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On the use of the first-order approximation in the kinetic analysis of TPR profiles

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Abstract

A theoretical investigation was carried out on the analysis of TPR profiles by the power-law kinetic model. Attention was focused on the use of the first-order approximation, with the aim to assess its limits in the procedure for estimating the activation energy of reduction. Numerical simulations performed by solving the non-isothermal mass-balance equations for the gaseous and solid species indicated a high sensitivity of the reduction patterns to the reaction order with respect to the solid. This quantity was found to exert a considerable influence on both the temperature at peak maximum and the peak shape.

A large number of TPR profiles was generated, assuming reaction orders other than unity and activation energies ranging from 80 to 100 kJ mol^{-1}. These profiles were interpreted by means of the first-order power-law model. The results obtained showed that the unjustified assumption of the first-order approximation may introduce significant errors in the estimate of the activation energy. In several cases, real and estimated values differed by more than 30%. In order to provide some guidelines for a correct kinetic analysis, the causes responsible for such misinterpretation were investigated from both a qualitative and quantitative point of view.

Keywords: Kinetic analysis; Power-law model; Reduction kinetics; Temperature-programmed reduction

Nomenclature and units

A	reactor cross-sectional area/cm^2
c	hydrogen concentration/μmol cm^{-3}

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E_a	activation energy/kJ mol^{-1}
F	volumetric flow-rate/cm^3 s^{-1}
H	peak asymmetry
k	rate constant/cm^3 μmol^{-1} s^{-1}
k_0	pre-exponential factor/cm^3 μmol^{-1} s^{-1}
L	reactor length/cm
m	reaction order with respect to hydrogen
N	number of experimental points
q	reaction order with respect to solid
r	reaction rate/μmol cm^{-3} s^{-1}
R	universal gas constant/J mol^{-1} K^{-1}
s	amount of solid per unit volume of reactor/μmol cm^{-3}
S	solid amount/μmol
t	time/s
T	temperature/K
V	reactor volume/cm^3
W	peak width at half height/K
z	axial coordinate/cm

Greek symbols

β	heating rate/K s^{-1}
ε	percentage error (Eq. (15))
ξ	hydrogen consumption rate/μmol s^{-1}
Φ	objective function (Eq. (14))/μmol^2 s^{-2}

Subscripts

calc	calculated
exp	experimental
M	peak maximum
0	initial or inlet

1. Introduction

Temperature-programmed reduction (TPR) is a powerful thermoanalytical technique for the characterization of reducible solids. Since its first appearance in 1975, this technique has been applied in a variety of scientific fields, including coal chemistry, corrosion science and heterogeneous catalysis [1–3]. In this latter area, TPR is now becoming a very important analytical tool, due to its high sensitivity and simplicity. Moreover, reduction experiments can be performed under conditions close to those experienced by the catalyst in its industrial use. This fact makes chemical and structural information derived from TPR measurements more valuable than data obtainable from experiments performed under controlled analytical conditions such as high vacuum or inert atmospheres.

Quantitative analysis of TPR profiles is quite a demanding task because of the possible occurrence of mass-transfer limitations interfering with chemical kinetics, and for the need to provide an appropriate kinetic description for the reduction process. The influence of transport phenomena on the intrinsic chemical kinetics has been extensively investigated [4,5] and relationships have been developed to diagnose the presence of diffusional limitations, based on the concepts of the effectiveness factor and mass-transfer coefficient [6,7]. It should be noted that interferences induced by diffusional effects or axial dispersion within the reactor can be avoided or, at least, minimized by proper design of TPR experiments. In particular, the particle size and flow conditions have been proved to be the most important factors to take into consideration [8,9]. Similarly, the choice of an adequate kinetic expression always represents a critical step, due to the lack of rigorous selection criteria [10–12].

Because of the complexity of the reduction process, no generally applicable model exists. The basic models which have been postulated and used for the analysis of gas–solid reacting systems include the homogeneous model, the sharp interface model, the nucleation model, the grain model and the crackling core model [13, 14]. Each of them provides a more or less detailed description of only some of the phenomena taking place in the reactor. Furthermore, in their original derivations they do not account for changes in the structural properties of the solid that may accompany the reduction process [15].

