Transient kinetics in heterogeneous catalysis by metals

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Abstract

This paper tries firstly to remember the origin of kinetic models in heterogeneous catalysis. The change of catalysis from an art to science induced by the introduction of the concepts of Langmuir is presented in Section 1.

In Section 2, deficiencies contained in these concepts as applied, where one site is associated to one chemisorbed radical, are developed. Namely the curious contradictions obtained in the analysis of the hydrogen inhibiting term on the rate of hydrogenolysis reactions are analysed.

In Section 3, attention is drawn on information obtained by use of labelled molecules. These studies indicated a similar H_2 inhibiting term on the only adsorption step. The interpretation of that effect results in the development of a multisite adsorption model.

Section 4 introduces the interest and advantages of the use of the chemical transient method. Simultaneously, its technical limitations are briefly presented.

Sections 5 and 6 are devoted to the application of the transient method to two very different but important catalytic reactions. The first of these examples makes evident the interest in the combination of labelled molecules with chemical transient effects, to determine the rate, direct and inverse, of the successive elementary steps of the model reaction that is ethane hydrogenolysis. The second example, the CO–H_2 reaction, is much more complex as the catalytically working surface is built during the transient phase, thus dramatically changing the surface properties. If it does not allow, as in the previous example, to obtain quantitative determinations of the rate of the elementary steps, it anyway provides unique information leading one to propose a new reaction scheme.

One of the aims of this paper is to support the still large importance of kinetic studies in heterogeneous catalysis, a topic dear to Michel Boudart with whom one of us (A. Frennet) had the honour and pleasure to work. © 2000 Published by Elsevier Science B.V.

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1. Catalysis, from an art to a science

The phenomenon of catalysis has been recognised a long time before it became a science. In the first part of the 19th century, several research works related to what we now call catalysis had already been published. Let us mention the publication by Davy [1] and Doebereiner [2] of a description of the combustion of alcohol in the presence of platinum, and that of hydrogen in the presence of palladium and iridium wires by Dulong and Thenard [3,4] and on platinum by Faraday [5].

Catalysis received its first definition from Berzelius [6] in 1836, which Redeal and Taylor translated into English [7] a few years later:

"This new force, which was hitherto unknown, is common to organic and inorganic nature. I do not

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believe that it is a force quite independent of the electrochemical affinities of matter; I believe, on the contrary, that it is only a new manifestation of the same; but, since we cannot see their connection and mutual dependence, it will be more convenient to designate the force by a separate name. I will therefore call this force *the catalytic force* and I will call catalysis the decomposition bodies by this force in the same way that one calls by the name analysis the decomposition of bodies by chemical affinity."

Nevertheless this definition relating the phenomena to a "catalytic force" did not contain any explanation allowing a scientific interpretation of the observed catalytic phenomena.

A series of distinguished scientists, within which Faraday and Doebereiner suggested some false explanations, were discussed in an interesting paper by Schoenbein [8] in 1848.

It was only in 1894 that Ostwald made the first very important scientific analysis of the catalytic phenomena, but in the framework of the thermodynamics of the reacting system. He drew the attention of the scientific community to the fact that catalysis may not modify the thermodynamics of the reacting system and that, thus, catalysis can only affect the kinetics of the possible reactions in a chemical system. So he introduced one of the most important concepts characterising catalysis: kinetic selectivity. He presented his complete views on the non-effect of a catalyst on the equilibrium point of a reaction in 1902 [9,10].

During the 19th century, catalysis remained more an art than a science.

Kinetic data could only receive a real scientific treatment from the time Langmuir introduced the concept of chemisorption in 1912 [11]. He derived the "Langmuir isotherm" [12] from a simple kinetic treatment of the dynamic adsorption–desorption equilibrium. Langmuir himself first introduced its application to kinetics [13].

This concept has been successfully applied by renowned scientists, specialists of kinetics — for the first time by Sir Cyril Hinshelwood in 1928 [14] (mechanism of Langmuir−Hinshelwood) and Sir Eric Rideal [15–18].

The development of kinetic equations in the framework of the concepts used in homogeneous kinetics was not able to account for a typical feature of heterogeneous kinetics: an inhibiting term in the partial pressure of one of the reactants. The catalytic reaction presents important steps on the surface of the catalyst. As a consequence, the rate equation contains the product of the coverages in the residues of chemisorption of the two reactants. If competition for adsorption on the same sites is considered, this leads to an inhibiting term in the partial pressure of at least one of the reactants. That formalism thus allowed to render account for that unique feature that differentiates heterogeneous kinetics from homogeneous kinetics: a negative value of the order characteristic of the partial pressure of one of the reactants in the overall kinetic equation.

For decades, this concept of chemisorption leading to the formation of active intermediates on the surface of the solid has been used by the specialists of heterogeneous catalysis to analyse and interpret kinetic data.

During about a period of half a century, some of the basic ideas of the chemisorption process received some improvements. Many of them are based on the results provided by chemisorption studies showing that, in a general way, the surface of a metal does not behave as homogeneous and a series of causes for the heterogeneity of the surface has been developed, both on "a priori heterogeneity" and on "induced heterogeneity".

Others, taking such heterogeneity into account thus replaced the Langmuir isotherm. Let us remember the work published by Temkin [19,20] and Roginskii [21]. As an example, this has been successfully applied at first in the kinetic studies of ammonia synthesis [22].

On the other hand, Sir Hugh Taylor [23,24] introduced the concept of an "active site" not necessarily confounded with the "chemisorption site" and present on the surface in much more restricted amounts.

Some weakness anyway remained in all these analyses:

- The first one results from the assumption that a given surface radical intermediate in the reaction scheme needs only *one* site for adsorption.
- The second one is associated with the replacement, in a general way, of the steady-state assumption of the concentration of the active intermediates as introduced by Bodenstein by the equilibrium situation of the same steps. As remembered by Boudart [25], the following treatment is thus applied:
  - A reasonable scheme, composed of a succession of elementary steps is written.

○ One of these steps is considered as being rate determining (r.d.s.).

○ All steps following the r.d.s. are not significant for the overall kinetics.

○ The steps preceding the r.d.s. are at equilibrium.

This method of analysis of kinetic data has been applied to results obtained in a "flow reactor" under steady-state conditions of all characteristics, including catalytic activity for many years. During the first half of the 20th century, catalysis received most attention as seen from the gas phase. Recognised as being governed by the kinetics of the catalytic reaction, it remains that the most important features take place on the surface of the catalyst, which, in practice, is located in what has been called for decades "the black box".

In the 1960s, more attention started to be paid to the surface, and the structure of the catalyst. Correlations started to be established between the surface structure and the catalytic properties and led namely Boudart to introduce *the concepts of demanding character and of facile character of catalytic reactions*. In the same period, the development of the vacuum techniques allowed the study of metal surfaces by various physical techniques. Much hope was put on the information concerning the characteristics of surfaces. Many very interesting results were obtained on the characterisation of metal surfaces and provided a lot of information important for catalysis. Correlation between the activity for "demanding reactions" as compared to that for "facile reactions" [26] (Boudart) could be made with some surface default [27] (Somorjai).

In the case of catalytic reactions presenting essentially one possible product, and thus, no possibility of selectivity between different reaction routes, interesting information concerning the nature of the active intermediates could be obtained from surface science type experiments. Let us mention as examples the contribution to the determination of the reaction mechanism of ammonia synthesis by Ertl [28]. The dynamic behaviour of CO oxidation by O_2, explaining the observed kinetic oscillations that the reaction exhibits, constitutes certainly another example of the interesting information that the surface science techniques can provide [27,28]. Anyway, most of the physical techniques in surface science used involve electrons, imposing to work under relatively low-pressure conditions (generally below 10^{-8}–10^{-10} atm). In many important reactions, essentially those involving H_2,

like hydrocarbon transformations (hydrogenation, dehydrogenation, isomerisation, cyclisation, hydrogenolysis etc.) and like the synthesis from syngas reaction, the catalytic properties of the surface of the material used as catalyst are strongly dependent on the nature and coverages resulting from the interaction of the gaseous reactants with the initially bare surface. As these coverages and their nature are strongly dependent on the working conditions of pressure and temperature, the surface existing under real catalytic conditions (1–100 atm) is generally completely different from the one existing below 10^{-8} atm [29–31].

Kenzi Tamaru was within the first to draw the attention on the *importance of the surface of the catalyst in its catalytically working state*. In an important paper published in 1964, he extensively developed his statement that "*the most important properties of a catalyst are not those of a bare surface, but those of the surface in its catalytically working state.*" He insisted on the fact that the surface is not necessarily the same as that existing under other conditions (pressure, temperature etc.).

In a general way, metallic catalysts undergo a final reduction in situ before use.

It is well known in the industrial application of catalysis that, after the reduction procedure, a catalyst needs to be treated by the flowing gaseous reactants for a period of time, before steady catalytic properties are reached. This is then called the "activation procedure".

The phenomena measured in a laboratory reactor during that period (that is from the time where the flux of one of the reactants starts to flow in, till the time steady properties are measured) correspond to what is called "chemical transient kinetics".

In the following parts of this paper, we will review reasons of inadequacy of steady-state kinetic studies, choosing as an example the hydrogenolysis reaction of alkanes. Important difficulties resulting from the application of the above-mentioned treatment to steady-state kinetic data are analysed.

In Section 3, kinetic studies, still conducted under steady-state conditions, but using hydrogen for hydrogenolysis in the form of its stable isotope D_2, are discussed. This work leads to the introduction of the formalism associated with multisite adsorption [29–31].

This concept is rather different from that of "ensemble" in the sense of Ponec and Sachtler [32]. This multisite concept introduces in the kinetic equation of an elementary step a coverage surface function making the dependence of the rate of that elementary step on the partial pressure of one of the reactants and to the temperature to be of the same type as those measured on the rate of the overall catalytic reaction rate.

Section 4 will be devoted to a general introduction to transient kinetics, and more specifically to chemical transient kinetics [33].

Two very different extreme cases may be distinguished concerning the steady-state surface:

1. It is rather similar to the initial surface.
2. It is very different from the initial surface.

Experimental conditions needed for a quantitative analysis of transient kinetic data are presented and discussed.

Sections 5 and 6 are devoted to the application of the chemical transient method to two model systems.

In Section 5, hydrogenolysis of ethane under low-pressure conditions allows to exemplify the case where the steady active surface is rather similar to the starting surface.

In Section 6, the CO–H_2 reaction on a Co–Cu based catalyst provides a system where, in opposition to the preceding one, the active surface is completely different from the starting one.

2. Deficiencies of steady-state kinetics

The inadequacy of the classical analysis of steady-state kinetics is deduced here from the analysis of one of the most extensively studied model reactions, which is also one of the most highly demanding one: *ethane hydrogenolysis* [34]. This reaction is in general, on metal catalysts, characterised by an important inhibiting effect in hydrogen. Negative orders α as large as -2.5 [35,36] in the formal rate equation

$$R_H = k_H (p_{H_2})^{\alpha} (p_{HC})^{\beta} \tag{2.1}$$

are mentioned in the literature.

