Available online at www.sciencedirect.com

Journal of Catalysis 216 (2003) 89–97

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Classical kinetics of catalytic reactions

Gérald Djéga-Mariadassou [a,*] and Michel Boudart [b]

[a] Laboratoire Réactivité de Surface, Université Pierre et Marie Curie, UMR CNRS 7609 Case 178, 4, Place jussieu, 75252 Paris cedex 05, France
[b] Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

Received 16 July 2002; revised 16 October 2002; accepted 6 November 2002

Abstract

The present paper deals with a "reactivity approach" to complex catalytic reactions. It utilizes data obtained with a reactor and demonstrates the very important role of both rate constants and concentrations of adsorbed species, on catalytic cycle, activity, and selectivity. It develops a link between global kinetics and closed sequence of elementary steps. It emphasizes the aspects of "assisted" catalytic reactions, kinetic "coupling" of catalytic cycles, and selectivity.

Keywords: Assisted catalytic reactions; Kinetic coupling; Rate constants; Rates and selectivity

1. Introduction

During the past 40 years, numerous concepts have developed in the field of kinetics applied to heterogeneous catalysis [1]. In the kinetic approach no frontiers exist today between homogeneous, enzymatic, and heterogeneous catalysis. There is a consistent science which permits the definition of useful and efficient rate laws describing sequences of elementary steps. Comparison between an enzyme active site and a metallic site supported on an oxide became possible owing to the famous "turnover rate" concept.

The present paper deals with the "reactivity approach" to complex catalytic reactions. It tries to show the very important role of both rate constants and concentrations of adsorbed species on the turnover rate of catalytic cycles and selectivity. It emphasizes the aspects of "assisted" catalytic reactions, kinetic "coupling" of catalytic cycles, and selectivity.

The paper reviews the most important concepts and shows how they have been developed during the past 20 years in different fields of catalysis. It does not consider the "microkinetic" analysis of Dumesic et al. [2]. Some striking applications are presented including the cleaning of automotive gas exhaust and isomerization for obtaining high-octane gasoline.

2. Basic concepts and definitions

2.1. The quasi-steady-state approximation

The quasi-steady-state approximation (QSSA), used for computational codes such as Chemkin or Chemkin-surface, permits, in the latter case, to enter *all* elementary steps of a catalytic sequence and to optimize *all* rate constants and concentrations of *all* reaction intermediates.

The QSSA theory is based on three fundamental rules: (i) concentrations of intermediates are very low; (ii) the variation of the concentration of one intermediate is stationary, i.e., independent of time ($\mathrm{d[intermediate]}/\mathrm{d}t = 0$); (iii) consequently, rates of all steps in a sequence have the same value, once divided by *the stoichiometric number* σ_i, the number of times we need an i-elementary step in the sequence to obtain the overall chemical equation. The QSSA theory leads to the definition of a catalytic reaction as a *closed sequence*, the rate of which is the *turnover rate*, i.e., the rate per site. The reaction rate can be calculated from any i-step according to the following equation:

$$\text{reaction rate} = \text{net rate of the } i\text{-step}/\sigma_i.$$

As an example, let us consider the CO oxidation on a three-way catalyst (TWC), presenting a zero-valent noble metal active site, denoted by "*," such as Pt [3].

The global chemical reaction is

$$2CO + O_2 = 2CO_2; \quad \text{or} \quad CO + \tfrac{1}{2}O_2 = CO_2. \tag{1}$$

---

[*] Corresponding author.
E-mail address: djega@ccr.jussieu.fr (G. Djéga-Mariadassou).

0021-9517/03/$ – see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0021-9517(02)00099-4

The catalytic sequence can be considered as [3] (Sequence 1)

		σ_i	σ_i'
[1]	$CO + {}^* \mathrel{\bigcirc\!\!\!\!\!\rightleftarrows} {}^*CO$	2	1
[2]	$O_2 + {}^* \twoheadrightarrow O^*O$	1	$\frac{1}{2}$
[3]	$O^*O + {}^* \rightarrow 2\,{}^*O$	1	$\frac{1}{2}$
[4]	${}^*CO + {}^*O \rightarrow CO_2 + 2^*$	2	1

Overall equations: $2CO + O_2 = 2CO_2$ linked to σ_i
or $CO + \frac{1}{2}O_2 = CO_2$ linked to σ_i'.

Let us recall the nature of the symbols of elementary steps in a sequence: "one-way" or irreversible ($\rightarrow$), "two-way" or reversible, but far equilibrium ($\rightleftarrows$), or near equilibrium ($\mathrel{\bigcirc\!\!\!\!\!\rightleftarrows}$). The symbol ($\twoheadrightarrow$) stands for the rate-determining step [1].

The experimental and global rate law, over zero-valent rhodium, Rh/SiO_2 [4,6], Rh(111) [5], Rh(100) [5], and Rh/Al_2O_3 [4,7], obeys the following equation:

$$\text{rate} = k_{\text{global}}[O_2]^{\alpha}[CO]^{\beta} \quad \text{with } \alpha = +1 \text{ and } \beta = -1. \qquad (2)$$

In Sequence 1, *two elementary steps for dioxygen chemisorption–dissociation* are needed. (Let us note the same two steps are also required for the NO adsorption–dissociation process [8] in TWC.) This can be explained by *the high carbon monoxide coverage,* at least at low temperature, as is the case for CO oxidation over Pd [9]. Therefore, CO chemisorption (step [1]) is near equilibrium; step [2] means that when dioxygen sticks to the surface, *it cannot find the two adjacent sites* required for its dissociation. CO has to scavenge adsorbed oxygen atoms (step [4]) to provide the second adjacent free site for oxygen dissociation (step [3]).

2.2. The catalytic cycle

Working with the previous set of σ_i (Sequence 1), the catalytic cycle representative of the preceding four-step reaction is reported in Fig. 1 [10]. This cycle illustrates the "closed sequence" concept in opposition to an "opened sequence" which cannot lead to a cycle (nevertheless, QSSA applies to both sequences). All catalytic processes are closed sequences.