The model used most in temperature-programmed reduction, particularly in the absence of a detailed knowledge of the mechanism of reaction, is the homogeneous, or power-law, model [3]. Its great popularity relies on the fact that, despite its simplicity, it can be considered a good approximation of more sophisticated models and thus can be used for a rough estimation of kinetic parameters. This model assumes that the reaction between the reducing gas and the reducible species occurs uniformly throughout the solid and that the reaction rate (r) can be expressed as

$$r = kc^m s^q$$

where c is the concentration of gaseous species, s is the amount of solid per unit volume of reactor, and m, q are the two reaction orders.

In most of the literature dealing with the kinetic analysis of TPR profiles, both reaction orders are assumed to be unity [7, 16–18]. Although this assumption greatly simplifies the procedure for determining the activation energy of reduction, which is by far the most meaningful parameter characterizing the reducibility of a solid, it does not reflect a general feature of gas–solid reacting systems. Reaction orders with respect to the solid phase are frequently fractional [19]. Therefore the accuracy of the kinetic analysis may be completely lost if the first-order approximation is not fulfilled.

In this paper, an attempt is made to quantify the consequences of an unjustified assumption of first-order reactions on the estimate of the activation energy. The way in which the two reaction orders affect TPR profiles was investigated first. Then TPR peaks were generated assuming reaction orders other than unity. These profiles were analysed by a first-order kinetic expression and the resulting activation energy was compared with that used to generate the simulated TPR curves. For the simulation and analysis of profiles, the TPR device was treated as a plug-flow reactor [12]. As is well known, the possibility of modelling the real system by means of such a reactor configuration is not restricted to the case of low conversions, as occurs for the differential reactor scheme [5,12]. This makes the results reported here quite general and, hence, directly transposable to a variety of experimental situations.

2. Kinetic model of the reduction process

The kinetic model was developed by considering the heterogeneous reaction system as a semi-continuous Plug-Flow Reactor (PFR) in which the following reaction takes place

$$\mathrm{MeO} + \mathrm{H_2} \rightarrow \mathrm{Me} + \mathrm{H_2O}$$

where MeO and Me denote the metal oxide and the metal, respectively.

In this type of reactor, the concentrations of the different species, as well as the reaction rate, are assumed to vary monotonously in the axial direction and to be uniform in each section normal to the reactor axis [20]. A differential mass-balance for the hydrogen, and a finite mass-balance for the reducible species, over the reactor volume, yield the following equations

$$\frac{F}{A}\frac{\partial c(z,t)}{\partial z} + r(c,s,T) + \frac{\partial c(z,t)}{\partial t} = 0 \tag{1}$$

$$r(c,s,T) + \frac{\partial s(z,t)}{\partial t} = 0 \tag{2}$$

where F is the volumetric flow-rate, A is the cross-sectional area of the reactor, c is the hydrogen concentration, r is the reduction rate and s is the amount of the reducible species per unit volume of reactor.

The functional dependence of the reaction rate on the reactant concentrations can be expressed, according to the power-law model, as

$$r(c,s,T) = k(T)c^{m}s^{q} \tag{3}$$

where $k(T)$ is a temperature-dependent rate constant, for which the Arrhenius equation can be used

$$k(T) = k_0 \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \tag{4}$$

It should be stressed that the quantity c in Eq. (3) represents the hydrogen concentration at the gas–solid interface, and that this is equal to the bulk hydrogen concentration only if mass-transfer limitations in the gas phase are negligible. Under other conditions, the two quantities may be considerably different and an additional relation is needed to evaluate them separately.

It may be convenient to write the derivative $\partial s/\partial t$ in terms of the heating rate (β), as

$$\frac{\partial s(z,T)}{\partial t}=\frac{\mathrm{d}T}{\mathrm{d}t}\frac{\partial s(z,T)}{\partial T}=\beta\frac{\partial s(z,T)}{\partial T} \tag{5}$$

In a large number of practical situations, Eq. (1) can be further simplified by assuming quasi-steady-state conditions for the hydrogen. This hypothesis implies that the residence time of the gaseous phase within the reactor is much smaller than the characteristic reaction time. Under such conditions, Eq. (1) becomes

$$\frac{F}{A}\frac{\partial c(z,t)}{\partial z}+r(c,s,T)=0 \tag{6}$$

Finally, by substitution of Eqs. (3)–(5) into Eqs. (2) and (6), the following set of partial differential equations is obtained

$$\frac{F}{A}\frac{\partial c(z,t)}{\partial z}+k_0\exp\left(\frac{-E_a}{RT}\right)c(z,T)^m s(z,T)^q=0 \tag{7}$$

$$k_0\exp\left(\frac{-E_a}{RT}\right)c(z,T)^m s(z,T)^q+\beta\frac{\partial s(z,T)}{\partial T}=0 \tag{8}$$

