (Fig. 2, 8 min of reaction), the deconvolution between the second and third peaks is not possible because the exact profiles of the peaks are not known. For this reason it is proposed to compare with the isothermal measurement (Table 1, column 6) the sum of the two peaks in the TPR results (Table 1, column 4).

A good agreement is found between the TPR and isothermal measurements for the first peak. The result for the second and third peaks shows some values smaller for the TPR experiment than for the isothermal run. This is probably due to some slight difference in the experimental conditions for the two studies such as the partial pressure of CO or the temperature of the reaction, which may affect the kinetics of the formation of the adsorbed species.

According to the results of the isothermal experiments (8) and Mössbauer experiments (9), the third peak at higher temperatures which appears after a period of 8 min of CO/H<sub>2</sub> reaction is attributed to the hydrogenation of the bulk carbide and is not considered in the present study.

#### *Interpretation of the Data by a Kinetic Model for Hydrogenation*

In Part I (15) it has been shown that a kinetic model based on sequential hydrogenations of some CH<sub>x</sub> adsorbed species into CH<sub>4</sub>, involving two, three, or four steps with the same rate constant, explains the experimental data obtained during the reaction under isothermal conditions. In particular, it has been shown that the mechanism

of hydrogenation with one limiting step is not likely and in the case of the more hydrogenatable species we have shown that two steps with the same rate may be involved.

Depending on the number of steps with the same rate, the evolution of the rate of CH<sub>4</sub> formation under isothermal conditions as a function of the time of hydrogenation can be determined (15). The following is found (15):

(1) one limiting step

$$\phi = kC_0He^{-kHt}$$

(2) two steps with same rate

$$\phi = C_0(kH)^2te^{-kHt}$$

(3) three steps with same rate

$$\phi = \frac{C_0(kH)^3}{2}t^2e^{-kHt}$$

(4) four steps

$$\phi = \frac{C_0(kH)^4}{6}t^3e^{-kHt}$$

where  $C_0$ , expressed as C-atom per unit area, is the initial surface coverage of carbonaceous species;  $k$  is the rate constant [ $k = A \exp(-E_r/RT)$  where  $E_r$  is the activation energy of hydrogenation];  $H$  is the hydrogen chemisorption coverage at the temperature  $T$ ; and  $t$  is the duration of the isothermal hydrogenation.

These equations lead to different curves of CH<sub>4</sub> production versus the time of hydrogenation, the curves being a function of the number of steps involved.

The same equations can be used to make a computer simulation of the shape of the CH<sub>4</sub> production under TPR conditions [linear increase in the temperature  $T = (T_0 + \alpha t)$ ] using reasonable values of various parameters. Values for  $C_0 = 10^{14}$  C-atom/cm<sup>2</sup>,  $H = 10^{11}$  H-atom/cm<sup>2</sup>, preexponential factor  $10^{-2}$ , activation energy  $E_a = 117$  kJ/mol, and linear rate of the increase of the temperature  $\alpha = 5$  K/s were used.

Figure 3 gives the result of the simulation for one limiting step and for three steps with the same rate constant. It can be ob-

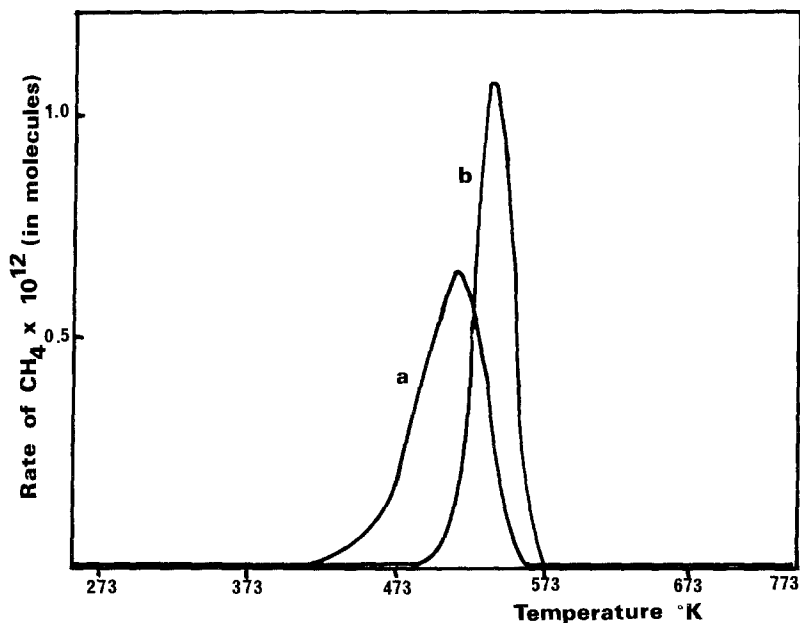


FIG. 3. Computer simulation of TPR experiment. Effect of the kinetic mechanism of the hydrogenation. (a) Mechanism with one limiting step; (b) mechanism with three steps with the same rate constant.

served that in contrast to the isothermal hydrogenation conditions, the number of steps has little effect on the shape of the TPR  $\text{CH}_4$  production. In all cases, an asymmetric peak is detected similar to TPD peaks of the first order (2, 11). Only the base of the peak is larger and the value of the maximum rate higher, depending on the number of steps. However, these observations cannot be used directly to interpret experimental data. This comment shows that TPR experiments do not reveal the mechanism of the hydrogenation by a simple observation of the production of  $\text{CH}_4$ .