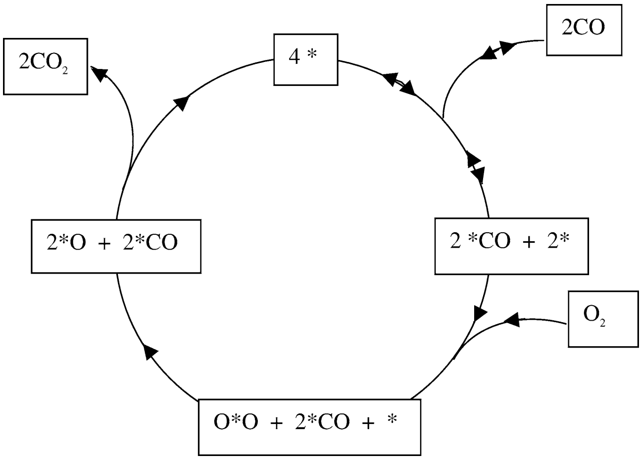
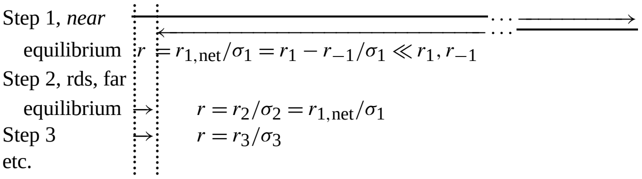


Fig. 1. Catalytic cycle for the global reaction: $2CO + O_2 = 2CO_2$ [10].

2.2.1. *The rate of reaction is $r = r_i/\sigma_i$*

A very good way of representing the rates of catalytic steps, according to the Japanese school [11], is as follows:



Step 1 cannot be strictly at equilibrium for the reaction to proceed. If all steps are far equilibrium, there is no rds.

2.2.2. *The overall reaction rate $r = r_{i,\text{net}}/\sigma_i$*

The overall reaction rate is consistent with the differential definition of rate (batch continuously stirred reactors): $r = d\xi/dt = (1/\nu_i)\,dn_i/dt$ (ξ being the extent of reaction, ν_i the stoichiometric coefficient [$\nu_i > 0$ for an i product and < 0 for an i reactant], and n_i the number of i moles).

The turnover rate is the rate with which the cycle turns over, per catalytic site.

2.3. How to obtain a good rate law

The primary goal of kinetics is to describe the chemical transformation. The methodology developed hereafter permits the following:

(i) To integrate all previous theories and models such as Langmuir–Hinshelwood (L–H), Eley–Rideal (E–R), Lindemann, etc.; those models have to be considered only as *particular cases of the present general kinetic approach*. Some rate equations can *mathematically "look like"* L–H or E–R equations, but their kinetic parameters are not L–H or E–R ones.
(ii) To directly calculate the turnover rate.
(iii) To solve any kinetic system.

There are three classical equations to solve the kinetics and obtain the rate law:

1. Application of QSSA: $r_i/\sigma_i = r_{i+1}/\sigma_{i+1}$. The concept of *rate-determining step* (*rds*), *if it exists,* also has to be applied. There is still confusion in published papers on this concept. Many still consider that the rds is a "slow elementary step." The adjective "slow" is generally not clear; some think of it in terms of "rate constant" and others in terms of "rate of reaction." In a catalytic cycle, if all steps turn over at the same rate (taking into account the σ_i value), there is no "slow step." In conclusion, it must be considered that the "rds" is a step "*far equilibrium and generally coupled with a step near equilibrium*" [1]. Boudart and Tamaru have given another, more general definition: *the rds is the*

step whose rate constant appears in the rate equation. This is also the case, for instance, for SN2 noncatalytic reactions in organic chemistry.

2. Definition of equilibrium constants, if there are elementary steps near equilibrium.
3. Balance on the density of active sites, "[L]."
   The concept of the *most abundant reaction intermediate* (*mari*) has to be considered for completing this third rule. It will be helpful for simplifying the balance on [L]. Let us note there can be some ambiguity on the [L] determination: it is generally determined by specific chemisorption of molecular probes such as H_2, O_2, ($H_2 + O_2$) [12–14], CO [15–21], N_2O [22–24], NO [25,26], or probe reactions [26,27] in the case where the metal is at a very low concentration in a complex catalytic material (e.g., TWC catalysts). This kind of chemisorption leads to a *total* number of active sites, even if, statistically, they are leading to different products, via different routes of reaction (kinetic coupling).

Application of the method to the oxidation of CO:

1. $r = r_2/\sigma_2 = r_2 = k_2[O_2][^*] = r_{\mathrm{rds}}$. (3)

Note that steps [3] or [4] can also be used for calculating the rate of reaction. In the case of step [3], the equation is $r_3 = k_3[O^*O][^*][L]^{-1}$. It is proportional to the probability of finding the two surface species (O^*O;*) side by side; therefore, the dimension of rate is that of [L] and not $[L]^2$. This is the reason why $[L]^{-1}$ has to be introduced in the rate equation [28]. Both surface species have to be calculated.

Step [3] can be the driving force for regulating the rate of all other steps in the catalytic cycle, as CO oxidation can only proceed once dioxygen has been dissociated:

$$r = r_3/\sigma_3 = k_3[O^*O][^*][L]^{-1}. \tag{4}$$

The concentration of "O^*O" species can be calculated if we consider the equality between the rates of steps [2] and [3].

$$r = k_3[O^*O][^*][L]^{-1} = k_2[O_2][^*]. \tag{5}$$

Step [2] introduces $[O_2]$; it is far equilibrium and permits calculation of the overall reaction rate. It is the rate-determining step (rds), *CO being the *mari*.

2. Step [1] being considered *near equilibrium*, a first approximation can be made in treating step [1] with its equilibrium constant:

$$K_1 = [^*CO]/[CO][^*]. \tag{6}$$

3. The balance on active sites will lead to the calculation of surface species.

$$[L] = [^*] + [O^*O] + [^*O] + [^*CO] \approx [^*] + [^*CO]. \tag{7}$$

Here is the simplification due to the *mari* concept.

We need to calculate the concentration of free sites (5) to obtain the rate equation. From (7) we have

$$[L] \approx [^*]\bigl(1 + [^*CO]/[^*]\bigr). \tag{8}$$

Therefore, using the K_1 equation, the rate of reaction is given by

$$r = k_2[O_2][L]\big/\bigl(1 + K_1[CO]\bigr) \approx k_2[O_2][L]\big/K_1[CO], \tag{9}$$

taking advantage of the fact that $K_1[CO] \gg 1$ because *CO being the *mari* (high CO surface coverage) means that $[^*CO]/[^*]$, which is equal to $K_1[CO]$, is very large. Partial orders toward O_2 and CO are therefore $+1$ and -1, respectively, and the experimental rate expression (2) is verified.

The reaction has been studied by Engel and Ertl [29,30] on the (111) face of a single crystal of palladium. By separate relaxation measurements, they measured the rate constant of step [4] and determined its activation energy, which was found to be equal to 25 $\mathrm{kcal\,mol^{-1}}$. The pre-exponential factor was found to be equal to 1.1×10^{-3} $\mathrm{cm^2\,s^{-1}}$, for $[L] = 10^{15}$ $\mathrm{cm^{-2}}$. For $T > 550$ K, and $P_{\mathrm{CO}} < 10^{-6}$ Torr, Conrad et al. [31] have found that islands of oxygen are formed at the surface. Carbon monoxide molecules diffuse on the surface and the formation of CO_2 takes place at the periphery of these islands. The rate of reaction is given by step [4] with $[^*O] = \mathrm{const}$ and $[L] = [^*]$. In this case $r = \mathrm{const} \times k_4[L]K_1[CO]$.