The initial and boundary conditions associated with these equations are

$$c(0,T)=c_0 \quad \text{for } T\geq T_0 \tag{9}$$

$$s(z,T_0)=s_0 \quad \text{for } 0\leq z\leq L \tag{10}$$

where c_0 is the hydrogen concentration at the reactor inlet, s_0 is the initial amount of solid per unit volume of reactor, T_0 is the initial temperature and L is the reactor length. The solution of the two equations provides the functions

$$c=c(z,T) \tag{11}$$

$$s=s(z,T) \tag{12}$$

that describe how the hydrogen and the reducible solid concentrations vary during the reduction and along the reactor axis. The first relationship, calculated at $z=L$, gives the hydrogen concentration at the reactor outlet. The theoretical TPR profile, namely the temperature dependence of the hydrogen consumption rate (ξ), can then be easily obtained as

$$\xi(T)=F[c_0-c(L,T)] \tag{13}$$

3. Results and discussion

The partial differential equations expressing the mass-balance relationships for the two reactants over the TPR device were solved numerically by a fourth-order Runge–Kutta technique. Integration was carried out using a temperature step of 1 K and a z-axis step equal to $L/10$. Smaller steps were found to produce no variations in the results obtained.

A first series of numerical simulations was performed with the aim of quantifying the influence exerted by the two reaction orders on the peak shape and position. A large number of TPR profiles was then generated, for assigned values of the activation energy (in the range 80–100 kJ mol^{-1}) and of the reaction orders. These data were analysed by setting $m = q = 1$ in the model equations, in order to evaluate the effect of the first-order approximation on the estimated activation energy.

3.1. *Effect of reaction orders on peak shape and position*

Simulations were carried out using the values reported in Table 1. These values are close to those usually adopted in TPR experiments [11, 12]. The two reaction orders were varied between 0 and 2. Some results, showing the hydrogen consumption rate as a function of temperature, are presented in Fig. 1. The first plot is relative to $m = 1$, and shows the effect of q on TPR profiles. The second plot is relative to $q = 1$, and indicates the influence of m. Similar reduction patterns were obtained by considering different sets of values for the quantities listed in Table 1.

From Fig. 1, it clearly appears that TPR profiles are much more sensitive to q than to m: variations of m in the range from 0 to 2 cause only limited changes in the peak shape and position. In contrast, variations of q result in remarkable modifications of the reduction profile. The effects of decreasing q are a shift of the peak maximum towards higher temperatures, a decrease of the maximum hydrogen consumption rate, and a rather pronounced tailing of the profile.

For a better evaluation of such effects, the influence of the reaction orders on three parameters characterizing the TPR peak was investigated. The three TPR characteristics are:

- the temperature at peak maximum (T_M);
- the peak width at half-height (W);
- the peak asymmetry (H), defined so as to be equal to 1 for symmetric peaks, > 1 for left-tailed peaks and < 1 for right-tailed peaks (Fig. 2).

If the TPR peak is regarded as a probability distribution curve, T_M, W and H can be related to the moments of the corresponding probability density function [21]. The results obtained are reported in Table 2.

Table 1
Numerical values used in the computer simulations

Parameter	Numerical value
Volumetric flow-rate (F)	1 cm^3 s^{-1}
Hydrogen concentration at the reactor inlet (c_0)	2 μmol cm^{-3}
Reactor volume (V)	$6 \cdot 10^{-2}$ cm^3
Reactor cross-sectional area (A)	0.785 cm^2
Initial solid amount (S_0)	300 μmol
Heating rate (β)	0.1 K s^{-1}
Pre-exponential factor (k_0)	10^6 cm^3 μmol^{-1} s^{-1}
Activation energy (E_a)	90 kJ mol^{-1}

