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ERRORS IN EVALUATION OF THE KINETIC PARAMETERS IN TEMPERATURE PROGRAMMED REDUCTION

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The possibility to determine the kinetic parameters for temperature programmed reduction of Cu/Fe_3O_4 using only one TPR profile is analyzed. The same data are analyzed both by Friedman's iso-conversional method and another one previously derived and published by the authors. One shows that taking into account the experimental restrictions of Monti and Baiker, the Friedman's method, although gives values of the activation energy smaller than the real values, indicates a very similar dependence of these on the reduction degree. On the basis of some synthetic data one shows that the errors are very large when these recommendations are neglected, being possible to determine a false dependence on the degree of reduction.

Keywords: *activation parameters, experimental parameters influence, iso-conversional method*

Introduction

Temperature programmed reduction (TPR) is an experimental method very often used to characterize the reducibility of some oxide catalysts. In most cases TPR is used to evidence the variations of the reducibility due to differences in composition, the preparation method or the applied pre-treatment. In literature there are many such works, but only a few papers report evaluations of the kinetic parameters.

Methods like those of Kissinger [1] or of Coats and Redfern [2] developed to analyze thermogravimetric data were applied to determine kinetic parameters of TPR data [3–7]. The fact that the position and even the shape of the TPR profiles are influenced by experimental parameters like the flow rate, the hydrogen concentration in the reducing mixture or the mass of the sample, was neglected in these cases. It was taken into account in other cases [8–10], when the activation parameters were evaluated by simulation, when the TPR profile is the result of two or more overlapping processes. In all these cases the results are very probably affected by errors either because the experimental parameters that influence the position and shape of the TPR peak were neglected or because only one single TPR profile has been used to determine by simulation the activation parameters.

Like in any non-isothermal method to determine correctly the activation parameters from TPR data one needs to use at least three curves, obtained by three different heating rates, applying an adequate iso-conversional method. Sometimes one proceeds in this way succeeding to evidence the change of the reduction mechanism or to detect a compensation effect during the TPR process [11, 12].

One may note that always is given a special attention in determination of the kinetic parameters from data obtained in a non-isothermal measurement. We may note that wanting to determine activation parameters with the best accuracy there are applied various procedures. Sometime different iso-conversional method are applied trying to obtain the same kinetic parameters [13] or, at least, to evidence the differences obtained in this way [14]. Under other circumstances one compare the results obtained by appling the iso-conversional methods to those obtained by fitting method [15, 16]. Or, like in case of Jansen and Machado [17], there are trials to change the standard principles of a certain method.

In this paper we shall show that even applying iso-conversional methods the activation parameters may be determined with significant errors. This happened especially when one use a method that does not take into account the influence of the experimental parameters. It is in a way a particular case of those showed by Khawam and Flanagan [18]. According to them an incorrect application of an iso-conversional method can determine false results, *e.g.* an artificial dependence of the activation energy on the degree of conversion.

Before showing our results, in the case of TPR, we have to mention that Simon [19] analyzed fundamentals of the iso-conversional methods from the point of vue of

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their correctness, their applications and the physical meaning of the activation parameters obtained.

Analyzing the integral iso-conversional methods Gao *et al.* [20] showed that in these cases the errors in evaluation of the activation energy strongly depend on the accuracy of determining of the temperature integral. In cases of the differential methods, like that of Friedman [21], the errors could be more important because these use instantaneous values which are very sensitive to the noise of the experimental measurements [22, 23].

Preliminary results and procedures

When a TPR profile is the result of a superposition of two or more processes the only method to determine the activation parameters is to simulate the TPR curve. This means to integrate numerically the equation of the reaction rate [5, 24] taking into account the start conditions and all the values of the experimental parameters and trying to fit the computed curve to the experimental one. In such cases the errors are mainly related to the fact that one have to choose a kinetic model assuming a certain form for the conversion function. Having different conversion functions one determine different pairs of activation parameters.

This is more clearly understood if we try to determine the activation parameters when we have, at least apparently, in the TPR profile one isolated single peak. In such a case one applies the linear regression using the relationship [25]

$$\ln\frac{(2-\delta c)g(\alpha)}{T\delta c}=\frac{E}{R}\frac{1}{T}+\ln\frac{2p_0D_0}{Ac^0_{\mathrm{ox}}V_\mathrm{r}\,pT_0} \qquad (1)$$

where c^0_{ox} – concentration of the oxide at the initial moment, t=0, D_0 – flow rate in normal conditions of pressure and temperature, V_r – reaction volume, p and p_0 – pressure and normal pressure, T, T_0 – temperature and normal temperature, A – pre-exponential factor, E – activation energy, R – gas constant, T – temperature, δc – relative hydrogen consumption and $g(\alpha)$ – the Šesták–Berggren function [26]: $g(\alpha)=\alpha^\mathrm{m}(1-\alpha)^\mathrm{n}$.