2.4. The concept of "two-step catalytic reaction" [1]

From the preceding section it is obvious that Sequence 1 can be simplified to

(Sequence 2)

[1] $CO + {}^* \mathrel{\rlap{$\rightleftarrows$}\hspace{0.25em}\circ} {}^*CO$

[2] $O_2 + {}^* \twoheadrightarrow \ldots$

for establishing the rate expression. The reason is that step [2] is away from equilibrium, i.e., "one-way," and "does not come back." So kinetics does not "see" what happens after this second step. This is true, as far as there is no adsorbed species competing for occupying free sites; in this case, the two-step concept remains valid, but the competitive species will have to be considered in the balance on active sites. Steps [3] and [4] are kinetically *insignificant*.

2.5. How to select the two steps

We have to consider that all steps have the same rate (taking into account σ_i). Furthermore, it is not possible to calculate the rate with the "near-equilibrium step," which is treated as if it is *at* equilibrium (use of its equilibrium constant). The method and calculations bring us automatically to two steps (one of them can be the sum of several near-equilibrium steps). As a matter of fact, starting from any one of the four steps in Sequence 1, the calculation of intermediates goes throughout two possibilities: (i) the use of QSSA with the equality of the rates of steps (taking into account σ_i) and (ii) the use of the equilibrium constant. If there is no rds, then only (i) is useful. If there is no near-equilibrium step, there is no rds and two elementary steps will be used: the first one produces the *mari*; the second consumes it. In all cases where there is a *mari*, the system comes back to steps that permit one to obtain the rate equation versus concentrations of reactants and products [1].

2.6. What is the origin of the equality between the rates of catalytic steps in a cycle?

The origin is the *compensation* between the value of the rate constant k_i associated to the i intermediate and its concentration: the higher the k_i, the lower the concentration of the corresponding intermediate. For $\sigma_i = 1$,

$$
\begin{aligned}
&{}^{*}\text{ intermediate 1} \overset{k_1}{\rightarrow} {}^{*}\text{ intermediate 2} \overset{k_2}{\rightarrow} {}^{*}\text{ product}\\
&\quad\text{if } k_1 \gg k_2,\ \text{then [intermediate 1]} \ll \text{[intermediate 2]},\\
&\quad\text{but } r_1 = r_2.
\end{aligned}
$$

This simple relation can explain what is called a *very reactive intermediate*: it is an intermediate associated with a high rate constant.

2.7. Is the mari a very reactive intermediate?

The *mari* is probably not a very reactive intermediate as it is accumulating on the surface of the catalyst. Spectroscopic techniques permit us to observe the *mari*. In a catalytic cycle, if there is a very reactive intermediate, it will not be observed due to its low concentration and very high rate constant; consequently, a high consumption of this very reactive intermediate will probably be observed.

The deNO$_x$ process over zeolite-supported transition metal cations is a good example. There are two main theories. *The first* claims that organic nitroso compounds (RNO$_x$) are the intermediates in the selective reduction of NO$_x$ by hydrocarbons, their decomposition leading to N_2 in the presence of an excess of oxygen. These compounds are detected by IR spectroscopy. This means that they are probably very stable, and may be adsorbed on the support or any other site of the catalytic material, under experimental conditions for spectroscopic studies. Are they the “very reactive intermediates” *leading to* N_2? Their role in the NO$_x$ selective catalytic reduction (SCR) process still has to be demonstrated (no clear explanation has yet been given). *The second model* assumes the existence of $(NO)_2$ species on the cationic active sites, N_2O being the intermediate leading to N_2. In this case, when the deNO$_x$ process occurs, N_2O does not desorb but transforms to N_2. This is generally observed on a Rh-based catalyst that presents a high selectivity to N_2 in deNO$_x$ or TWC and means that the rate constant associated to N_2O at the temperature of light-off of the catalyst is very high and that contact time is long enough for N_2O decomposition to occur. We cannot claim that N_2O is not the intermediate leading to N_2, as it disappears from the gas phase and from the catalyst surface when the reaction occurs.

In conclusion, if the *mari* is probably not a very active intermediate, it is nevertheless very useful for simplifying the balance on [L] when establishing the rate equation.

Is there any other abundant surface species? Probably yes, but some of them can be only spectators of the reaction; i.e., they are not located on the active sites and do not participate in the reaction or the [L] balance.

According to QSSA, all steps in a catalytic cycle have the same rate (taking into account their σ_i) (Fig. 1). Therefore *there is no “slow step” in a catalytic cycle*. The *rds is not a slow step*. Two cycles can however turn over at different rates. This is the topic of the next section.

3. Assisted catalytic process

Let us now consider the case of isomerization of alkanes over bifunctional catalysts [32]. Three associated and successive cycles turn over to proceed to the overall reaction. They have no common adsorbed intermediate and thus are *not kinetically coupled* [30]. The global reaction can be considered as *an assisted catalytic process*. Fig. 2 demonstrates the functioning of the three cycles.

Designing new, efficient catalysts (i.e., producing multibranched isomers with a high-octane index) implies optimizing the *ratio* between the two functions: metallic [(de)hydrogenating function]/acid [isomerization function], i.e., the *number* and *quality* of sites for each function [34,35]. In the present case, the dehydrogenating function has to produce enough n-alkene species for cycle 2 to turn over without any limitation. Simultaneously, the third cycle has to be sufficiently efficient to hydrogenate i-alkene to i-alkane. *There is no true kinetic coupling*.

3.1. Reactivity approach of the reaction of isomerization

The global features of the isomerization of n-C$_7$ can be seen in Fig. 3. It reports the evolution of the concentration of the major products of n-C$_7$ isomerization: single-branched, multibranched, and cracked products. The concentration of n-C$_7$ is also reported to show its global consumption versus contact time. Comparison with the major products of reaction can be made. The reaction has been found to be first order with respect to n-C$_7$ [36]. It clearly appears that single-branched isomers are intermediates of reaction, going through a maximum characteristic of successive reactions. Multibranched isomers are secondary products going through another maximum leading to cracked products. Multibranched products only appear once single ones are formed. The same process is observed for cracked products with respect to multibranched ones.