Moreover, the temperature at the top of the peak for some given values of various parameters is only slightly affected by the number of steps (20 K between one limiting step and three steps with the same rate constant). Hence in an attempt to use the experimental data such as the temperature at the peak maximum to obtain some value for the kinetic parameter, the same expression must be found for the different cases (with or without a limiting step).

In the following, by use of the equation for the rate of the  $\text{CH}_4$  formation given above, a calculation is made to obtain a mathematical relation between the temperature at the maximum of the peak  $T_m$  and the kinetic parameters. This expression, using reasonable simplifications, should be the same for various possibilities concerning the hydrogenation mechanism (with or without limiting step). It should be useful for the determination of kinetic parameters and in particular the hydrogenation activation energy.

The same assumptions as those in Part I (15) are made. The concentration of adsorbed hydrogen is given by the Langmuir-type equation

$$H = \frac{\sqrt{\lambda P}}{1 + \sqrt{\lambda P}} H_0, \quad (1)$$

where  $P$  is the pressure of adsorption,  $H_0$  is the hydrogen concentration at the saturation point, and  $\lambda$  is the adsorption coefficient given by statistical theory. The equa-

tion which reveals the temperature effect is

$$\lambda = \frac{\text{constant}}{T^{5/2}} \exp\left(\frac{Q_a}{RT}\right),$$

where  $Q_a$  is the heat of adsorption.

All the equations are derived by using, at the maximum of the rate of  $\text{CH}_4$  formation, the equations

$$\left(\frac{d\phi}{dt}\right)_{T_m} = 0 \quad (\text{a})$$

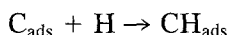
and

$$\left(\frac{dT}{dt}\right)_{T_m} = \alpha_m, \quad (\text{b})$$

where  $\alpha_m$  is the rate of linear increasing of  $T$ .

The various mechanism possibilities will be considered in succession.

(1) *One limiting step.*



( $\text{C}_a$  adsorbed carbonaceous species ( $\text{CH}_x$  structure)).

From Ref. (15) the rate of  $\text{CH}_4$  formation is given by

$$\phi = A e^{-E_r/RT} C_{\text{ads}} H$$

and from Eqs. (a) and (b) one has for the top of the peak

$$\alpha_m \frac{E_r}{RT_m^2} C_{\text{ads}} + \left(\frac{dC_{\text{ads}}}{dt}\right)_{T_m} + \frac{C_{\text{ads}}}{H} \left(\frac{dH}{dt}\right)_{T_m} = 0. \quad (\text{II}_a)$$

However,

$$-\frac{dC_{\text{ads}}}{dt} = A e^{-E_r/RT} C_{\text{ads}} H$$

and

$$\frac{1}{H} \cdot \frac{dH}{dt} = \frac{d \ln H}{dt}.$$

Using the approximation of the Langmuir model with  $\sqrt{\lambda P} < 1$  (hypothesis valid at high temperature), we have  $H = \sqrt{\lambda P} H_0$ , with  $\lambda$  related to the temperature as above.

It can then be written that

$$\frac{d \ln H}{dt} = \frac{-5}{4} \cdot \frac{1}{T_m} \cdot \alpha_m - \frac{1 \cdot Q_a}{2 RT_m^2} \cdot \alpha_m,$$

and by substitution in Eq. (II<sub>a</sub>) this becomes

$$\frac{E_r - \frac{1}{2} Q_a}{RT_m^2} = \frac{AH}{\alpha_m} e^{-E_r/RT_m} + \frac{5}{4} \cdot \frac{1}{T_m}. \quad (\text{II}_b)$$

A simpler equation between  $T_m$  and  $E_r$  can be obtained with a few approximations. Using some realistic values for the kinetic parameters, one finds that  $A = 10^{-2} \text{ cm}^2/(\text{s} \times \text{site})$ ,  $H = 10^{13} \text{ H-atom/cm}^2$ ,  $E_r = 125 \text{ kJ/mol}$ ,  $T = 400^\circ\text{C}$ ,  $\alpha_m = 10^\circ\text{C/s}$ , and  $Q_a = 84 \text{ kJ/mol}$ , and it can be observed that

$$\frac{5}{4} \cdot \frac{1}{T_m} \ll \frac{AH}{\alpha_m} e^{-E_r/RT_m}.$$

Now  $5/(4T_m)$  is smaller than the first term in Eq. (II<sub>b</sub>). This leads to

$$\frac{E_r}{RT_m} = \ln \frac{AH}{\alpha_m} - \ln \frac{E_r - \frac{1}{2} Q_a}{RT_m}. \quad (\text{II}_c)$$