The first attempt to render an account of the negative order has been published by Cimino et al. [37] in 1954. This analysis is based on an Hinshelwood–Langmuir

(H–L) type mechanism. They have applied the classical treatment. The chemisorption of the alkane results from the breaking of a C–H bond. This assumption results from the following observation: the catalytic exchange of hydrogen between an alkane and D_2 takes place generally at a much lower temperature than that at which hydrogenolysis is observed on the same catalyst. The hydrocarbon radical formed on the surface of the metal progressively dehydrogenates, till the formation of a radical able to induce the breaking of the C–C bond is achieved.

In that paper, as in the numerous works published later, the r.d.s. was considered to be the one involving the breaking of the C–C bond.

All the steps preceding that r.d.s. are assumed to be at equilibrium. In that work, the equilibrium of the successive steps preceding the r.d.s. was written as

$$C_2H_6 + S \leftrightharpoons (C_2H_x)_a + (6 - \tfrac{x}{2})H_2 \tag{2.2}$$
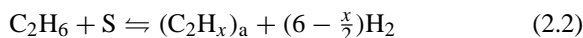
where S represents a free site. Neglecting the surface coverage by other radicals than the most abundant surface intermediate (MASI), here $(C_2H_x)_a$, and using the hypotheses of Langmuir for chemisorption, we get

$$k_1 p_{C_2H_6}(1 - \theta_{C_2H_x}) = k_1' \theta_{C_2H_x}(p_H)^{(6-(x/2))} \tag{2.3}$$

The r.d.s. was written in that paper as

$$(C_2H_x)_a + H_2 \rightarrow CH_y + CH_z \tag{2.4}$$
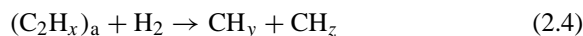
Finally, what we get is that the rate of the hydrogenolysis reaction is

$$R_H = k(p_{C_2H_6})^n (p_{H_2})^{1-n(6-(x/2))} \tag{2.5}$$

In this analysis, the inhibiting term in hydrogen pressure is thus related to the degree of dehydrogenation of the MASI. This kind of analysis has been applied by many authors [29–31], sometimes applying some modifications in the writing of the r.d.s., namely as the role of hydrogen is concerned. This induces slight modifications in the associated degree of dehydrogenation of the MASI to render account of a similar value of the order.

Such a reaction scheme, relating thus the inhibiting term in hydrogen to the degree of dehydrogenation of the MASI, has still been used even in the analysis of ethane hydrogenolysis using the transient kinetic method [38].

This type of treatment has anyway already received some criticism [33].

We would like to briefly remember here the two points of the criticisms that we consider as being the most important:

1. When the hydrogen pressure effect is measured in a wide pressure range (more than two orders of magnitude), the inhibiting term is not constant, i.e. it increases with the hydrogen pressure.

   On the other hand, when the hydrogen pressure dependence is measured at different temperatures, the order affecting the hydrogen pressure in the hydrogenolysis reaction becomes more negative when the temperature is lower.

   In the framework of an analysis where the importance of the negative order affecting the hydrogen pressure is related to the degree of dehydrogenation of the MASI, *the surprising conclusion is that the MASI is more dehydrogenated the higher the hydrogen pressure or the lower the temperature*!

2. The isotopic exchange between ethane and D_2 is characterised by a hydrogen inhibiting term in the H_2 pressure of the same type as the hydrogenolysis reaction [29–31]. We have already drawn the attention to the fact that, when exchange is measured [29–31], one needs, in order to measure only the exchange, to work at the chemical equilibrium of the system, and namely at adsorption–desorption equilibrium.

   The exchange rate may thus be considered as a trick to measure the adsorption rate at adsorption–desorption equilibrium.

   The inhibiting term in H_2 pressure needs then to be found in the adsorption rate equation of the alkane, and not the degree of dehydrogenation of the MASI.

3. Difference between homogeneous and heterogeneous kinetics: multisite adsorption

The effect of multisite adsorption on the writing of the rate equation of methane adsorption has been developed and analysed in the study of the isotopic exchange between methane and deuterium [39]. In this paper, the necessity of finding the inhibiting term in H_2 pressure in the adsorption rate equation is analysed in detail.

An attempt to render account for that inhibiting term has been published by Kemball [40] in 1966 on the basis of competition between H_2 and CH_4 for adsorption on the same sites. In this analysis, the concept of one chemisorbed radical on one chemisorption site is applied. This, of course, leads this author to conclude by admitting the inadequacy of such a model to render account for the important inhibiting term in H_2 pressure as measured.

In an extensive study of chemisorption on a series of metals in the form of evaporated metal films [41,42], it appears that the number of hydrogen chemisorption sites may be related to the number of metal surface atoms. In the chemisorption of methane, the first radicals resulting from the progressive dehydrogenation of the CH_4 molecule (CH_3 and CH_2) cover more than one chemisorption site as defined by the surface metal structure. This was first mentioned in 1963 [43]. Here, we would like to insist on the fact that this coverage of several sites by only one radical as in our model does not imply a multibonding of that radical to the surface [29–31]. This is thus in opposition to the model introduced by Martin [44]. Anyway, the formalism expressed in the rate equation is similar in both models.

The most important feature is that the use of such a model induces the appearance, in the rate equation of the elementary step of adsorption, of a function of the type θ_s^z, where θ_s represents the fraction of the free potential sites involved in the definition of the active site [29–31].

In the case of a surface essentially covered by hydrogen, this relation is written as

$$\theta_s = (1 - \theta_H) \tag{3.1}$$

If the chemisorption site for the chemisorption of an alkane to proceed is composed of an ensemble of z potential sites, as defined by the surface metal structure and assimilated to the hydrogen chemisorption site, the adsorption rate equation is then

$$R_a = k_a p_{HC} \theta_s^z \tag{3.2}$$

$$R_a = k_a p_{HC} (1 - \theta_H)^z \tag{3.3}$$

We have called the coverage function $G = \theta_s^z = (1 - \sum \theta_i)^z$ [29–31].

Eqs. (3.2) and (3.3) are to be compared to the formal rate equation of the same step:

$$(R_a)_{exp} = (k_a)_{exp} p_{HC} p_{H_2}^\alpha \tag{3.4}$$

The association of the hydrogen pressure effect, expressed by α, with the hydrogen coverage function $G = (1 - \theta_H)^z$ leads one to define α_G as

$$\alpha_G = \frac{\delta \ln G}{\delta \ln p/p_0} \tag{3.5}$$

Through the hydrogen adsorption constant, the function G contains a temperature dependence also, that may be written as

$$E_G = -R \frac{\delta \ln G}{\delta 1/T} \tag{3.6}$$

It has further been shown [45] and verified experimentally [46] that there is a correlation between α_G and E_G through the thermodynamics of H_2 adsorption:

$$E_G = -\alpha_G Q_{iso} \tag{3.7}$$

where Q_{iso} is the local isoteric heat of adsorption of hydrogen.

We have developed this formalism at the occasion of the study of the CH_4–D_2 exchange. It was of course interesting to study the system C_2H_6–D_2 where in addition to exchange, hydrogenolysis can also take place. This exchange has already been studied in the 1950s [47] by Kemball on metal films but under a hydrogen pressure range larger than 10 Torr. It happens that, in that pressure range, the temperature at which hydrogenolysis takes place is much higher (sometimes up to 100°C higher) than that at which exchange is already measurable. Exploring a much larger pressure range in hydrogen, it has been possible to find pressure conditions where, at the same temperature, one may go from conditions where hydrogenolysis is more important than exchange to conditions where exchange is more important than hydrogenolysis. Of course, there exists an intermediate H_2 pressure value where both exchange and hydrogenolysis proceed at an observed same rate [45].

As an example, results obtained on rhodium films at 50°C [48] are reproduced in Fig. 1. The H_2 pressure for which the two rates (hydrogenolysis and exchange) are equivalent is displaced by an important factor with temperature. This can be seen in Fig. 2 presenting results at 20°C, as compared to Fig. 1.
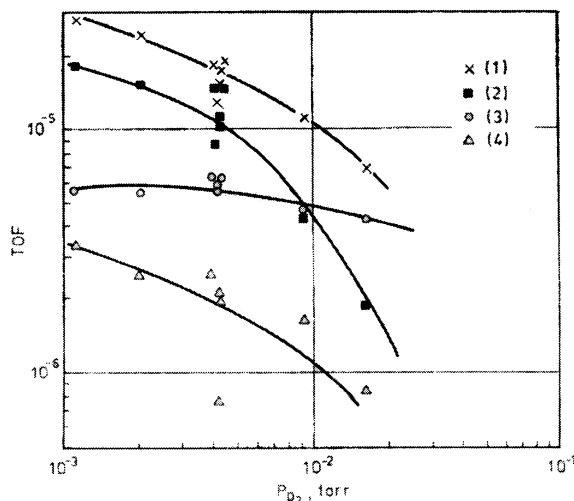

Fig. 1. C_2H_6–D_2 reaction at 50°C on Rh: (1) rate of adsorption of C_2H_6; (2) rate of formation of CH_4; (3) rate of multiple exchange; (4) rate of single exchange.

The extrapolation to the H_2 pressure range above 10 Torr met with a detailed analysis [49] and shows the consistency between our results in the low-pressure range and the difference in temperature where hydrogenolysis and exchange proceed as observed previously [47] at higher pressure.

The adsorption rate of ethane thus received more attention [50]. It immediately appeared that the only
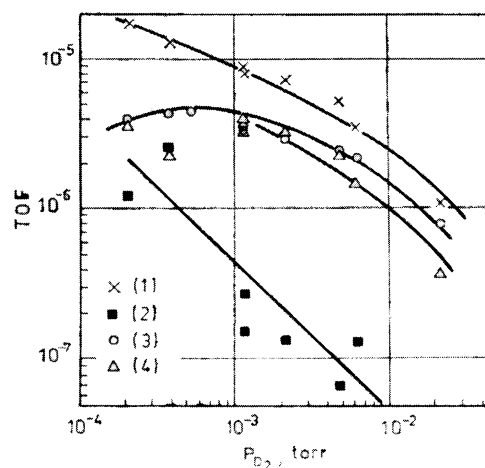

Fig. 2. C_2H_6–D_2 reaction at 20°C on Rh: (1) rate of adsorption of C_2H_6; (2) rate of formation of CH_4; (3) rate of multiple exchange; (4) rate of single exchange.
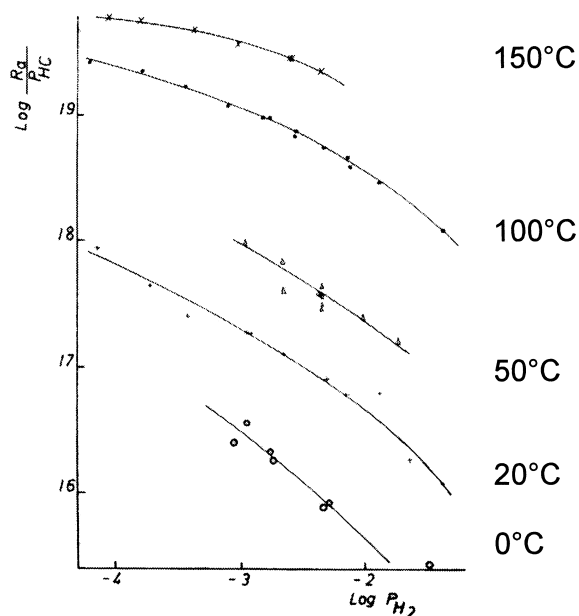
Fig. 3. Adsorption rate of C_2H_6 (R_a) on Rh as a function of H_2 pressure.