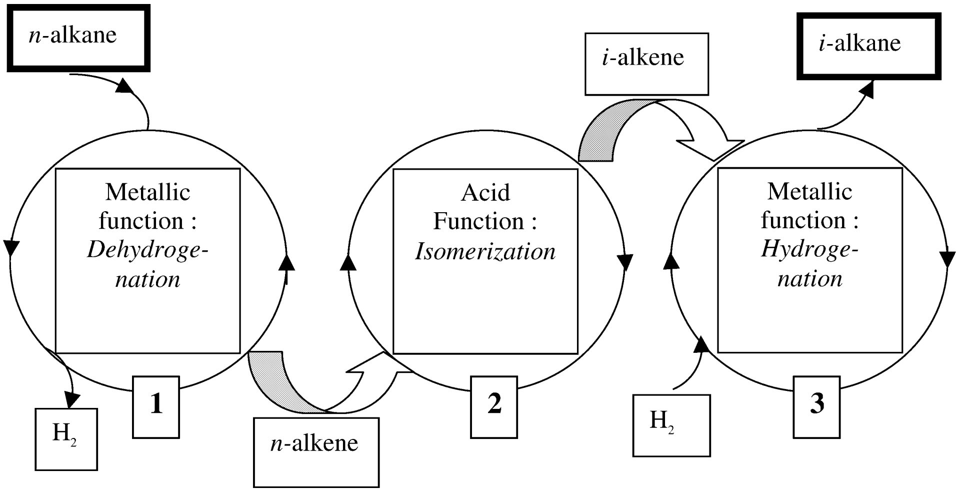


Fig. 2. Isomerization of n-alkane over an acid site *assisted* by a (de)hydrogenation metallic function over a bifunctional catalyst [32–35].

There are three kinetic approaches:

- If we only consider the kinetics of *consumption of* n-C_7 (Fig. 3), we shall get information on cycle 1, as n-C_7 is only concerned with cycle 1. Nevertheless, as we shall see, the *assisted process* will cause the rate of disappearance of cycle 1 to become that of cycle 2.
- If we consider the *global transformation of* n-C_7 to i-C_7, without looking at the distribution of isomers, we clearly start with cycle 1 (n-C_7) to achieve the reaction with cycle 3 (i-C_7). Nevertheless, the isomerization process occurs in cycle 2, which will give the rate for the whole process as long as cycles 1 and 2 turn over rapidly: this is the kinetic significance of optimizing the balance between (de)hydrogenation and acid activities of the bifunctional catalyst [34,35].
- If we now consider the global *isomer distribution* within mono- and multibranched compounds (Fig. 3), cycle 2 is concerned more specifically. The products detected at the outlet of the reactor in Fig. 3 are hydrogenated, and cycle 3 must be involved in the reaction. Cycle 3 must, however, turn over rapidly for hydrogenating iso-olefins as soon as they form.

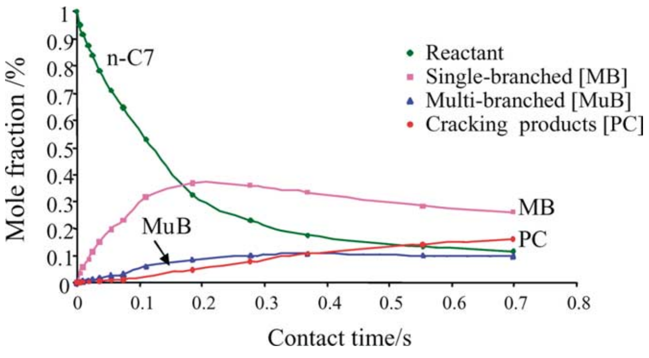


Fig. 3. Isomerization of n-heptane over an oxycarbide of tungsten $W_2C_{0.80}O_{0.68}$ at 623 K, under 0.6 MPa H_2 [36].

Let us go into greater detail in the reaction. It will permit us to link global kinetic data with the corresponding sequence of elementary steps. The global reaction for n-heptane isomerization, one of the model compounds for gasoline, is

$$n\text{-}C_7 = i\text{-}C_7. \tag{10}$$

The three cycles (Fig. 2) involve metallic (*) and acid sites ($\diamond H^+$). They can be described by a series of three sequences of elementary steps.

3.1.1. 1st cycle: dehydrogenation of n-heptane to n-heptene (n-C7=) over a metallic site

The net reaction for this cycle is

$$n\text{-}C_7 = n\text{-}C_7{}^{=} + H_2 \tag{11}$$

$$\begin{array}{llll}
 & & & \sigma_i \\
[1] & n\text{-}C_7 + 2^* \rightleftarrows {}^*n\text{-}C_7{}^{=\,*} + H_2 & K_1 & 1 \\
[2] & {}^*n\text{-}C_7{}^{=\,*} \rightleftarrows n\text{-}C_7{}^{=} + 2^* & K_2 & 1
\end{array}$$

Thermodynamics tells us that the *experimental* ratio n-$C_7{}^{=}/n$-C_7 is generally near equilibrium (about 0.5% under 0.6 MPa H_2, at 623 K). This means that the *1st cycle is near equilibrium*, and correspondingly, the two steps can be treated using their equilibrium constants for calculating the intermediate concentrations. Nevertheless, this cycle presents a rate of consumption of n-C_7 (Fig. 3). Taking into account the fact that n-C_7 is only consumed in cycle 1, the cycle turns over quite rapidly *to restore the equilibrium*, once n-$C_7{}^{=}$ has been consumed by the second cycle (Fig. 2). Cycle 1 has *intrinsically* a very high turnover rate, which leads rapidly to thermodynamic equilibrium. Consequently, it can be concluded that *the rate of disappearance of* n-C_7 *must be that of cycle* 2 *consuming the olefin*. Disregarding the hydrogenolysis of n-C_7 leading to minor products, and the formation of some alkyl-cyclopentane isomers over metallic sites, Fig. 3 corresponds to the consumption of the reactant, *on metallic sites* (*cycle* 1), simultaneously with the formation of monobranched, multibranched, and cracking products, *on acid sites* (cycle 2). It can be seen that the disappearance of the reactant corresponds, within the limits previously described, to the formation of isomers and products of cracking occurring on the acid sites.

3.1.2. *2nd cycle: isomerization of* n-$C_7^=$ *over acid sites* ($\diamond H^+$)

The global reaction of cycle 2 is

$$n\text{-}C_7^{=} = i\text{-}C_7^{=}. \tag{12}$$

The sequence can be described as follows:

			σ_i
[3]	$n\text{-}C_7^{=} + \diamond H^+ \overset{\circ}{\rightleftarrows} \diamond n\text{-}C_7^+$	K_3	1
[4]	$\diamond n\text{-}C_7^+ \twoheadrightarrow \diamond i\text{-}C_7^+$	k_4	1
[5]	$\diamond i\text{-}C_7^+ \overset{\circ}{\rightleftarrows} i\text{-}C_7^{=} + \diamond H^+$		1

Olefin protonation, step [3], is near equilibrium and leads to the formation of the adsorbed carbenium ion $\diamond n\text{-}C_7^+$. Step [4] is far equilibrium and is therefore the rate-determining step. It could possibly be a "two-way" elementary step. For the sake of simplicity, it will be considered as a "one-way" step. It is clear that since the rds is a one-way step, *the kinetic law will not "see" the nature of isomers, as the step does not "come back." This is the reason why this kinetic approach will only lead to the global isomerization of* n-$C_7^=$.