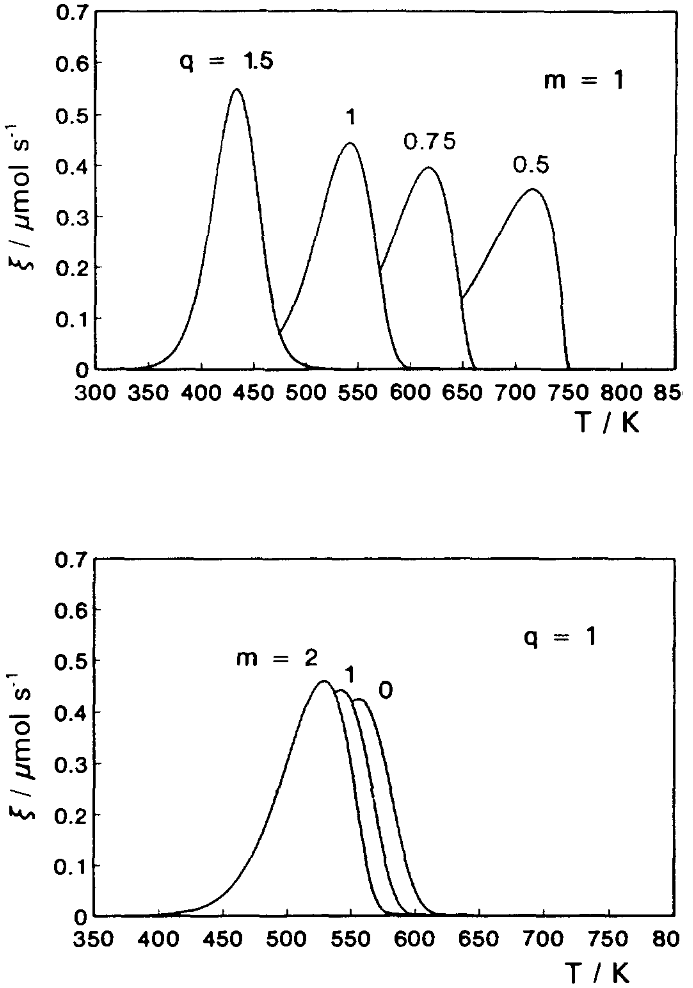

Fig. 1. Effect of reaction orders on the simulated TPR profiles (parameter values are listed in Table 1).

As can be observed, the temperature at which the reduction rate reaches a maximum, i.e. the peak position, is highly sensitive to q, whereas the effect of m is far less pronounced. Increases of m are accompanied by a decrease in T_M, i.e. by a shift of the reduction peak towards lower temperatures. For $m = 1$, an increase of q from 0.25 to 2 results in a decrease of T_M close to 500 K.

The peak width at half-height decreases as q is increased. Variations of q between 0.25 and 2 lead to decreases in width ranging from 39 K (for $m = 2$) to 49 K (for $m = 0$). For $0.25 < q < 1$, W increases as m decreases, whereas for $q \geq 1$, W is quite independent of m. Finally, the peak asymmetry exhibits a high sensitivity of q, particularly at lower q values. In the range $0.25 < q < 0.75$, the observed asymmetry is subjected to percentage variations close to 55%, whereas for $q > 0.75$ limited changes occur.

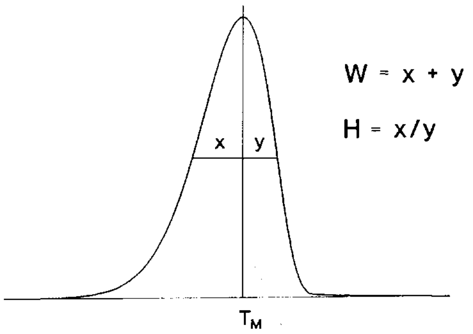

Fig. 2. Peak shape characterization: T_M is the temperature at peak maximum, W is the peak width at half height, and H is the peak asymmetry.

Table 2
Influence of reaction orders on the temperature at peak maximum (T_M), peak width (W) and asymmetry (H). Calculations were made using the values summarized in Table 1

	q					
m	0.25	0.5	0.75	1	1.5	2
			Temperature at peak maximum, T_M/K			
0	888	743	636	556	442	367
1	851	716	618	542	434	362
2	816	692	600	529	427	357
			Half-height peak width, W/K			
0	89	83	74	64	51	40
1	84	80	72	64	51	41
2	81	77	70	64	51	42
			Peak asymmetry, H			
0	3.45	2.19	1.55	1.37	1.04	1.00
1	3.94	2.20	1.77	1.46	1.13	1.05
2	4.06	2.35	1.80	1.56	1.32	1.10