To obtain a practical relationship between  $E_r$  and  $T_m$  it can be considered that the last term of Eq. (II<sub>c</sub>) is smaller than the first and therefore a simple relation between  $E_r$  and  $T_m$  can be proposed:

$$E_r = RT_m \ln \frac{AH}{\alpha_m}. \quad (\text{II}_d)$$

By introduction of this value of  $E_r$  into Eq. (II<sub>c</sub>), one can propose a more precise relationship,

$$E_r = RT_m \ln \frac{AH}{\alpha_m} - \ln \left( \frac{1}{T_m} \left( \ln \frac{AH}{\alpha_m} \right) - \frac{1}{2} \frac{Q_a}{RT_m^2} \right), \quad (\text{II}_e)$$

which is close to the form found in TPD of the second order (2) (in agreement with the computer simulation),

$$E_d = RT_m \left[ \ln \frac{\nu}{\alpha_m} - \ln \frac{1}{T_m} \left( \ln \frac{\nu}{\alpha_m} \right) \right],$$

$\nu$  being the frequency factor.

(2) *Two steps with the same rate.*



The calculation is similar to that developed in Eq. (II<sub>1</sub>) above but starts with the rate of CH<sub>4</sub> formation:

$$\phi = Ae^{-E_r/RT}CH_{\text{ads}}H$$

and

$$\frac{dCH_{\text{ads}}}{dt} = kC_{\text{ads}}H - kCH_{\text{ads}}H.$$

Using Eqs. (a) and (b) for the top of the peak, one finds a relationship between  $T_m$  and  $E_r$ ,

$$\begin{aligned} E_r - \frac{1}{2} Q_a \\ \frac{RT_m^2}{\alpha_m} \\ = \frac{AH}{\alpha_m} e^{-E_r/RT} \left( 1 - \frac{C_{\text{ads}}}{CH_{\text{ads}}} \right) + \frac{5}{4} \frac{1}{T_m}, \quad (\text{II}_d) \end{aligned}$$

which can be simplified by omitting the term  $5/(4T_m)$  as in Eq. (II<sub>b</sub>) above and considering that  $CH_{\text{ads}} > C_{\text{ads}}$  at the top of the peak. This leads to the same equation as (II<sub>c</sub>) and then to (II<sub>0</sub>) and (II<sub>1</sub>).

(3) *Three or four steps.* The treatment is the same as that in Eq. (II<sub>d</sub>) with the following simplifications: for three steps  $CH_{2\text{ads}} > CH_{\text{ads}}$  and for four steps  $CH_{3\text{ads}} > CH_{2\text{ads}}$  at the maximum of the peak. This leads to the same equation as (II<sub>c</sub>) and then to (II<sub>0</sub>) and (II<sub>1</sub>).

Therefore in all cases, with or without limiting steps, the same relationships between  $T_m$  and  $E_r$  can be proposed, namely, Eqs. (II<sub>0</sub>) and (II<sub>1</sub>), depending on the level of simplification. This agrees with the simulation.

## DISCUSSION

The kinetic interpretation of the temperature-programmed reaction reveals different kinetic parameters acting significantly on the observed results.

(a) *Mechanism of the Hydrogenation*

Under the isothermal hydrogenation conditions, the mechanism strongly affects the shape of the curve of the production of CH<sub>4</sub> versus the time of hydrogenation (15). In TPR this parameter is not so important. With some minor assumptions, the relationship between the temperature at the maximum of the peak and the other kinetic parameters is the same independent of the presence or absence of a limiting step. The computer simulation (Fig. 3) reveals slight differences between different mechanisms.

(b) *Activation Energy*

As in TPD, the species with different hydrogenation activation energies give different peaks in proportion to their respective quantities: the higher the activation energy the higher is the value of  $T_m$ .

This explains the presence of, at least, three peaks (after 8 min of CO/H<sub>2</sub> reaction) in the observed TPR spectrum, due to the presence of three carbonaceous species on the iron catalyst (depending on the time of the CO/H<sub>2</sub> reaction). This result is in agreement with the results observed in the isothermal hydrogenation conditions (15).