3.1.3. *3rd cycle: hydrogenation of* i-$C_7^=$ *over metallic sites* (*)

The net reaction is

$$i\text{-}C_7^{=} + H_2 = i\text{-}C_7. \tag{13}$$

The cycle follows a four-step Horiuti–Polanyi sequence [1].

		σ_i
[6]	$H_2 + 2^* \overset{\circ}{\rightleftarrows} 2^*H$	1
[7]	$i\text{-}C_7^{=} + 2^* \overset{\circ}{\rightleftarrows} {}^*i\text{-}C_7^{=}{}^*$	1
[8]	${}^*i\text{-}C_7^{=}{}^* + {}^*H \rightarrow {}^*i\text{-}C_7H + 2^*$	1
[9]	${}^*i\text{-}C_7H + {}^*H \rightarrow i\text{-}C_7 + 2^*$	1

3.1.4. *Kinetics of first cycle*

Experimentally, the reaction is first order related to n-C_7. As the cycle is near equilibrium when n-olefin is consumed by cycle 2, cycle 1 restores the equilibrium concentration of n-olefin. We have no access to the intrinsic turnover rate of cycle 1 if it is higher than that of cycle 2. We must demonstrate that the global kinetics of isomerization, which is linked to the consumption of the reactant, is first order with respect to n-C_7.

3.1.5. *Global kinetics of isomerization: concept of two-step catalytic reaction* [1]

The isomerization reaction occurs on acid sites. Therefore, the balance on active sites will be made on this kind of site (metallic sites are not considered for the kinetic law, if they are very active). As step [4] is the rds, far from equilibrium, this global kinetic law of isomerization does not "see" isomers. Therefore, the whole kinetics can be simplified to the two following steps:

[10]	$n\text{-}C_7 + \diamond H^+ =\!\!\circ\!\!= \diamond n\text{-}C_7^+ + H_2$	K_{10}
[4]	$\diamond n\text{-}C_7^+ \twoheadrightarrow \ldots$	k_4

Step [10] is global; it is the sum of steps [1]–[3]. Therefore $K_{10} = K_1K_2K_3$. Step [10] produces the *mari* and step [4] consumes it. Applying the general method for obtaining the rate law, it is easy to obtain the following equation (14),

$$r = \frac{[L]k_4K_{10}[n\text{-}C_7]/[H_2]}{1 + (K_{10}[n\text{-}C_7]/[H_2])}, \tag{14}$$

where [L] is the density of *acid* sites.

The ratio on the right-hand side of (14) is a generalized Langmuir adsorption isotherm that can be approximated by means of [1]

$$\bigl(K_{10}[n\text{-}C_7]\big/[H_2]\bigr)^{\alpha} \tag{15}$$

with $0 \leqslant \alpha \leqslant 1$. Hence,

$$r = k_4[L]\bigl(K_{10}[n\text{-}C_7]\big/[H_2]\bigr)^{\alpha}, \tag{16}$$

with $0 \leqslant \alpha \leqslant 1$. Experimentally, it was found that $\alpha = 1$ for the reaction reported in Fig. 3.

3.1.6. *Kinetics of cycle 2*

Single- and multibranched isomers and products of cracking are reported in Fig. 3. They are the major products formed in cycle 2. n-Heptene is not present due to its very low concentration regulated by thermodynamics. n-Heptane is reported but it pertains only to cycle 1. Nevertheless, the meaning of this n-C_7 plot is that the kinetics of consumption of n-heptane in cycle 1 is driven by cycle 2.

The kinetic evolution of isomer concentrations versus contact time is that of successive reactions. This is in agreement with Guisnet et al. [35].

3.2. *Assisted decomposition of NO by a hydrocarbon in the presence of an excess of dioxygen*

Another clear example of assisted catalysis is the deNO$_x$ reaction, in lean burn conditions, over an oxide-supported transition metal cation. Berger [37] and Gorce [38] have proposed a detailed mechanism of the *assisted decomposition of NO* by a hydrocarbon in the presence of an excess of oxygen. It was concluded that three different catalytic features were needed to ensure the removal of NO$_x$. The first feature allowed the decomposition of NO to N_2, whereas the two other features allowed the oxidation of NO to NO_2 and the partial oxidation of the hydrocarbon via NO_2. In such a mechanism, the partially oxidized hydrocarbons finally achieve their complete oxidation when reacting with the oxygen left over from NO decomposition. Fig. 4 reports the general scheme for such a reaction. The three functions

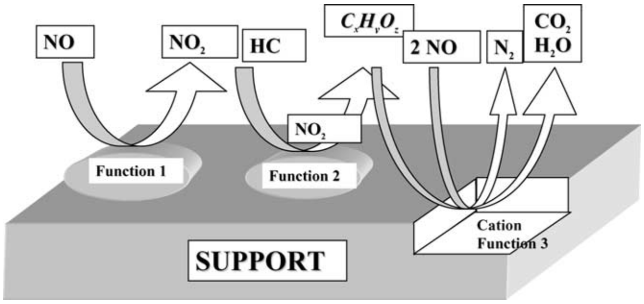


Fig. 4. A general model for a three-function deNO$_x$ catalyst [37,38].

correspond to three catalytic cycles *with no kinetic coupling*.

The kinetics of this system have not yet been done.

4. Kinetic coupling *in* and *between* catalytic cycles

4.1. Kinetic coupling between catalytic cycles. General definition

An ensemble of rate constants can represent a kinetic coupling. Fig. 5 reports a general case.

Intermediate$_{\text{ads}}$ pertains to three catalytic cycles. The first leads to its formation with rate constant $k_{\text{formation}}$. This adsorbed intermediate now has four possibilities. It can return to the first cycle, if the corresponding step is two-way (go and return). It can desorb if $k_{\text{desorption}}$ is considerable enough related to the three other rate constants. It can continue to react in two other cycles *kinetically coupled*, to produce P_1 and P_2. The selectivity will be given by the ratio P_1/P_2. When the two first elementary steps characterized by $k_1^{(1)}$ and $k_1^{(2)}$ are considered, selectivity is given by the ratio of the two corresponding rates, i.e., by the ratio of the corresponding two rate constants. This is valid as long as $P^{(1)}$ and $P^{(2)}$ do not transform into each other. That is often the case in hydrotreating.