It is obvious that applying Eq. (1) one have to assume a certain form for the conversion function. In Table 1 we may note that proceeding so in case of the TPR profile of Cu/Fe_3O_4, obtained by heating the sample by 5 K min^{-1}, one obtains for different values of *m* and *n* very different values of the activation parameters having in all these cases values of the correlation factor larger than 0.99. As one may see in this table it is difficult to decide which pair of values are the best in case the TPR of Cu/Fe_3O_4. Similar results one obtains in case of the TPR profiles recorded when the heating rate is 10 or 15 K min^{-1}.

Table 1 The values of the activation parameters, *E* and *A*, determined by linear regression, as well as of the correlation factor *r* function of the Šesták–Berggren exponents *m* and *n* for a heating rate of 5 K min^{-1}

m	*n*	E/kJ mol^{-1}	A/m^3 mol^{-1} s^{-1}	*r*
0.1	0.3	51.3	5.7	0.992
0.1	0.4	57.6	6.9	0.996
0.1	0.5	63.9	8.0	0.997
0.1	0.6	70.2	9.2	0.996
0.1	0.7	76.5	10.3	0.994
0.1	0.8	82.8	11.4	0.992
0.2	0.3	41.8	4.2	0.992
0.2	0.4	48.1	5.4	0.996
0.2	0.5	54.4	6.5	0.996
0.2	0.6	60.7	7.6	0.994
0.2	0.7	67.0	8.8	0.991
0.3	0.3	32.3	2.7	0.992
0.3	0.4	38.5	3.8	0.995
0.3	0.5	44.8	5.0	0.993
0.4	0.3	22.8	1.2	0.991

Analyzing all these data by Friedman's iso-conversional method [21] one noticed that the reduction of the Cu/Fe_3O_4 catalyst consists of at least 3 different processes [12]. In temperature ranges where the activation energy depends on the degree of reduction a compensation effect evidenced too. Using Eq. (1) to analyse the same data one obtained similar results, but shifted towards higher temperatures by 5 kJ mol^{-1}. Although this difference is not large, this happened both because in Friedman's equation all the experimental parameters are neglected and the reaction rate equation has been, in a way, simplified. This time the difference is not large because in the experiments it was taken into consideration the recommendation of Monti and Baiker [5] to choose the flow rate of the reducing mixture, the concentration of the hydrogen in this and the amount of the sample (that has to be reduced) in such a way to have a small hydrogen consumption even at the maximum. As we shall show in the following when we neglect this recommendation, i.e. when the relative hydrogen consumption (at the maximum) is large, the errors become important.

To prove this we generated three different TPR curves for which the activation parameters are identical, but being characterized by different Šesták–Berggren exponents. These synthetic TPR curves generated with β=5 K min^{-1}, are shown in Fig. 1.

The values of the experimental parameters used in simulations were equal to those of the real experiments [10–12]: c_in=4 mol m^{-3}, V_r=2·10^{-7} m^3, p=p_0=101325 Pa, T_0=293 K, D_0=3.3·10^{-7} m^3 s^{-1}. The three

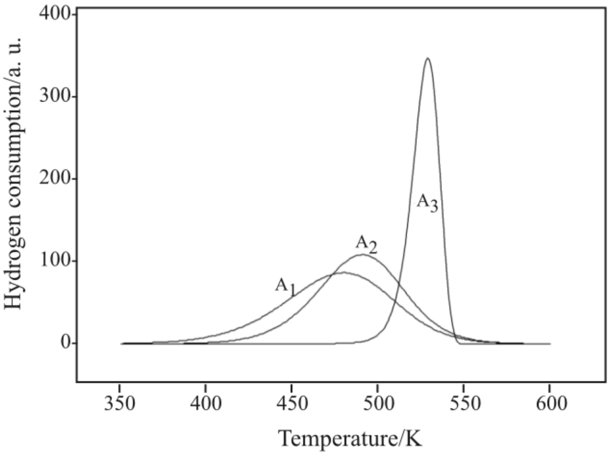

Fig. 1 The synthetic TPR curves, for β=5 K min^{-1}, characterized by the same activation parameters – E=71 kJ mol^{-1} and A=6·10^4 m^3 mol^{-1} s^{-1}, but different Šesták–Berggren exponents. A_1 – m=0, n=1.3, A_2 – m=0.3, n=1.3, A_3 – m=0.8, n=0.8

heating rates corresponding to the three TPR curves were 5, 10 and 15 K min^{-1}, respectively.