(c) *Hydrogen Chemisorption*

Equations (II<sub>0</sub>) and (II<sub>1</sub>) reveal two effects of this parameter, first the surface concentration in H and second the heat of adsorption. Equation (I<sub>0</sub>) reveals that if, for a given value of the hydrogenation activation energy of an adsorbed species, the hydrogen concentration decreases (for example by poisoning during the CO/H<sub>2</sub> reaction) the temperature of the peak maximum increases. This explains the shift observed in the experimental results. The effect is less important in TPR than in an isothermal experiment (15). For the isothermal conditions, a reverse proportionality is found between  $t_m$  (time of the appearance of the maximum) and  $H$ , while in the TPR experiment,  $T_m$  is in inverse proportion with the logarithm of  $H$ .

According to the sign of  $\partial T_m/\partial Q_a$ , Eq. (II<sub>b</sub>) shows that an increase in the heat of adsorption leads to a decrease in  $T_m$ . The place of  $Q_a$  in Eq. (II<sub>1</sub>) shows that this parameter is only a factor of a second order.

(d) *The Heating Rate  $\alpha_m$*

Equation (I<sub>0</sub>) reveals that an increase in the  $\alpha_m$  value gives an increase in the temperature at the maximum, in a way similar to the TPD experiment.

In order to obtain the values of the hydrogenation activation energy of various species, using Eqs. (II<sub>0</sub>) or (II<sub>1</sub>) and the experimental determination of  $T_m$ , some values for the kinetic parameters must be introduced. The parameter  $\alpha_m$  is 5 K/s (from the experimental conditions). From Part I (15) the heat of adsorption value for hydrogen  $Q_a$  is 84 kJ/mol. For the preexponential factor  $A$  of the second order reaction, the classical  $(kT)/(hS) = 10^{-2}$  is used ( $k$  is Boltzman's constant,  $h$  Planck's constant,  $T$  temperature, and  $S$  density of sites per square centimeter assuming  $S = 10^{15}/\text{cm}^2$ ). The last parameter,  $H$ , the hydrogen atom concentration at temperature  $T_m$ , is not well determined. Chemisorption measurements of  $\text{H}_2$  were made previously (18); i.e., we had 90  $\mu\text{mol}$ s of H per gram of catalyst and we measured 17  $\text{m}^2$  per gram of catalyst for the metallic iron surface. This gives a surface density at room temperature of  $3.1 \times 10^{14}$  H-atoms per square centimeter. However, during the reaction some sites disappear by poisoning and their exact number is unknown. It is proposed to take a range of reasonable values of  $H$  which gives a range of values of  $E_r$ .

For the first species, in the case of 0.5 min of  $\text{CO}/\text{H}_2$  reaction when  $T_m$  has a value of 210°C (Fig. 2) it is found that

using  $H = 10^{13}$  H-atom/ $\text{cm}^2$

$$\text{Eq. (II}_0\text{): } E_r = 95.7 \text{ kJ/mol}$$

$$\text{Eq. (II}_1\text{): } E_r = 110.3 \text{ kJ/mol}$$

using  $H = 10^{11}$  H-atom/ $\text{cm}^2$

$$\text{Eq. (II}_0\text{): } E_r = 76.9 \text{ kJ/mol}$$

$$\text{Eq. (II}_1\text{): } E_r = 92.8 \text{ kJ/mol.}$$

For the second species, in the case of 2 min of  $\text{CO}/\text{H}_2$  reaction when  $T_m = 398^\circ\text{C}$  and considering the value of  $H$  smaller than that of the first species,

$H = 10^{12}$  H-atom/ $\text{cm}^2$

$$\text{Eq. (II}_0\text{): } E_r = 120.0 \text{ kJ/mol}$$

$$\text{Eq. (II}_1\text{): } E_r = 141.2 \text{ kJ/mol}$$

$H = 10^{10}$  H-atom/ $\text{cm}^2$

$$\text{Eq. (II}_0\text{): } E_r = 94.5 \text{ kJ/mol}$$

$$\text{Eq. (II}_1\text{): } E_r = 118.3 \text{ kJ/mol.}$$

The values found for  $E_r$ , in particular those from the more accurate Eq. (II<sub>1</sub>), are in good agreement with those obtained from the isothermal experimental data (15) and with the literature data.

#### CONCLUSION

The present paper confirms the conclusion based on the data recorded during the hydrogenation of carbonaceous species formed during the  $\text{CO}/\text{H}_2$  reaction on the  $\text{Fe}/\text{Al}_2\text{O}_3$  catalyst. Three carbonaceous species can be detected after 10 min of reaction. Two are surface species and the third is the carbide species. The kinetic model proposed in Part I (15) for the hydrogenation of the species by a mechanism involving at least two steps having the same rate constants is in agreement with the observed results. However, the discussion of various possible mechanisms shows that TPR is not the right experiment to confirm this point.

The correct determination of the hydrogenation activation energy using TPR results requires the characterization of the evolution of the hydrogen chemisorption as a function of the time of the  $\text{CO}/\text{H}_2$  reaction. This is the next program of this work.



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