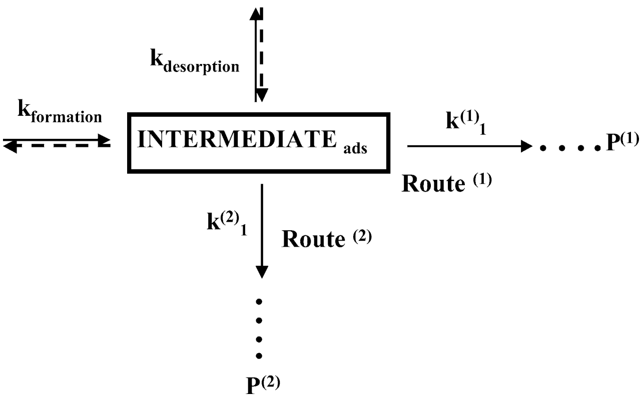


Fig. 5. Ensemble of rate constants for regulating the selectivity of reactions.

4.2. *Kinetic coupling in coupled catalytic cycles* [39]

The effect of hydrogen pressure on enantiomeric selectivity for hydrogenation of an alkene in the presence of a soluble organometallic chiral catalyst has been studied in Halpern's laboratory [40–43]. These data have led Boudart and Djéga-Mariadassou [39] to show the importance of kinetic coupling in shifting selectivity with pressure when two catalytic cycles are coupled in two parallel reactions.

4.2.1. Coupled catalytic cycles

The alkene is labeled “O” and the two catalytic cycles are coupled through “*” (Fig. 6). They are treated as two-step catalytic reactions.

They lead to two enantiomers labeled L and R respectively for left and right cycles (Fig. 6). Two *mari* have been assumed, $^*\mathrm{O}^{\mathrm{L}}$ and $^*\mathrm{O}^{\mathrm{R}}$. The surprising feature is that the major active intermediate $^*\mathrm{O}^{\mathrm{L}}$ leads to the minor product P^{L}, whereas the minor intermediate $^*\mathrm{O}^{\mathrm{R}}$ leads to the major enantiomer P^{R}.

The total concentration of active sites is

$$[\mathrm{L}] = [^*] + \left[^*\mathrm{O}^{\mathrm{L}}\right] + \left[^*\mathrm{O}^{\mathrm{R}}\right]. \tag{17}$$

4.2.2. Case of medium hydrogen pressure

Let us define:

- ${r_1}^{\mathrm{L}}$, ${r_{-1}}^{\mathrm{L}}$ and ${r_1}^{\mathrm{R}}$, ${r_{-1}}^{\mathrm{R}}$ the forward and reverse rates of the left and right first steps of the two coupled cycles (Fig. 6)
- ${r_2}^{\mathrm{L}}$ and ${r_2}^{\mathrm{R}}$ the second step rates.

Applying the QSSA, we obtain

$${r_1}^{\mathrm{L}} - {r_{-1}}^{\mathrm{L}} = {r_2}^{\mathrm{L}} \quad \text{and} \quad {r_1}^{\mathrm{R}} - {r_{-1}}^{\mathrm{R}} = {r_2}^{\mathrm{R}}. \tag{18}$$

This leads to

$$\frac{[^*\mathrm{O}^{\mathrm{L}}]}{[^*\mathrm{O}^{\mathrm{R}}]} = \frac{{k_1}^{\mathrm{L}}}{{k_1}^{\mathrm{R}}} \frac{{k_{-1}}^{\mathrm{R}} + {k_2}^{\mathrm{R}}[\mathrm{H}_2]}{{k_{-1}}^{\mathrm{L}} + {k_2}^{\mathrm{L}}[\mathrm{H}_2]}. \tag{19}$$

The selectivity is the ratio of overall rates:

$$\frac{[\mathrm{P}^{\mathrm{R}}]}{[\mathrm{P}^{\mathrm{L}}]} = \frac{{k_2}^{\mathrm{R}}}{{k_2}^{\mathrm{L}}} \frac{{k_1}^{\mathrm{R}}}{{k_1}^{\mathrm{L}}} \frac{{k_{-1}}^{\mathrm{L}} + {k_2}^{\mathrm{L}}[\mathrm{H}_2]}{{k_{-1}}^{\mathrm{R}} + {k_2}^{\mathrm{R}}[\mathrm{H}_2]} = \frac{r^{\mathrm{R}}}{r^{\mathrm{L}}}. \tag{20}$$

4.2.3. Case of low hydrogen pressure

At low pressure, in each cycle, ${r_{-1}}^{\mathrm{L}} \gg {r_2}^{\mathrm{L}}$ and ${r_{-1}}^{\mathrm{R}} \gg {r_2}^{\mathrm{R}}$; i.e., $^*\mathrm{O}^{\mathrm{L}}$ and $^*\mathrm{O}^{\mathrm{R}}$ accumulate on the surface. Since ${r_1}^{\mathrm{L}} > {r_{-1}}^{\mathrm{L}}$ and ${r_1}^{\mathrm{R}} > {r_{-1}}^{\mathrm{R}}$ for the reaction to proceed, at low pressure we have ${r_1}^{\mathrm{L}}, {r_{-1}}^{\mathrm{L}} \gg {r_2}^{\mathrm{L}}$ and ${r_1}^{\mathrm{R}}, {r_{-1}}^{\mathrm{R}} \gg {r_2}^{\mathrm{R}}$. These inequalities tell us that the first steps are near equilibrium (see Section 2.1, the arrow scheme), and steps 2 are the *rds* in each cycle (Fig. 6b).

Therefore,

$${k_{-1}}^{\mathrm{L}} \gg {k_2}^{\mathrm{L}}[\mathrm{H}_2] \quad \text{and} \quad {k_{-1}}^{\mathrm{R}} \gg {k_2}^{\mathrm{R}}[\mathrm{H}_2],$$