Fig. 4. C_2H_6 adsorption: rate according to reaction (3.8).

adsorption rate of ethane presents the same type of dependence towards H_2 pressure and towards temperature as hydrogenolysis does. Fig. 3 represent the rate of ethane adsorption per unit ethane pressure at negligible hydrocarbon coverage on the surface. One question anyway remained: does the adsorption step proceed by an H–L type mechanism:

$$RH + zS \rightleftharpoons R_a + H_a \qquad (3.8)$$

or by a reactive mechanism such as Rideal type mechanism:

$$RH + H_a + zS \rightleftharpoons R_a + H_2 + wS \qquad (3.9)$$
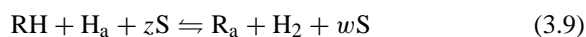
The results of Fig. 3 are plotted according to the rate equation parameters derived from the H–L mechanism (Fig. 4) and from the Rideal mechanism (Fig. 5).

It is clearly evident that this analysis leads one to favour the Rideal type mechanism [51] where the surface function G_R is thus of the type

$$G_R = \theta_H (1 - \theta_H)^z \qquad (3.10)$$

In the particular case remembered here, the value of z is of about 8. For methane, it had been admitted to be of about 6–7 [51].
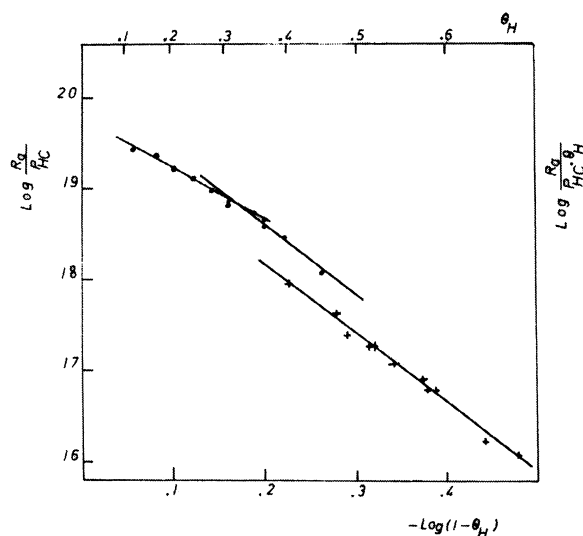
The importance of the surface coverage function appears in Fig. 6, where the values of the coverage functions G_R and G_D are plotted as a function of θ_H for different values of z. G_D is the coverage function in the case of an H–L type reaction mechanism.

The values of the two functions G_D and G_R do differ at θ_H values lower than 0.5, but become more
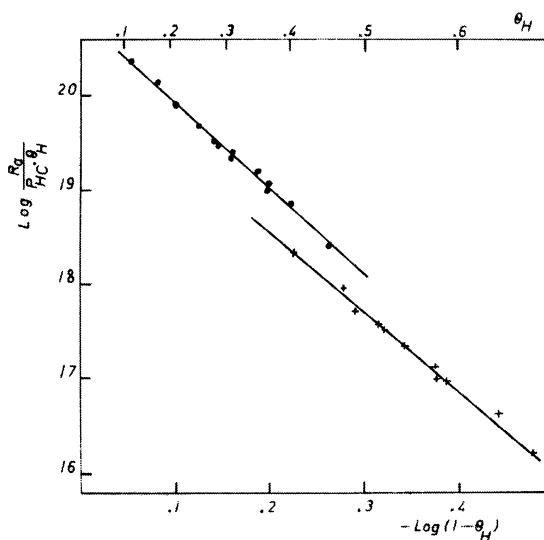

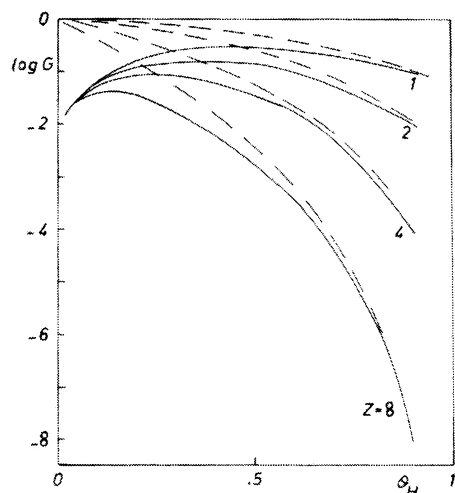Fig. 5. C_2H_6 adsorption: rate according to reaction (3.9).

Fig. 6. Variation with H coverage (θ_H) of the functions $G_D = (1 - \theta_H)^z$ (dashed line) and $G_R = \theta_H(1 - \theta_H)^z$ for some values of z.

and more equivalent the more the θ_H value is above 0.5. We would here like to insist on the very important variation of G for rather small variations of the values of θ_H in the 0.5–1 range as soon as the value of z is larger than 4.

As this function contains the hydrogen coverage, it also contains, through the hydrogen adsorption–desorption fast phenomena, a dependence towards the H_2 pressure and the temperature.

These dependencies have been extensively analysed [29–31], and presented in Eqs. (3.5) and (3.6). This analysis leads to *the important conclusion* that in heterogeneous catalysis *the rate equation of an elementary step*, and not only that of the adsorption step, as presented here [51], may contain a pressure dependence towards one of the reactants and a temperature dependence presenting variations of their values with variations of the experimental conditions of the same type and of the same importance as those characterising the global reaction rate. This represents a fundamental difference with homogeneous kinetics where for elementary steps, order and stoichiometry are confounded and thus have constant values. By combination of reasonable assumed elementary steps, one tries to reproduce the measured order of the global reaction rate characterising the pressure dependencies towards one of the reactants. Let us

remember that the classical procedure of analysis of kinetic measurement obtained in catalysis at steady state is based on the same assumption. The classical treatment is thus often inadequate and there is a need for direct information concerning elementary steps.

Several procedures exist. One is to work with labelled molecules, and preferably with stable isotopes.

Another is to try to exploit the chemical transient kinetic phenomena following a positive or a negative step in the partial pressure of one of the reactants.

We have extensively remembered facts and ideas already published [29–31,33,41,42,51] in order to use it as support to stress the importance of chemical transient kinetic studies as compared to only steady-state kinetic studies.

4. The transient kinetic method

Already in 1939, Wagner and Hauffe introduced the method [52]. It was only about two decades later that Tamaru started applying it, who recognised within the various interesting features the possibility of deriving from transient kinetics information concerning the adsorption of the reactants during surface catalysis [53].

From that time, the method has been applied to several reactions like hydrocarbon hydrogenolysis and isomerisation [54–59] and mostly to the methanation reaction from CO–H_2 reaction, as will be more analysed extensively in Section 6 of this paper.

A series of reviews on transient kinetics have been published. Let us remember the works by Kobayashi [60–61], Wagner [62], Bennet [63], Happel et al. [64], Tamaru [65].

The transient method consists of the analysis of the composition of the gas flowing out a reactor during the period of adaptation of a catalytic system to a perturbation of one of the parameters controlling the kinetics of the heterogeneous catalytic reaction.

The temperature is an important parameter governing the kinetics of a reaction. Anyway, it is practically quite impossible to impose temperature variations of a catalytic system fast enough to induce what could be a step of temperature as compared to the rate of adaptation of the catalytically reacting system in most cases.

On the other hand, a step in the gas-phase composition is practically possible.

Several types of such variations may be applied as given in the following.

4.1. Isotopic composition

In some reactions like the CO–H_2 reaction or ammonia synthesis, when steady-state conditions have been reached, the inlet of one of the reactants of natural isotopic composition is replaced by a quantitatively equal inlet value of the same reactant, but labelled with a stable isotope like C^{13}, O^{18} or N^{15}.

We do not treat this case here.

4.2. Chemical composition

A step, positive or negative, of the partial pressure of one of the reactants is applied by abruptly changing the value of the inlet flow rate of one of the reactants.

This may be realised in the form of pulses: that is a positive step, followed by a negative one after some period of time, but without reaching steady state.

In this paper, we analyse and exemplify the case where a step of the partial pressure of one of the reactants is applied from zero to a steady-state value. After steady-state conditions have been reached, the inlet of that reactant is turned off and the relaxation of the system is measured. In the examples developed hereafter, the first part is called "build up transient" and the second one "back transient".

Such transient studies are most fruitful, if surface composition variations may be derived from the variations of the gas-phase composition at the outlet of the flow reactor.

This implies the following during the transient phenomena:

1. The behaviour and composition of the surface of the catalyst are identical in each point. It is thus clear that the reactor must behave as closely as possible to a well-mixed reactor, presenting neither composition nor temperature gradient.
2. The transport from the outlet of the reactor to the analytical device is of the plug-flow type, in order to avoid any induction of distortion of the gas composition during the variations of the gas-phase composition.
3. Use of a mean for continuously measuring all variations of volumetric flow rate out of the reac-

tor. This may be achieved by the use of an inert internal standard.

Within the limitations characteristic of the study of such transient kinetics, let us mention two main causes:

1. A "step" of the gas-phase composition in the reactor is not a perfect one. One may, if the transport in the inlet pipes is of plug flow type, impose a real step of the inlet flow rate of one of the reactants.

    Let us mention that this is best realised by switching from the inlet of an inert gas to the inlet of the second reactant in order to minimise any abrupt variations of the total volumetric flow rate.

    But the reactor has a dead volume that needs to be filled or to be emptied. If the reactor behaves sufficiently well as a well-mixed reactor, this phenomenon is characterised by a time constant τ_g.

    In the practical case of a laboratory type flow microreactor where the dead volume presents a lower limit value in the range of $1\ cm^3$ and of volumetric flow rates in the maximum range value of $1\ cm^3/s$, the value of τ_g may be as low as 1 s, which represents a limit value.

    It is clear that, in order to measure the chemical transient in the catalytic system, this system needs to exhibit transient periods that are long as compared to τ_g.
2. Another limitation is associated with the analytical system.

    If the chemical reacting system is simple enough, mass spectrometers (MS) able to scan and record the necessary number of masses in delays compatible with the requirements associated with the rate of composition variations exist. Such a mass spectrometer presents the advantage of providing the rough data "on-line", and thus, allows applying an adequate feedback.

    If the chemical system is not simple enough, an analysis by gas chromatography (GC) is needed, involving a fast sampling system, which is presently available in the form of a multiloop-sampling valve. The inconvenience of such an analytical system is the lack of information "on-line".

Further more, if the reacting system contains labelled molecules *and leads* to a complex composition of products, an expensive high performance GC-MS is needed.

4.3. The determination of the net adsorption–desorption rate

The value of this net adsorption–desorption rate is determined as follows.

The general equation of a dynamic flow reactor is

$$\left(\frac{dn_g}{dt}\right)_i = \left(\frac{dn_i}{dt}\right)_i - \left(\frac{dn_o}{dt}\right)_i + \left(\frac{dn_d}{dt}\right)_i - \left(\frac{dn_a}{dt}\right)_i \quad (4.1)$$

where $(dn_g/dt)_i$ is the variation with time of the number of moles of component i in the gas phase of the reactor, $(dn_i/dt)_i$ the molar flow rate of component i entering the reactor, $(dn_o/dt)_i$ the molar flow rate of component i going out of the reactor, $(dn_d/dt)_i$ the molar desorption rate of component i and where $(dn_a/dt)_i$ is the molar adsorption rate of component i.