Some trends of the functions $T_M(q)$, $W(q)$ and $H(q)$ are shown in Fig. 3. Because of the decreased sensitivity of T_M, W and H to m, only profiles relative to $m = 1$ have been plotted. These curves can be used to evaluate the sensitivity of TPR profiles to q for reaction orders with respect to the solid species different from those reported in Table 2. The plots also indicate the non-linear dependence of T_M, W and H on q, with the exception of the function $W(q)$ in the range $0.25 < q < 1.75$, which can be approximated by the linear relation: $W = 93.8 - 29.2\,q$.

All these considerations clearly demonstrate that the reaction order with respect to the solid phase plays a key role in determining the shape and position of the reduction peak. Thus we can suppose that if the reduction kinetics do not follow a first-order rate

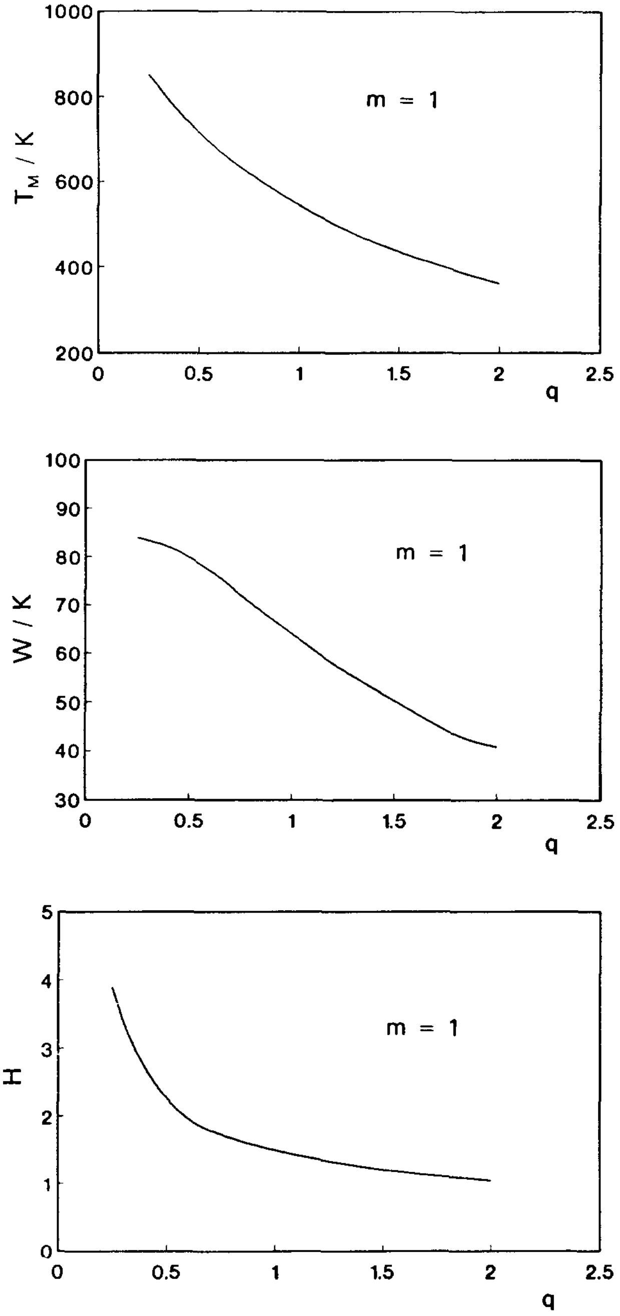

Fig. 3. Effect of reaction orders on T_M, W and H.

law and the two reaction orders are assumed to be unity, considerable errors may affect the estimate of the remaining kinetic parameters.

3.2. Estimation of the activation energy from TPR data

Simulated reduction patterns were generated assuming the reaction orders (m', q') and the activation energy (E'_a) listed in Table 3. The values of the remaining quantities were maintained unchanged and equal to those reported in Table 1. The simulated profiles were calculated using a temperature step of 2K, and the number of experimental points was close to 120.