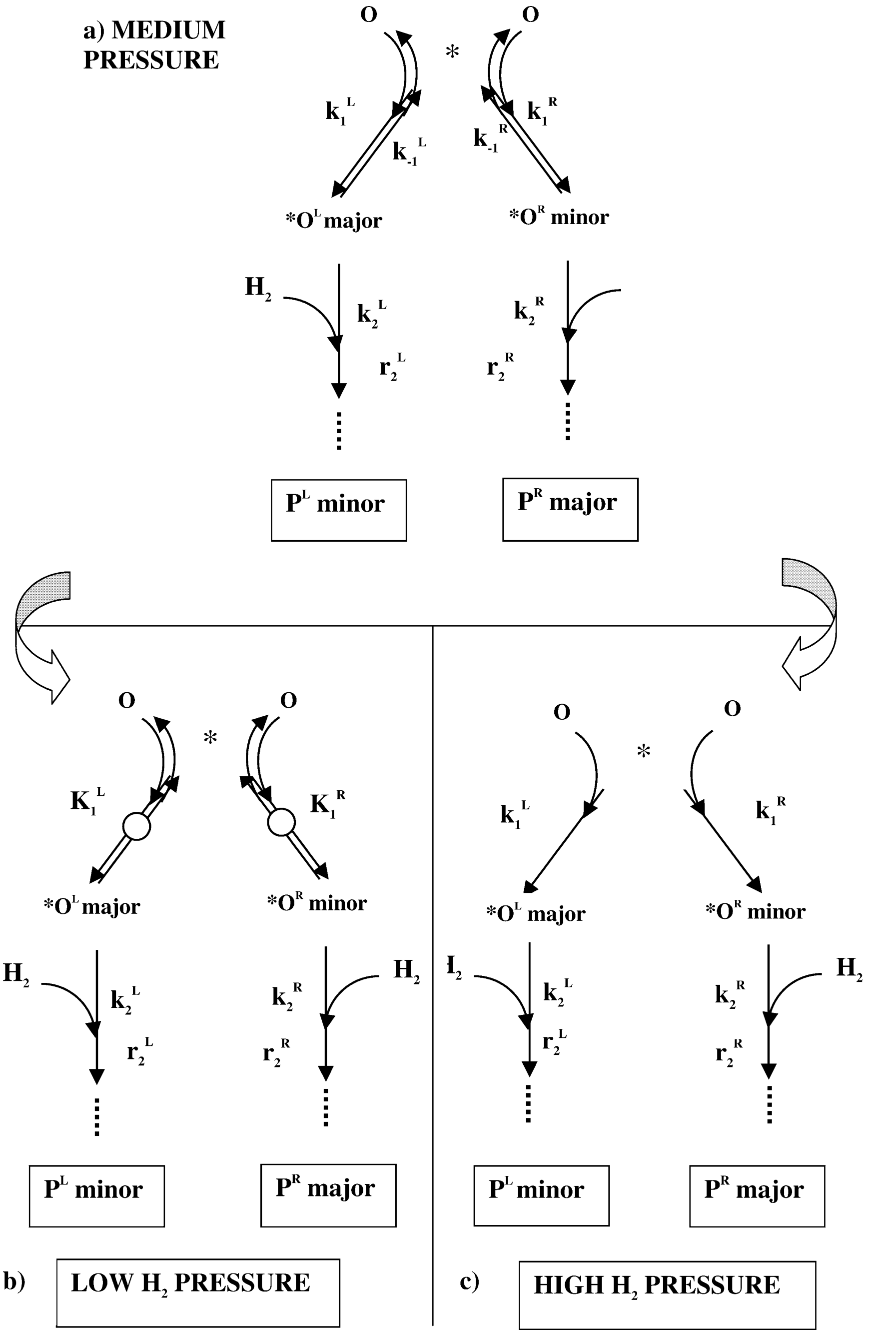


Fig. 6. Scheme of the coupled catalysis cycles for hydrogenation of an alkene (O) in the presence of a soluble organometallic chiral catalyst (*). $K_1{}^R = k_1{}^R/k_{-1}{}^R$; $k_1{}^R$ and $k_{-1}{}^R$ being the forward and reverse rate constant of the step respectively. $K_1{}^L = k_1{}^L/k_{-1}{}^L$; $k_1{}^L$ and $k_{-1}{}^L$ being the forward and reverse rate constant of the step respectively.

and (20) transforms to

$$\frac{[P^R]}{[P^L]} = \frac{k_2{}^R}{k_2{}^L}\frac{K_1{}^R}{K_1{}^L}, \qquad \text{(20bis)}$$

whereas (19) transforms to

$$\frac{[{}^*O^L]}{[{}^*O^R]} = \frac{K_1{}^L}{K_1{}^R}. \qquad \text{(19bis)}$$

$[P^R]/[P^L] = 54.8$ and $[{}^*O^L]/[{}^*O^R] = 10.6$ according to kinetic parameters from Landis and Halpern [40].

4.2.4. At high hydrogen pressure

$k_{-1}{}^L \ll k_2{}^L[H_2]$ and $k_{-1}{}^R \ll k_2{}^R[H_2]$; the kinetic coupling *in* each cycle is such that steps 2 “pump away” more and more $^*O^L$ and $^*O^R$ intermediates. In such a case $r_2{}^L \gg r_{-1}{}^L$ and $r_2{}^R \gg r_{-1}{}^R$ and steps 1 now become “one-way” reactions (Fig. 6c). Consequently, $r_1{}^L = r_2{}^L$ and $r_1{}^R = r_2{}^R$.

Selectivity transforms to

$$\frac{[P^R]}{[P^L]} = \frac{k_1{}^R}{k_1{}^L} \qquad \text{(20ter)}$$

and

$$\frac{[{}^*\mathrm{O}^\mathrm{L}]}{[{}^*\mathrm{O}^\mathrm{R}]} = \frac{k_1{}^\mathrm{L} k_2{}^\mathrm{R}}{k_1{}^\mathrm{R} k_2{}^\mathrm{L}}. \tag{19ter}$$

$[\mathrm{P}^\mathrm{R}]/[\mathrm{P}^\mathrm{L}] = 2$ and $[{}^*\mathrm{O}^\mathrm{L}]/[{}^*\mathrm{O}^\mathrm{R}] = 280$ according to kinetic parameters from Landis and Halpern [43].

It must be noted that selectivity does not depend on hydrogen pressure at both low and high pressure, but it does depend on pressure between low and high pressure. Kinetic coupling *in* and *between* catalytic cycles clearly justifies why $[{}^*\mathrm{O}^\mathrm{L}]_\mathrm{major}$ leads to $[\mathrm{P}^\mathrm{L}]_\mathrm{minor}$ and $[{}^*\mathrm{O}^\mathrm{R}]_\mathrm{minor}$ leads to $[\mathrm{P}^\mathrm{R}]_\mathrm{major}$. As can be seen more particularly at high pressure, rate constants of the second steps play a very important role in the consumption of the *mari*.

The methodology used in this paper has introduced assumptions of quasi-equilibria, rds, mari, kinetic coupling, and assisted catalytic processes [1], etc., which appear as a result of Dumesic et al. microkinetics methodology requiring no new assumptions [2].

5. Conclusion

Application of the quasi-steady state approximation to catalysis has led to a method for determining rate equations in complex catalytic reactions. A computational program such as Chemkin Surface is based on this theory. A catalytic reaction corresponds to a set of i elementary steps. It is a closed sequence that can be represented by a catalytic cycle. The rate of a catalytic cycle is given by the net rate of an i step divided by its stoichiometric number σ_i. There is a compensation effect between the concentration of an adsorbed species and its associated rate constant which regulates the turnover rate of the catalytic cycle. In a closed sequence, elementary steps can be near or far from equilibrium. In many cases two-step catalytic reactions can be defined.