The net adsorption–desorption rate of component i is

$$R_i = \left(\frac{dn_d}{dt}\right)_i - \left(\frac{dn_a}{dt}\right)_i \quad (4.2)$$

which is also equal to

$$R_i = \left(\frac{dn_o}{dt}\right)_i - \left(\frac{dn_i}{dt}\right)_i + \left(\frac{dn_g}{dt}\right)_i \quad (4.3)$$

which may also be written as

$$R_i = \frac{N_a}{RT} p_i \left(\frac{dv}{dt}\right)_{out} - (\phi_i)_{in} + \frac{N_a}{RT} V_r \left(\frac{dp}{dt}\right)_i \quad (4.4)$$

where p_i is the partial pressure of component i as measured at the outlet of the reactor, $(dv/dt)_{out}$ the instant volumetric flow rate out of the reactor as derived from the measured initial volumetric flow rate and the variations of the inert gas pressure used as internal standard, $(\phi_i)_{in}$ the flow rate into the reactor of component i, V_r the volume of the reactor and where $(dp/dt)_i$ is the instant variation of the partial pressure of component i at the outlet of the reactor.

As an example in a very simple case, that is the isotopic exchange between CH_4 and D_2 [66], Fig. 7 represents theoretically the phenomena as observed on a precious metal surface. Steady-state conditions of D_2 flow in the reactor containing the catalyst are established at a constant given temperature.

The build up transient starts by establishing the CH_4 flow. After steady-state conditions are attained concerning the CH_4 (CP_4 with P for protium) and the sum of the deuterated methane partial pressures (CP_xD_{4-x}), the methane inlet is turned off. The dashed area represents the amount of methane, and thus, of carbon, which did not come out of the reactor, and which thus stays on the surface:

Using the equation

$$(\theta_c)_t = \int_0^1 \left(\sum R_i\right) \quad (4.6)$$

It is possible to calculate at any moment what the coverage is. This of course may be conducted as well during build up as during back transient. Of course, such a treatment has some meaning only in the case of a gradientless reactor. It is then possible to transform the rough data, expressed as a function of time, in a dependence in its variations with coverage.
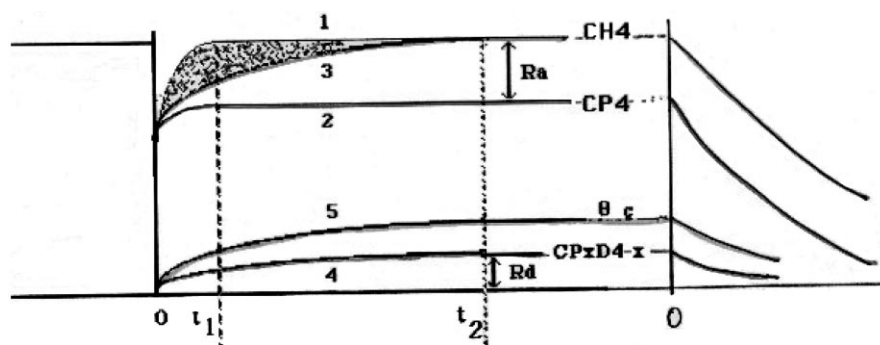
Two extreme cases are exemplified hereafter.

Fig. 7. Transient experiment of a CH_4–D_2 exchange reaction.

In the first one, the coverage of active intermediates as formed during the transient experiment is very small and the catalytic properties of the surface remain quite constant all along the transient experiment.

In the second one, the surface composition is completely modified during the transient experiment, associated with important variation of the catalytic behaviour of the surface.

In the first case, the surface behaves as homogeneous during the transient and the various rates present an exponential variation.

We may then thus write, for a build up transient

$$R_\propto - R_t = \exp\left(-\frac{t}{\tau_s}\right) \tag{4.7}$$

where $R_\propto$ is the rate of formation of any of the products at steady-state activity, and R_t is the same rate at any time t.

τ_s is the time constant characteristic of the build up of the surface intermediate implied in the formation of the considered product to reach steady-state coverage.

In the case of a back transient, the rate of appearance of each of the products obeys the following equation:

$$R_t = R_\propto \exp\left(-\frac{t}{\tau_s}\right) \tag{4.8}$$

When such equations are obeyed, we may also write for the surface intermediate responsible for the appearance of that species in the gas phase that

$$\frac{\mathrm{d}\theta_i}{\mathrm{d}t} = v_i \theta_i \tag{4.9}$$

where v_i contains the temperature dependence as well as the pressure or coverage dependence of the permanent reactant.

The following is thus derived:

$$v_i = \frac{1}{\tau_s} \tag{4.10}$$

In the equation

$$(R_i)_\propto = v_i \theta_i \tag{4.11}$$

R_i is to be expressed in TOF.

As we have developed above, values of τ_s smaller than τ_g are to be avoided. This means that one may only study systems where $\tau_s > \tau_g$. As in practice the lower limit for τ_g is of about 1 s, systems to be studied by the transient method have to be characterised by a value of τ_s larger than 1 s, or values of v smaller than 1 s (Table 1).

On the other hand, if steady state is to be reached within reasonable working delays, τ_s needs to be smaller than 10^4 s, or v larger then 10^{-4} s.

The corresponding coupled values of $R_\propto$ and θ associated with values of v ranging from 10^{-4} to 1 s (grey part) need to be characteristic of the catalytic system in order for one to be able to apply chemical transient kinetic studies.

As simultaneously $R_\propto$ and θ are dependent on the total pressure under which the catalytic reaction is conducted, the possibility of applying the chemical transient method also depends on the pressure range used.

Values of R and v depend much more on the total pressure than θ, which is most generally in the range 10^{-3}–10^{-1} in the case of a surface that keeps its catalytic properties during a chemical transient. It thus clearly appears that, for transient kinetic studies to be measurable, there is an upper limit in the pressure of the reactant that is included in v, which is characteristic of the frequency factor affecting the r.d.s.

Table 1
Values of v according to Eq. (4.10), in the logarithmic form

$\log \theta$	$\log R$									
	−8	−7	−6	−5	−4	−3	−2	−1	0	1
−4	−4	−3	−2	−1	0	1	2	3	4	5
−3	−5	−4	−3	−2	−1	0	1	2	3	4
−2	−6	−5	−4	−3	−2	−1	0	1	2	3
−1	−7	−6	−5	−4	−3	−2	−1	0	1	2
0	−8	−7	−6	−5	−4	−3	−2	−1	0	1

It becomes clear, as will be exemplified in the study of C_2H_6–D_2 (Section 5), that if a chemical transient measurement can be made in a rather low-pressure range (10^{-3}–1 Torr), it becomes quite impossible in the atmospheric pressure range and above.

We will show that, in the other more complex case (CO–H_2, Section 6) where the behaviour of the catalyst changes during a transient, there also appears a limit range of pressure where the chemical transient method may be applied.

5. The C_2H_6–D_2 reaction under transient conditions

This study concerns the case where the coverage of active intermediates reached at steady state is very small and thus where the properties of the working surface are nearly the same as those of the initial surface. Let us remember that steady-state conditions are established for the deuterium flow rate, and thus, the D_2 pressure before starting.

Transient kinetic studies have been realised on the C_2H_6–D_2 under the same conditions where steady-state measurements have been conducted and presented in Section 3 (Figs. 1 and 2).

On the right-hand side part of Figs. 1 and 2, it appears clearly that most of the adsorbed ethane molecules desorb in the form of multiply-exchanged molecules and that the rate of hydrogenolysis is much smaller. The classical concept of the breaking of the C–C bond being rate determining and associated with the steps preceding the r.d.s. being close to equilibrium applies. At the point where the ethane exchange rate is equal to hydrogenolysis rate, it is more difficult to define an r.d.s.

We present hereafter the results of a transient kinetic study under conditions close to those corresponding to that point [48], that is a D_2 pressure of 4.3×10^{-3} Torr, that of ethane being about 10 times smaller. Let us draw the attention to the fact that, under these pressure conditions, we are in the Knudsen region and diffusion of gases is directly associated with the conductance of the reactor. As these measurements were made in a UHV system, the conductance of which is more than 10 l/s and the average volumetric flow rate out of the reactor is lower than 0.05 l/s, one may consider that the system behaves as a well-mixed one. As the volume
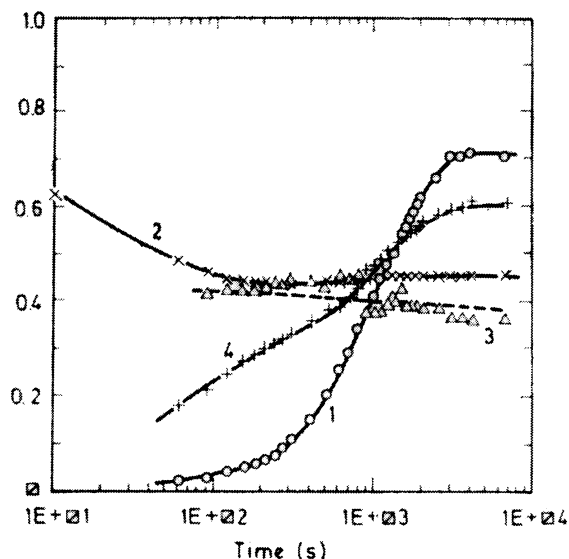

Fig. 8. C_2H_6–D_2 build up transients at 50°C on Rh — variation of pressures with time: (1) CD_4 — 2×10^{-5} Torr; (2) C_2P_6 — 10^{-4} Torr; (3) C_2P_5D — 5×10^{-6} Torr; (4) C_2D_6 — 10^{-5} Torr.

of the reactor is of the order of 2 l, the time constant τ_g is thus in the range of 40 s.

The variations of the partial pressure of the hydrocarbons flowing out of the reactor with time measured in a build up experiment are presented in Fig. 8.

The equivalent graph of the pressure variations in the back transient following the build up after it had reached steady state is given in Fig. 9. Using Eq. (4.6), it is possible to calculate the instant in–out mass balance in carbon atoms ($d\theta_c/dt$) and the variations of the mean coverages in carbon atoms by integration of the instant in–out mass balance with time. These results, expressed in terms of θ_c, are shown in Fig. 10. The values of θ_c are calculated as the number of carbon surface atoms per hydrogen chemisorption site.

As far as the build up is concerned, Fig. 11 represents the variation with time (in the log form) of the rate of light ethane C_2P_6 (P for protium) adsorption (R_a), of the rate of formation of the deuterated hydrocarbons (single exchanged ethane (R_{SE}), multiply-exchanged ethane (R_{ME}) and methane (R_H), resulting from hydrogenolysis) in terms of TOF.