In order to estimate the activation energy of reduction, these data were analysed by minimization of the following objective function

$$\Phi = \sum_{i=1}^{N} (\xi_{i,\mathrm{exp}} - \xi_{i,\mathrm{calc}})^2 \tag{14}$$

where N is the number of points relative to each simulated profile and ξ is the hydrogen consumption rate. The subscripts exp and calc denote simulated and calculated quantities, respectively. The estimates of the activation energy obtained by setting $m = q = 1$ in the model equations are summarized in Table 3, along with the percentage error ε defined as

$$\varepsilon = 100\frac{|E'_a - E_a|}{E'_a} \tag{15}$$

where E_a is the activation energy value for which Φ reaches a minimum.

Table 3

Influence of reaction orders on the estimated activation energy. The superscript ′ denotes values used to generate the simulated TPR profiles. E_a is the activation energy obtained by setting $m = q = 1$ in the model equations and ε is the percentage error (see Eq. (15))

Reaction orders				
m'	q'	E'_a/kJ mol^{-1}	E_a/kJ mol^{-1}	ε
1	0.5	90	120	33
1	1.5	90	71	21
1	2	90	59	34
0	1	90	93	3
0.5	1	90	91	1
1.5	1	90	89	1
2	1	90	88	2
1	0.5	80	107	34
1	1.5	100	79	21
1	2	100	65	35
0	0.5	90	125	39
2	2	90	58	36

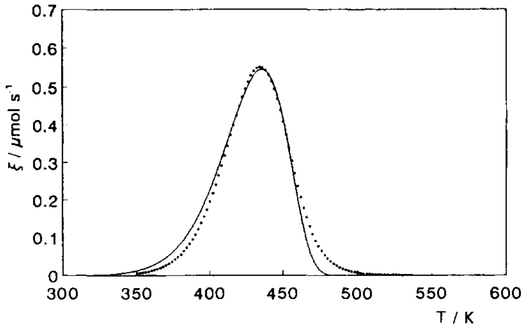

Fig. 4. Correlation of TPR profiles by the power-law model. Points represent data simulated by assuming $m = 1$ and $q = 1.5$. The solid line is the best-fit curve derived from the first-order approximation.

A comparison between the real and estimated activation energies indicates that the first-order approximation may introduce significant errors in the estimation procedure. The percentage differences between E'_a and E_a are in the range 1–39%. As expected, very limited errors ($\varepsilon < 3$) occur when TPR profiles relative to $m' \neq 1$ and $q' \neq 1$ are considered. The analysis of profiles with $m' = 1$ and $q' \neq 1$ leads to considerably larger errors ($21 < \varepsilon < 34$). Finally, the situation becomes even worse (percentage differences close to 40%) when both m' and q' are different from unity.

The explanation of these results is to be found in the influence of reaction orders on the peak shape and position. Due to the high sensitivity of the reduction patterns to q, a small variation of this quantity from unity produces a remarkable effect on the hydrogen consumption rates. The apparent activation energy obtained even by minimization of Φ gives values very different from the true ones. However, despite such a discrepancy, the experimental and calculated profiles may appear to be in fairly good agreement, as is shown in Fig. 4, where a typical example is reported. The points plotted in the figure were generated by setting $m' = 1$, $q' = 1.5$ and $E'_a = 90$ kJ mol^{-1} in the model equations. The best-fit curve was obtained using the first-order approximation, from which an activation energy of 71 kJ mol^{-1} was derived. Thus, despite the good quality of the correlation (the calculated temperature at the peak maximum is 436 K against 434 K and the corresponding hydrogen consumption rate is 0.54 μmol s^{-1} against 0.55 μmol s^{-1}), the percentage error in the estimate of the activation energy is more than 20%.

4. Conclusions

The results reported in the present study strongly demonstrate the need for verifying the hypothesis of unitary reaction orders prior to analysis of the temperature-programmed reduction kinetics by the simplified power-law model. This holds, in particular, for the reaction order with respect to the solid species, which was found to have a significant influence on the resulting reduction patterns. Particular care should thus be devoted to estimating the exact value of this quantity. The analysis of TPR profiles should involve a preliminary estimation of reaction orders, for instance by means of isothermal reduction experiments [22]. Alternatively, the two reaction orders could be evaluated, along with the activation energy, from a single TPR profile. This method requires a greater computational effort, due to an increased number of parameters to be estimated from the experimental data. In any case, a good fit between the experimental and calculated profiles does not provide a sufficient criterion to assess the reliability of the kinetic analysis, particularly if the comparison is restricted to the region around the peak maximum.

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