Several catalytic cycles can participate in a reaction. If there is no common adsorbed intermediate, an “assisted catalytic process” can be defined. This is the case in alkane isomerization (bifunctionality) and in reduction of NO in the presence of a hydrocarbon in lean conditions.

If the same adsorbed species pertains to different catalytic cycles defining various reaction routes, there is a kinetic coupling of the corresponding catalytic closed sequences. As the concentration of the adsorbed species is the same for all routes, *the unique driving force of the system remains as the rate constants*. Selectivity depends on the relative values of rate constants, which also depend on temperature.

Acknowledgments

We greatly acknowledge the editors for inviting us to contribute to this 40th birthday celebration issue. G.D.M. also thanks his collaborators, W. Nicholas Delgass for helpful discussions, and Michel Che, who willfully encouraged him to participate in this paper.

References

[1] M. Boudart, G. Djéga-Mariadassou, Cinétique des Réactions en Catalyse Hétérogène, Masson et Cie, Paris, 1982;
M. Boudart, G. Djéga-Mariadassou, Kinetics of Heterogeneous Catalytic Reactions, Princeton University Press, Princeton, NJ, 1984.
[2] J.A. Dumesic, D.F. Rudd, L.M. Aparicio, J.E. Rekoske, A.A. Trevino, The Microkinetics of Heterogeneous Catalysis, in: ACS Professional Reference Book, American Chemical Society, Washington, DC, 1993.
[3] I. Manuel, C. Thomas, C. Bourgeois, H. Colas, N. Matthess, G. Djéga-Mariadassou, Catal. Lett. 77 (2001) 193;
I. Manuel, Doctoral thesis, Université Pierre et Marie Curie, Paris, 2002.
[4] S.H. Oh, C.C. Eickel, J. Catal. 128 (1991) 526.
[5] C.H.F. Peden, D.W. Goodman, D.S. Blair, P.J. Berlowitz, G.B. Fisher, S.H. Oh, J. Phys. Chem. 92 (1988) 1563.
[6] N.W. Cant, W.K. Hall, J. Catal. 54 (1978) 372.
[7] Y. Yu, J. Catal. 87 (1984) 152.
[8] R. Burch, P.J. Millington, A.P. Walker, Appl. Catal. B 4 (1994) 65.
[9] G. Ertl, M. Neumann, Z. Phys. Chem. (N.F.) 90 (1974) 127.
[10] G. Djéga-Mariadassou, F. Fajardie, J.F. Tempère, J.M. Manoli, O. Touret, G. Blanchard, J. Mol. Catal. A 161 (2000) 179.
[11] K. Tamaru, Dynamic Heterogeneous Catalysis, Academic Press, London, 1978.
[12] H.L. Gruber, J. Phys. Chem. 66 (1962) 48.
[13] J.E. Benson, M. Boudart, J. Catal. 4 (1965) 704.
[14] Y. Barbaux, B. Roger, J.P. Beaufils, J. Germain, J. Chim. Phys. 67 (1970) 1035;
M.A. Vannice, J.E. Benson, M. Boudart, J. Catal. 16 (1970) 348.
[15] P.H. Emmett, S. Brunauer, J. Am. Chem. Soc. 59 (1937) 310 and 1553.
[16] W.A. Pliskin, R.P. Eischen, Adv. Catal. Relat. Subj. 10 (1958) 1.
[17] D.J.C. Yates, J.H. Sinfelt, J. Catal. 8 (1967) 348.
[18] T.A. Dorling, R.L. Moss, J. Catal. 7 (1966) 378.
[19] R.F. Baddour, M. Modell, U.K. Heusser, J. Phys. Chem. 72 (1968) 3621.
[20] D. Cormack, R.L. Moss, J. Catal. 13 (1969) 1.
[21] Y.L. Lam, M. Boudart, J. Catal. 50 (1977) 530.
[22] T.J. Osinga, B.G. Linsen, W.P. Van Beek, J. Catal. 7 (1967) 277.
[23] J.J.F. Scholten, J.A. Konvalinka, Trans. Faraday Soc. 65 (1969) 2465.
[24] B. Echevin, S.J. Teichner, Bull. Soc. Chim. Fr. (1975) 1487.
[25] F. Fajardie, J.F. Tempère, G. Djéga-Mariadassou, G. Blanchard, J. Catal. 163 (1996) 77.
[26] L. Salin, C. Potvin, J.F. Tempère, M. Boudart, G. Djéga-Mariadassou, J.M. Bart, Ind. Eng. Chem. Res. 37 (1998) 4531.
[27] J.J.F. Scholten, in: B. Delmon, P. Grange, P. Jacobs, G. Poncelet (Eds.), Preparation of Catalysts, II, Elsevier, Amsterdam, 1979, p. 685.
[28] M. Boudart, in: H. Eyring (Ed.), Physical Chemistry, Vol. 7, Academic Press, New York, 1975, p. 362.
[29] T. Engel, G. Ertl, Chem. Phys. Lett. 54 (1978) 95.
[30] T. Engel, G. Ertl, J. Chem. Phys. 69 (1978) 1267.
[31] H. Conrad, G. Ertl, J. Kuppers, Surf. Sci. 76 (1978) 323.
[32] J.H. Sinfelt, H. Hurwitz, J.C. Rohrer, J. Phys. Chem. 64 (1960) 892.
[33] M. Boudart, in: Kinetics of Chemical Processes, Prentice-Hall, Englewood Cliffs, NJ, 1968, p. 240, reissued by Butterworth-Heinemann, Stoneham, England, 1991.
[34] F. Ribeiro, C. Marcilly, M. Guisnet, J. Catal. 78 (1982) 267.
[35] M. Guisnet, F. Alvarez, G. Giannetto, G. Pérot, Catal. Today 1 (1987) 410.
[36] T.L.H. Pham, Doctoral thesis, Université Pierre et Marie Curie, Paris, 2002.
[37] M. Berger, Doctoral thesis, Université Pierre et Marie Curie, Paris, 1988.
[38] O. Gorce, Doctoral thesis, Université Pierre et Marie Curie, Paris, 2001.
[39] M. Boudart, G. Djéga-Mariadassou, Catal. Lett. 29 (1994) 7.
[40] J. Halpern, D.P. Riley, A.S.C. Chan, J.J. Pluth, J. Am. Chem. Soc. 99 (1977) 8055.
[41] J. Halpern, Science 217 (1982) 401.
[42] J. Halpern, Pure Appl. Chem. 55 (1983) 99.
[43] C.R. Landis, J. Halpern, J. Am. Chem. Soc. 109 (1987) 1746, 6217.