An equivalent treatment applied to the back transient and plotted in Fig. 12 as rates and θ_c values in the form of log as a function of t shows that the desorption phenomena obey an exponential decay very well.
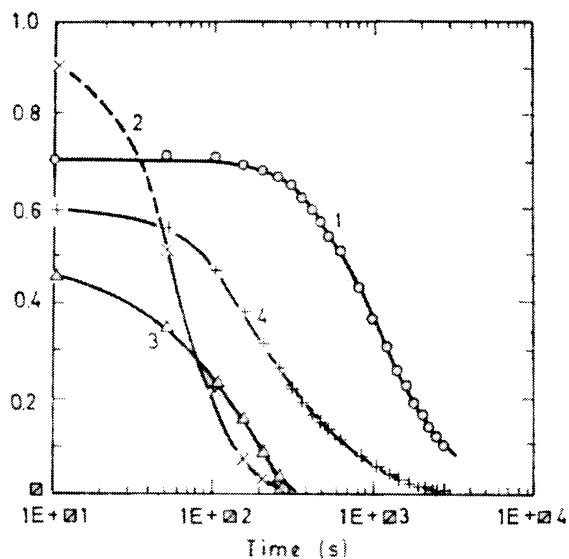
Fig. 9. C_2H_6–D_2 build up transients at $50°C$ on Rh — variation of pressures with time: (1) CD_4 — 2×10^{-5} Torr; (2) C_2P_6 — 10^{-5} Torr; (3) C_2P_5D — 5×10^{-6} Torr; (4) C_2D_6 — 10^{-5} Torr.

The information obtained in the very first part of that back transient (Fig. 13) shows that the rate of single exchange variations follows the variations of light ethane pressure, both variations characterised by a value of $\tau \cong 60 \, \text{s} = \tau_g$. This supports the model we have proposed for the single exchange reaction. The adsorption site [50] is composed of a hydrogen-chemisorbed atom associated with an ensemble of z "potential" sites as defined by the structure of the metal surface. Adsorption then takes place
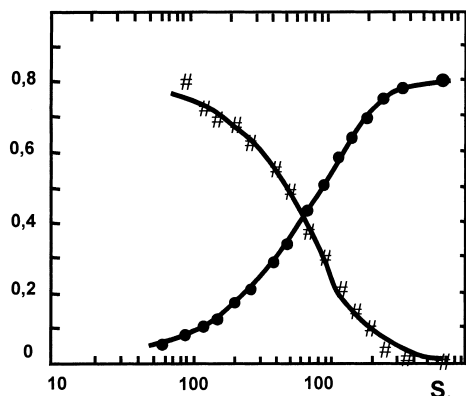

Fig. 10. C_2H_6–D_2 build up transient. Variations of $d\theta_c/dt$ — 2×10^{-5} (#) and θ_c — 2×10^{-2} (●) with time.
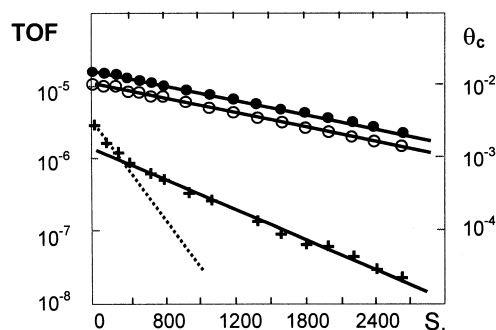
Fig. 11. Variations with time of R_a — 2×10^{-5} (×), R_{SE} — 2×10^{-6} (★), R_{ME} — 4×10^{-6} (+), R_H — 10^{-5} (○).
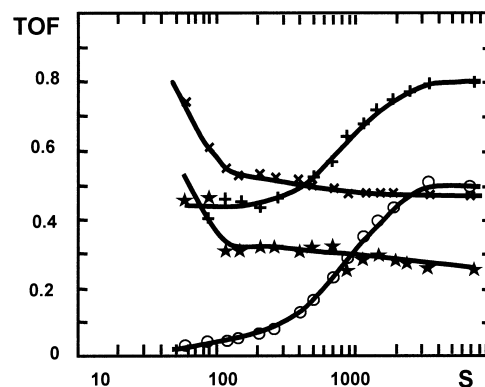

Fig. 12. C_2H_6–D_2 back transient. Decay of θ_c (●), R_H (○) and R_{ME} (+) with time.

through the formation of an associative complex with the hydrogen adsorbed atom on the metal surface. As the hydrogen adsorption–desorption phenomena correspond to a very fast reaction, as measured by
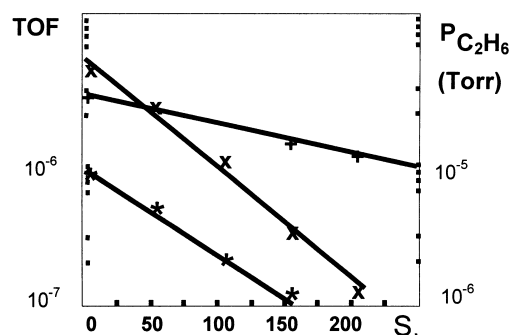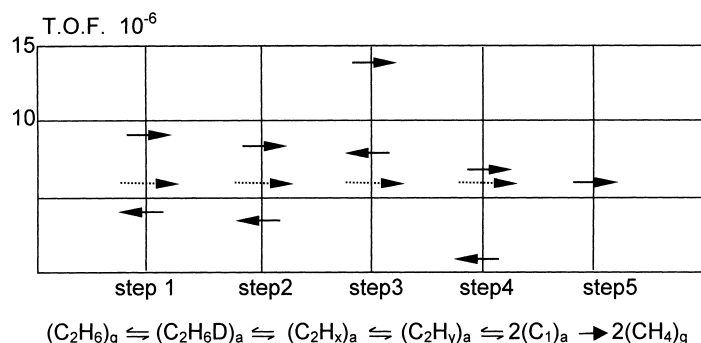

Fig. 13. C_2H_6–D_2 back transient. Decay of $P_{C_2H_6}$ (×), R_{SE} (★), R_{ME} (+) with time.

$$(C_2H_6)_g \leftrightharpoons (C_2H_6D)_a \leftrightharpoons (C_2H_x)_a \leftrightharpoons (C_2H_y)_a \leftrightharpoons 2(C_1)_a \rightarrow 2(CH_4)_g$$

Scheme 1.

the H_2–D_2 exchange, as compared to the rate of hydrocarbon adsorption reaction, the H atoms bonded to the metal surface are D atoms. The decomposition on the surface complex thus leads, and can only lead to single exchange.

This reaction scheme of the adsorption step of ethane is associated with a reaction scheme of the desorption step involving directly a hydrogen molecule and has met with extensive analysis [68]. It is written as

$$(C_2H_6)_g + H_a + zS$$
$$\leftrightharpoons (C_2H_7)_a \leftrightharpoons (C_2H_5)_a + H_2 + wS \qquad (5.1)$$
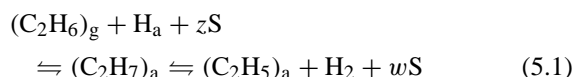
Through the term θ_s^w in the desorption rate equation,

$$R_d = k_d \theta_{C_2H_5} \theta_s^w p_{H_2} = k_d \theta_{C_2H_5} p_{H_2}^{\alpha_d} \qquad (5.2)$$

The measured H_2 pressure dependence α_d presents in the low H_2 pressure range a value approaching 1 which is in agreement with a value of w (Eq. (5.1)) much smaller than z [67]. This value of α_d progressively decreases with increasing the D_2 pressure [68].

A very important conclusion to keep in mind is the H_2 pressure dependence of the value of τ_s, introducing a value of H_2 pressure making τ_s reach progressively the value of τ_g (cf. Section 4: the transient method).

This transient research work met with extensive analysis [69]. This analysis based on both the results of transient measurements and steady-state measurement combined with the use of labelled molecules (here D_2) made it possible to decompose the catalytic reaction in its successive elementary steps.

As presented in the following scheme, the direct and reverse rate of each of the successive steps as they

are at the steady state of the catalytic reaction could be calculated (Scheme 1).

Their values are represented in plain arrows. In dotted arrows appear the net value of the rate of each step, which is the difference between the direct rate and the reverse rate. This net rate is at steady state the same for each step. It clearly appears that there is no determining step.

Another important conclusion concerns the coverages. Values of total carbon coverage are obtained from in–out mass balance and give similar results in build up and back transient. Most important is that the value of the coverage derived from the use of Eq. (4.10), that relates R, θ and τ_s, leads to a carbon coverage value in good agreement with that derived from in–out mass balance [68].

Let us remember that the steady-state coverage of hydrocarbon surface intermediate is, in the concerned experiments, rather low, in the range of 1–2%; when the steady-state coverage is more important, the phenomena become more complex [29–31,33].

6. Chemical transient studies lead to a new insight in the mechanism of syngas reaction

The CO–H_2 reaction remains one of the greatest challenges in catalysis [70–75]. Although the synthesis of a very large number of organic products is allowed by thermodynamics, the simultaneous equilibrium should anyway lead to the formation of CH_4 in more than 99% of the cases. Thus, the synthesis of some particular products is a question of kinetics, and thus, a catalytic problem also.

From the time the study of the CO–H_2 began, till now, many types of mechanisms have been proposed. Among the most discussed questions in the literature are the type of adsorption [76–83], the nature of the monomer, the first carbon–carbon bond formation, and the number of sites and monomers (CO, CH_x, CH_xO_y etc.) involved ([84–94]). A large number of results are presented in the literature that are sometimes in agreement with each other and sometimes not. Anyway, the general consensus is that carbene ($=CH_2$) species are responsible for the chain growth mechanism and CO insertion for the formation of oxygenates. In all these reaction schemes, the catalyst is a metal surface.

Among the different methods involved in studying this reaction, two important types of transient experiments are presented in the literature: isotopic transients and chemical transients. In an isotopic transient, the chemical steady state of the catalytic system is not affected, thus introducing no chemical perturbation of the catalytically working surface. The relation generally used viz.

$$R_{TON} = \theta_i \tau^{-1}$$

relates the coverage of intermediates i, θ_i, that is the MASI under steady-state conditions. The CO–H_2 reaction received most attention using this type of transients ([95–104] — about methanation, [105–114] — about FT reaction). Chemical transients have not often been used for the CO–H_2 reaction, and have been mostly limited to the methanation reaction [115–117].

These two kinds of transients are complementary. Indeed, as isotopic transients keep the catalytically working surface constant, it is possible to determine quantitative values of the parameters characteristic of some elementary steps. But it is not possible to measure the effect of the coverage on the activity and on the selectivity, while this is possible with chemical transients. Reciprocally, chemical transients do not allow quantitative determinations concerning elementary steps.

The results presented here were obtained by using chemical transients.

The build up transients were realised by substitution of an He flow by a flow of CO at the same flow rate value without changing the H_2 flow. The initial time t_0 corresponds to the moment where the CO starts entering the reactor. This moment is given by the beginning of the He disappearance.

When steady state is reached, the CO flow is replaced by an He flow in order to measure the relaxation of the system. This constitutes a back transient.

The following pages aim to exemplify the richness and the amount of information that are provided by such chemical transient experiments. Furthermore, it represents a typical example of transients where the "catalytically working surface" is very different from the initial one.

6.1. The system studied

The results discussed here are a part of a work done on Co–Cu based catalysts [118–120] prepared by co-precipitation. The active surface area of this catalyst was measured by CO adsorption at room temperature and has the value of 90×10^{19} CO at./g Co–Cu.

In order to give some characteristics of the catalytic properties of the catalyst used, results of a study of the total pressure effect on the selectivity are represented in Fig. 14. At 0.1 atm atmosphere pressure of the CO–H_2 system diluted in Ar with an H_2/CO ratio of 2, only CH_4 and CO_2 are formed in equal quantities. At atmospheric pressure, hydrocarbon chains are formed in addition to CH_4 and CO_2. Under 60 bar pressure, alkanes, alkenes and alcohols are mainly formed. Typically, Fig. 14 shows that the selectivity towards CH_4 and CO_2 decreases as the pressure increases, the chain length increases as the pressure increases (α_{SF}) and alcohols are formed but only under high pressure.

The distribution of products obtained under atmospheric pressure and 60 bar obeys the Anderson–Schulz–Flory (ASF) law. Therefore, two of the important parameters of the ASF model, L_{SF} and α_{SF},
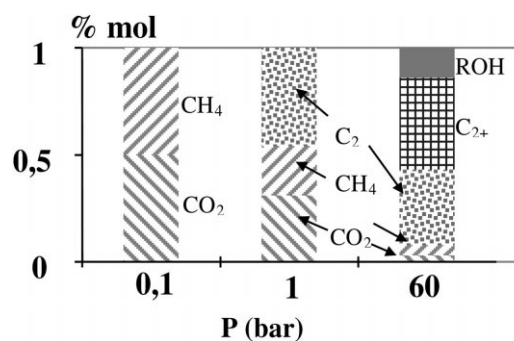

Fig. 14. Effect of total pressure on the selectivity. H_2/CO = 2. The flow is regulated in order to keep the conversion below 10%.
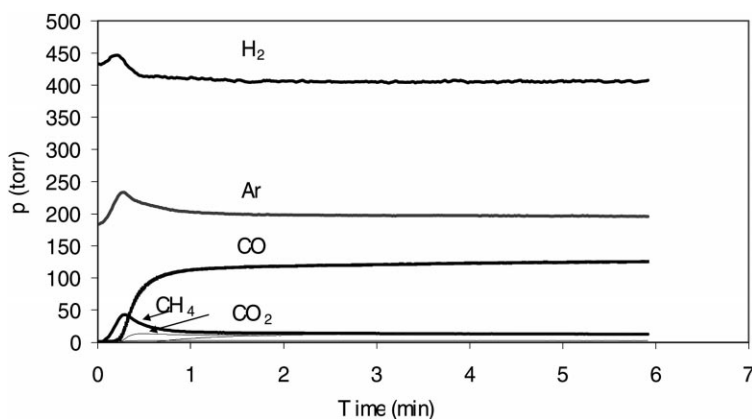
Fig. 15. Pressures as functions of time from the CO entrance in the reactor to steady state.

are used in the discussion. $L_{SF} = R_L/R_T$ and $\alpha_{SF} = R_L/(R_T + R_L)$ with R_L being the lengthening rate and R_T the termination rate.

6.2. Results from a build up of the surface

The crude results consist of the evolution of the partial pressures recorded at the outlet of a laboratory flow microreactor by a quadripolar mass spectrometer as a function of time during the transient period. The geometry of that reactor is such that it behaves rather well as a well-mixed reactor, whereas the pipes in, and essentially out, of the reactor leading to the analytical device have a diameter such that the flow is of the plug flow type. So there is no distortion at the inlet of the analytical device of the gas-phase composition at the outlet of the reactor with time during that composition variation. This has been verified by analysing the gas-phase composition out of that reactor by switching, in the presence of a catalyst, the flow of one inert gas (He) by another one (Ar) [121,122].

An inert gas used as internal standard and introduced at a constant molecular flow rate allows one to take account of all volumetric flow rate variations. It is thus easy to transform, for each of the gaseous components, the pressure variations in molecular flow rate variations out of the reactor. By use of Eq. (4.4) developed in Section 4, the adsorption and desorption rates are calculated at any moment.

A typical example is developed concerning a reaction conducted at total atmospheric pressure and

270°C with an H_2/CO ratio of 3. Fig. 15 represents the variation of the pressures with time.

The products appear following a sequence:
1. As soon as CO enters the reactor, CH_4 formation is observed.
2. After a certain period of time depending on the experimental conditions, CO, C_2H_6 and CO_2 appear simultaneously.
3. C_3H_6, C_4H_{10} and C_5H_{12} appear successively in a sequence corresponding to the number of carbon atoms in the molecule.
4. H_2O is only formed near the steady state.

Fig. 16 shows the calculated variation of the appearance rate of the various products as a function of time.

The next transformation is to calculate from in–out mass balance the coverage of oxygen and carbon atoms. Fig. 17 compares the total amounts of carbon and oxygen atoms in the products with the amount of CO molecules consumed. The coverage steady state is reached when the number of CO molecules consumed is equal to the number of C and O atoms in the products formed.

By integration (Eq. (4.6)), the number of carbon and oxygen atoms remaining on the surface may thus be calculated at any moment. Fig. 18, where the carbon and oxygen coverages are plotted as a function of time, shows that the carbon and oxygen coverages at steady state are larger than the monolayer and that the oxygen coverage is more important than that of carbon.

Finally, from the combination of the data of the two last graphs, the evolution of the selectivity all along
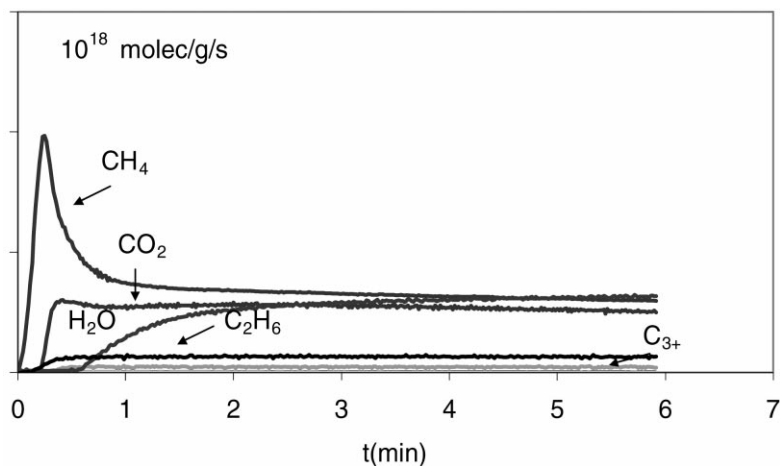
Fig. 16. Formation rates as functions of time from the CO entrance in the reactor to steady state.

the build up of the surface by plotting the reaction rates is given as a function of the carbon coverage in Fig. 19 and oxygen coverage (Fig. 20).

As shown in Fig. 19, chain lengthening, appearance of C_2H_6, and CO_2 formation start to take place simultaneously with the appearance of CO in the gas phase. This corresponds in Fig. 20 to a coverage of oxygen atoms of about 50×10^{19} O at./g Co–Cu. At the same time, CH_4 formation reaches a maximum and decreases. The first carbon–carbon bond is formed as soon as CO molecules appear in the

gas phase. The presence of CO in the gas phase thus seems to be a condition for the carbon insertion. This constitutes an argument in favour of CO being the monomer.

Three different transients were carried out with the same steady hydrogen pressure but with three different values of CO steady pressure. In Fig. 21, both α_{SF} and L show a direct and monotonous dependence towards the CO pressure. Fig. 22 represents the variations of α_{SF} and L versus the carbon coverage, for the first of the three experiments. Their dependence towards the
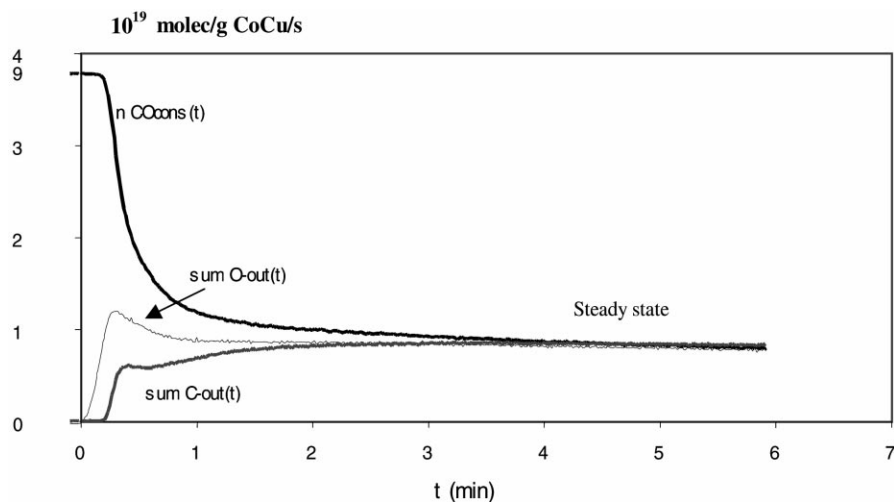

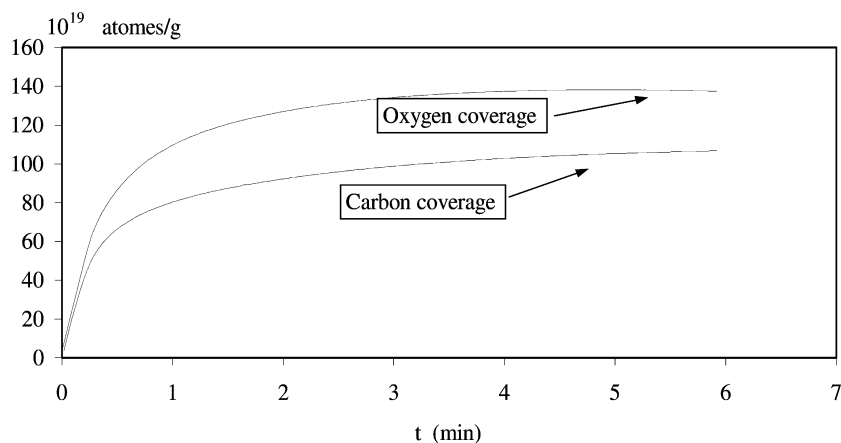Fig. 17. Sum of the O and C atoms going out of the reactor vs. time.

Fig. 18. Coverages vs. time during the build up.

number of surface carbons is more complex and not monotonous. CH_x seems thus not to be the monomer involved in chain lengthening.

The lengthening stops increasing as soon as p_{CO} has reached its steady value, whereas the coverage continues to reach its maximum value. The fact that the α_{SF} value does not change with the coverage in a long range of θ confirms the independence of α_{SF} from the coverage. CH_x is thus not the monomer, as is often suggested.

CO_2 also appears when CO is present in the gas phase, a long time before water formation. CO_2 can thus not be the result of the water gas shift (WGS) reaction.

Water, the last product formed, appears when the other partial pressures have reached their maximum steady values.

The sequence of the appearance of hydrocarbons shows that chain lengthening proceeds by means of a monomer containing only one carbon atom, which is in agreement with the ASF model.

6.3. Back transient or emptying

As soon as the CO flow is stopped and is replaced by a flow of He, one observes the emptying of the gas phase, followed by a peak of CH_4 production and finally the emptying of CO_2 and the C_{2+} hydrocarbons
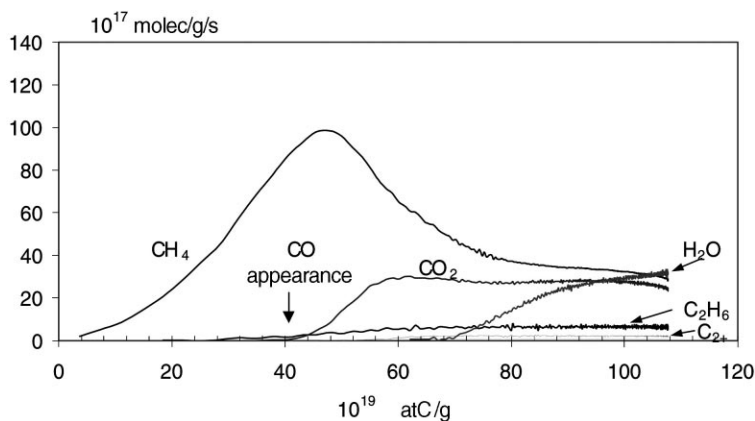

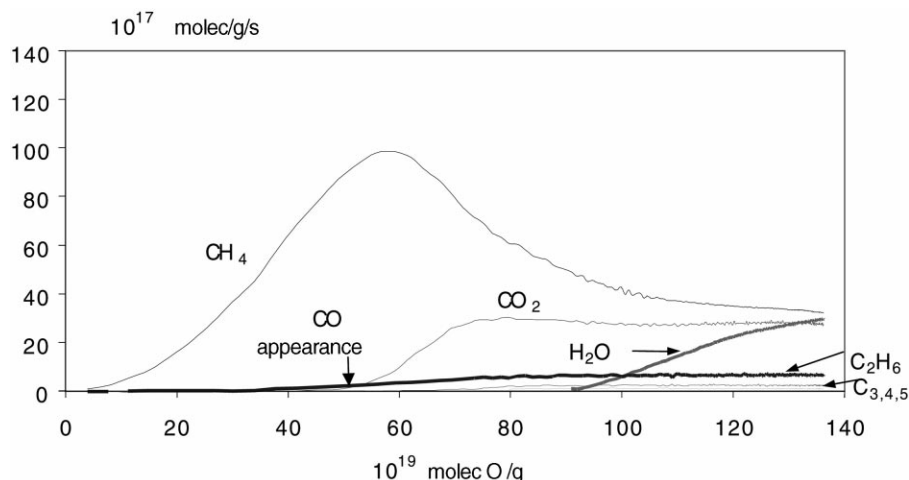Fig. 19. Formation rates of the product of reaction vs. the C coverage.

Fig. 20. Formation rates vs. the O coverage.

from the surface. Water production stays unaffected for a long period and starts to decrease after the complete disappearance of the other products.

The comparison between the product time constants is more useable after having normalised the values of the pressures. Therefore, in Fig. 23, all the pressure values are divided by their steady-state values. $p_{\text{norm}} = p/p_{\infty}$. The He pressure is normalised following $p_{\text{norm}} = (p_{\infty}^{\text{He}} - p^{\text{He}})/p_{\infty}^{\text{He}}$.

The two normalised curves characterising the behaviour of He and CO pressures overlap, which means that CO disappears from the gas phase as He appears.

This correlation allows one to conclude that CO is adsorbed in an irreversible way.

The CH_4 curve exhibits a completely different profile from that of C_{2+}, meaning that part of the CH_4 is not produced from pre-existing CH_x radicals at steady state but from the C_1 MASI.

The decay of C_{2+} production is exponential and is characterised by the same time constant within each other, which is in agreement with the ASF hypothesis. It also means that C_{2+} is present on the surface in the form of its last precursor state.
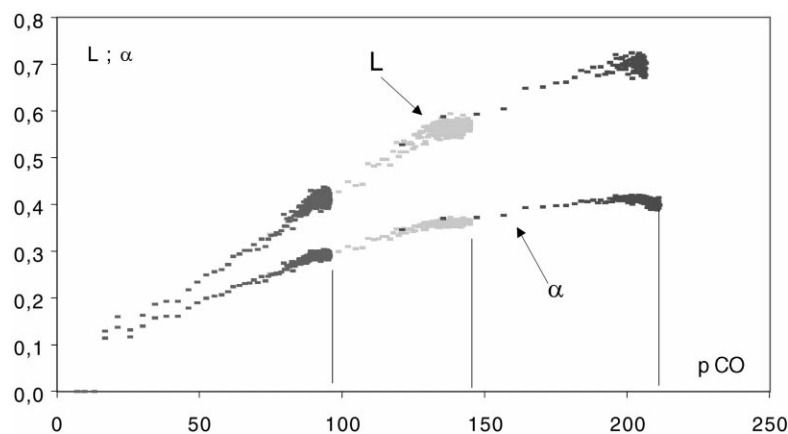
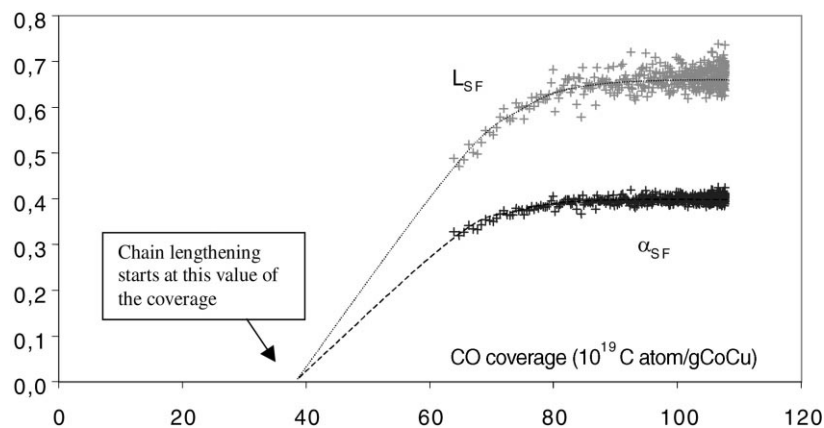Fig. 21. Evolution of α_{SF} and L all along the build up.

Fig. 22. Evolution of L_{SF} and α_{SF} vs. the C coverage during a build up.

Furthermore, CO_2 disappears in the same way as C_{2+} and independently of CO. The H_2O behaviour is completely different from those of the other products. H_2O continues to be formed, while the others have completely disappeared. H_2O thus comes from the catalyst reduction.

6.4. Combination of the results of the build up and of the emptying

Table 2 presents the values of coverages obtained from several build ups and emptyings realised under different conditions.

The amount of carbon atoms staying on the surface (Eq. (4.6)) under steady-state conditions at the end of the build up and the amount of carbon atoms desorbed during the emptying are of the same magnitude. The carbon deposition is thus reversible.

On the other hand, the same comparison between the values of O coverage shows a difference of about 50×10^{19} oxygen atoms, which is equivalent to half of the number of chemisorption sites as measured by CO chemisorption at room temperature. Such oxygen coverage corresponds also, during the build up, to the coverage where the selectivity of the catalyst changes from methanation to chain lengthening and CO_2
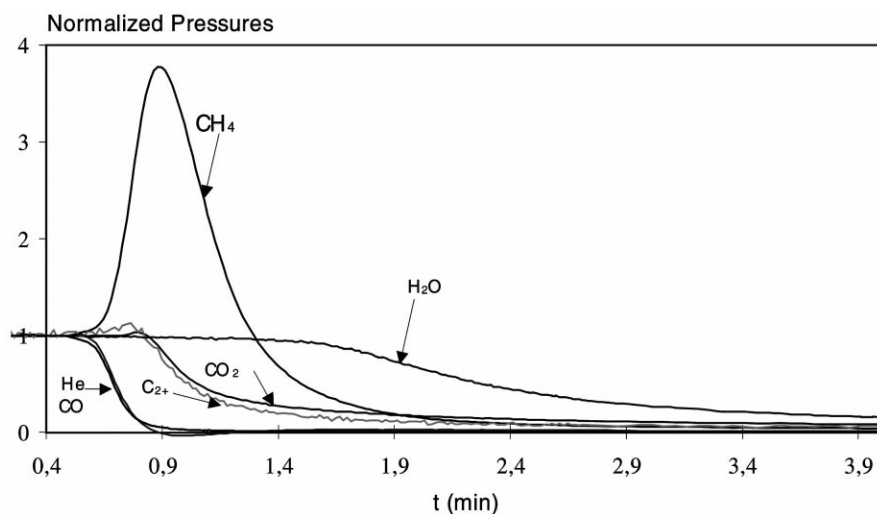

Fig. 23. Relaxation of the system. Normalised values of the pressures with time.

Table 2
Values of coverages from the build up and back transient

Experimental conditions			C coverages — n_C (at./g Co–Cu)		O coverages — n_O (at./g Co–Cu)			
p_{H_2} (Torr)	p_{CO} (Torr)	H_2/CO	Build up	Empty	Build up	Empty	Remaining	Mechan.
437	210	2	98	76	110	52	58	114
411	129	2.9	104	89	135	80	55	134
400	95	4.5	94	94	130	84	46	138
530	126	3.7	93	78	145	76	69	114
411	129	2.9	104	89	135	80	55	134
286	139	2	97	104	115	84	31	161

Table 3
p_{CO} effect[a]

H_2/CO	p_{H_2} (Torr)	p_{CO} (Torr)	CO conversion (%)	α_{SF} — gas	α_{SF} — surface
15	445	29	91	0.08	0.10
3.6	431	119	25	0.30	0.23
2.8	427	153	15	0.36	0.33
2.0	432	212	8	0.40	0.40

[a] $p_{H_2} = $ constant, $T = 270°C$, $d = 28\,cm^3/min$.

production. Another important conclusion is that the catalyst surface working under reaction conditions is thus not the metallic surface.

As mentioned above, the rate of hydrocarbon formation at steady state obeys the ASF distribution. During the emptying, the integration of the product desorption curves also obeys the ASF distribution.

Tables 3 and 4 allow one to compare the values of α_{SF} for the product distribution under steady-state conditions with the α_{SF} values of the distribution of the desorbed radicals.

It appears from Tables 3 and 4 that the distributions on the surface and in the gas phase are equivalent, independently of the temperature, the pressure and the conversion in the studied ranges.

As soon as CO has disappeared from the gas phase, the chain lengthening stops. The monomer is

Table 4
Effect of temperature on the values of α[a]

T (°C)	CO conversion (%)	α_{SF} — gas	α_{SF} — surface
200	3	0.40	0.40
262	14	0.38	0.42
272	21	0.35	0.36
278	32	0.35	0.34

[a] $H_2/CO = 2.2$, $p_{H_2} = 479\,Torr$, $p_{CO} = 217\,Torr$.

thus not on the surface. If it were the case, chain lengthening would continue independently of the presence of the CO_g. The resulting desorbed molecule distribution would differ from the product distribution in the gas phase under steady-state conditions. This is a further argument in favour of the CO molecule being the monomer and not the CH_x on the surface.

6.5. Model proposition

From all this information and all the conclusions, we suggest a model that explains the steps of the surface construction from a fresh surface to a surface working under steady-state conditions:

- Phase 0: the surface construction starts on a metallic surface in equilibrium with H_2.
- Phase 1: all the in-going CO molecules adsorb. In addition, some of them are hydrogenated in CH_4. No CO molecule is detected, while the increase in C and O coverage proceeds.
- Phase 2: from a given coverage, CO does not adsorb quantitatively anymore. C_2H_6 appears in the gas phase together with CO, and the C_{2+} chains are formed one after the other. Simultaneously, CH_4 production decreases. This may be associated with a
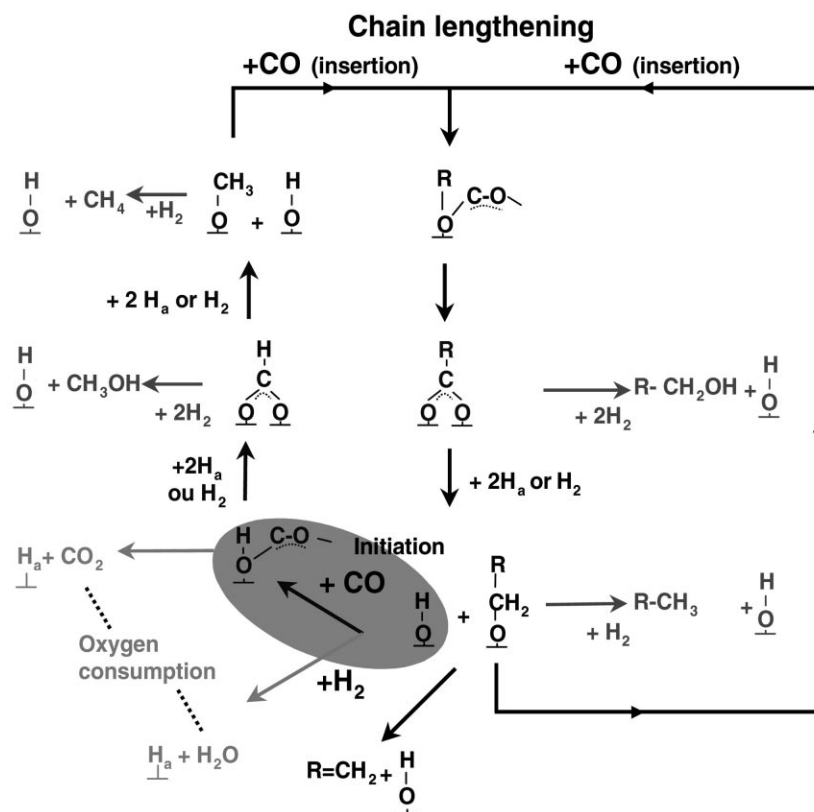
Fig. 24. Suggested reaction scheme for the CO–H$_2$ reaction.

reaction of CO$_g$, which increases the pressure, with a fraction of surface carbon atoms.

- Phase 3: simultaneously with the H$_2$O appearance in the gas phase, all the products reach their steady value, while the coverage continues to increase. The C and O coverages together reach a value that is about three times that of the CO monolayer.

6.6. Description of the proposed mechanism

The reaction scheme presented in Fig. 24 allows one to render account for all the observations. It is divided into two sequences of steps.

The left part of the scheme corresponds to the initiation step leading to the C$_1$ precursor formation. It may also lead to the formation of C$_1$ products (CH$_4$ and/or CH$_3$OH). The initiation step in this scheme consists of the insertion of one CO molecule within a surface hydroxyl to form a surface radical of the type of a formate. The progressive hydrogenation of that precursor may lead to methanol and to CH$_4$ formation, on the basis of kinetic selectivity on the same site. The hydrogenated carbon atom here bonds to an oxygen and not to the metal surface and may react with one CO molecule to form the first carbon–carbon bond. This insertion is of the same type as the one corresponding to the initiation step on the OH radical. The only difference is that here the H atom of that OH is replaced by a CH$_x$. Thus, it also constitutes the chain-lengthening step. Thus, in this scheme, at steady state, the initiation step and the chain lengthening are of the same nature. It consists of CO insertion, while only the nature of the surface radical is different.

The middle part of the scheme represents the steps leading to the C$_{2+}$ hydrocarbons, alcohols and alkenes. The CO insertion within the alkyl radical is preceded by the reaction of the CO molecule with the O bond to the metal. It is noteworthy that, in this scheme, the selectivity of hydrocarbons/oxygenates involves only one precursor.

The two steps characterised in the scheme by a grey arrow are those through which most of the oxygen atoms brought to the surface by the CO insertion step are consumed. One results in the reaction of an OH surface group with hydrogen (most desired step). The other results in the decomposition of the radical of the surface intermediates resulting from the initiation step instead of leading to formate-type surface radical. It then represents the much less desired selectivity towards CO_2 formation, but that does not correspond to the Boudouart reaction.

6.7. Discussion of the results in the framework of our reaction scheme

This reaction scheme makes it possible for one to explain the following:

- The general behaviour during build up as during back transient.
- The important peak of only CH_4 formation during the back transient.
- The presence of half of the monolayer atoms not desorbing and the distribution of the oxygen atoms under steady-state conditions.
- The number of chemisorbed radicals at steady state compatible with the extent of the surface in opposition to the total number of O and C atoms if they were dissociated on the surface.

In Table 5, we consider the total number of CH_4 molecules to be composed of two parts. One is calculated from the ASF distribution of the C_{2+} molecules. The second one is obtained from the difference between the total number and the one calculated from the ASF distribution. It is associated with the number of CH_4 molecules coming from the hydrogenation of the formates that may no longer undergo chain lengthen-

ing due to lack of CO. We must keep in mind that CO_2 is also the result of formate decomposition. The sum of the number of CO_2 molecules and the second type of CH_4 gives thus the number of formates that were present on the surface under steady-state conditions.

The next column represents the total number of hydrocarbon radicals, which is in agreement with the ASF distribution. The sum of these two last numbers gives the total number of surface radicals present on the surface.

The number of oxygen atoms on the surface is calculated by the sum of two times the number of formates (one formate contains two oxygen atoms) and the number of hydrocarbons (one hydrocarbon radical is bonded to the surface by means of one oxygen atom). This total number of radicals is given in the last column of Table 5.

The total number of oxygen atoms, calculated by application of the mechanism, is remarkably similar to the number of oxygen atoms that remained on the surface as measured at the end of a transient build up.

On the other hand, the number of surface radicals (formates and hydrocarbons radicals) is always a little bit smaller than the number of sites. It is now possible to evaluate a distribution of the intermediates on the surface. Under steady-state conditions, the formates occupy 50–60% of the surface, the hydrocarbon chains in the formation occupy 25–30% and hydroxyls 10–30% of the surface. The presence of hydroxyls is of course necessary to allow the reaction to start.

6.8. Conclusions

The results of the mass balance presented here show that the C and O steady-state coverages are two to three times that of the monolayer. The comparison

Table 5
Distribution according to the mechanism[a]

H$_2$/CO	CH$_4$ total	CH$_4$ ASF	CH$_4$ formate	CO$_2$	Formate	$\sum$ HC$_{surf}$ radicals	$\sum$ Surface radicals
2.0	51	13	38	10	48	18	66
2.9	50	17	33	22	55	24	79
4.5	53	21	32	23	55	28	83
3.7	50	17	33	13	46	22	68
2.9	50	17	33	22	55	24	79
2	57	20	37	29	66	29	95

[a] $n_m = 90 \times 10^{19}$ C at./g Co–Cu; $T = -270°C$.

of the results of the build up and of the back transient shows that the carbon atoms are reversibly adsorbed. On the other hand, half of the oxygen monolayer remains on the surface at the end of the emptying and can only be eliminated by reduction at higher temperature. Based on the model, a calculation of the atomic distribution within the surface radicals allows one to quantitatively explain this difference in the mass balance. In our model, the catalytic working surface under reaction conditions is composed of half of the oxygen monolayer bonded to the metallic surface. This view differs strongly from the one generally considered in the literature where the catalytic surface is the metallic surface.

The mass balance allows also to calculate a distribution of the surface radicals in which the number of surface radicals is smaller than the number of CO chemisorption sites. In that distribution of surface radicals, the most abundant intermediate is the formate, which also indicates the position of the r.d.s. The presence of such formates on the surface has already been discussed [71] but used in a different way in the reaction scheme.

The reaction mechanism proposed is in opposition to the mechanisms using CH_x as a monomer for the lengthening. In this last model, the monomer necessary to explain the selectivity towards alcohols, which often is CO, is different from the one leading to chain lengthening. Such mechanisms are also sometimes associated with two types of sites. On the contrary, the mechanism proposed here involves a kinetic selectivity on only one radical for the hydrocarbon/alcohol selectivity. Thus, only one site is involved, that is an oxygen atom bonded to the metallic surface.

7. General conclusion

We have tried to put in evidence the power of transient kinetic measurements as compared to the more limited information that steady-state kinetics is able to provide.

At first, we would like to insist on that catalysis may not modify the requirements imposed by the thermodynamics of a chemical reacting system. On the other hand, catalysis concerns the kinetics of the reactions allowed by thermodynamics.

In some simple systems, like the $CO–O_2$ system, only one product can be formed. Catalysis can thus only modify the rate of that reaction. It is derived from the work by Ertl [28] that the catalytically active site is directly defined by the surface of the metal catalyst. Furthermore, it clearly appears from that work that in such a case the physical methods of surface science are powerful to elucidate the catalytic phenomena.

On the other hand, in many systems, a wide variety of products can be formed. Two cases have to be distinguished:

- In the first one, the catalytic properties are directly defined by the metal surface of the catalyst. The coverages by the active surface intermediates remain very small under catalytically working conditions. During transient experiments, the rate of formation of the various products follows monotonous variations [33]. The $C_2H_6–D_2$ system under low-pressure conditions presented in Section 5 of this paper constitutes an example of such a case. Coupled with the use of labelled molecules, it allows to determine the real rate, back and forth, of elementary steps of the catalytic reaction.

- In the second case, the catalytically active surface is not directly defined by the metal surface and is progressively built up during a transient experiment. So, in the case of the $CO–H_2$ reaction (see Section 6), it is clear that the properties of the bare surface are very different from the one at steady state at pressures higher than atmospheric pressure. At much lower pressure (below 10^{-1} atm), the catalytic surface keeps its simple methanation properties at steady-state activity, as in the first part of the transient measured at atmospheric pressure [118].

In most cases where the working surface needs to be created from reaction between the initially bare surface and the gas phase, the synthesis of some products goes through a maximum. For hydrocarbon transformations, hydrogenolysis reaction is observed first. The activity for that reaction goes through a maximum. Some time after that maximum, other reactions [54–59] appear, like isomerisation, cyclisation etc. In such cases, the transient is unique for providing information on the evolution of the catalytic properties.

The analysis of only chemical transient kinetic studies in the $CO–H_2$ reaction has proven this method to be very powerful not only for the understanding of the

catalytic reaction scheme but also for the determination of the surface composition defining the catalytic properties. The fleeting character of some of the surface intermediates makes the transient studies a unique method for the understanding of such catalytic reactions. It also provides interesting guidelines for further insight by other methods as, for example, the kinetic selectivity towards the various products (Section 6.6) should be related to the characteristics of the oxygen surface atoms acting as active sites. These characteristics might now be determined by the chemical shift in the XPS spectrum. Correlations could then be made with the selectivity as observed under high-pressure conditions towards hydrocarbons or oxygenates together with the composition of the multi-metallic catalyst. This extensive analysis highlights the still great importance of kinetic studies in catalysis.

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