The total hydrogen consumptions in all the simulations were the same because in all the cases it was considered that the masses of the oxide involved in the TPR process were also the same. We considered in these simulations that the quantity of the oxide (MO type, where M is a divalent metal) is 58·10^{-6} mol. Consequently, the oxide concentration into the reaction space was 290 mol m^{-3}.

All the TPR profiles simulated on the basis of the parameters presented in Table 1 are single processes, taking into consideration the request of Monti and Baiker [5]. Under these conditions, as we shall see in the next chapter, the values of the activation energy can be determined with a satisfactory accuracy even applying Friedman's method.

Finally we simulated another four single processes, four TPR experiments in which the quantity of the oxide, that has to be reduced, increases from 42·10^{-6} up to 630·10^{-6} mol. As we shall show in the next chapter in two of these four cases, when the requests of Monti and Baiker are neglected, the hydrogen consumption is very large and, consequently, the values of the activation energies, determined by Friedman's method, have significant errors.

Results and discussion

The values of the activation energies determined by Eq. (1), for various values of the degree of reduction, starting with 0.1 up to 0.9, are presented in Fig. 2. The values of the correlation factor were larger than 0.9999 in all the cases. As one can observe in Fig. 2

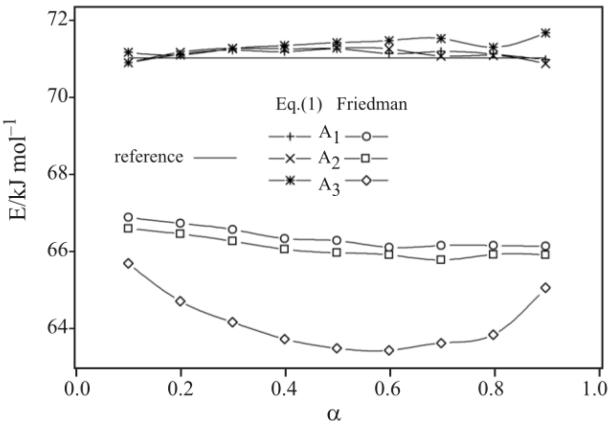

Fig. 2 The dependence of the activation energies, determined both by Friedman's method and Eq. (1), on the degree of reduction

the evaluated values of the activation energy are practically the same, close to 71 kJ mol^{-1}, with fluctuations smaller than 1.5% for all the curves, A_1…A_3, and any value of the degree of reduction.

We applied also Friedman's method to the same synthetic data, determining again the activation energies as function of the degree of reduction. The results of these evaluations are also presented in Fig. 2. The values of the correlation factor were again larger than 0.9999.

Analyzing these figures we may note that in this case the errors are significant, larger than those obtained in the case of the method given by Eq. (1). The largest errors were obtained in the case of the A_3 curve. In this case the errors are around 11%, but in the other cases they are reasonable, below 7%. In addition, we note that the fluctuations of the activation energies, when the degree of reduction varies from 0.1 up to 0.9, are smaller than 5% (even in the case when there were obtained the largest errors). Consequently, we have to consider, in every of these three cases, that the activation energy is constant. In other words in any of these cases the fluctuations of the activation energy do not suggest any overlap of some parallel processes.

Comparing the two methods we may note that the accuracy of Friedman's method is worse than that given by Eq. (1). In the case of the simulated TPR experiment, labeled by A_3, the errors are the largest. This curve is the narrowest and, consequently, around its maximum, the hydrogen consumptions into the reaction space is the largest. Due to this fact during this TPR simulated experiment the hydrogen concentration, c_r, into the reaction space decreases more than in the other cases.

According to the following relationship the general form of the equation of the reaction rate may be simplified, compressing the factors A, c_r and c_{ox}^0 in a single one, A':

$$\nu = A c_{\mathrm{r}} c_{\mathrm{ox}}^{0} g(\alpha)\exp\left(-\frac{E}{RT}\right) \cong A' g(\alpha)\exp\left(-\frac{E}{RT}\right) \quad (2)$$

obtaining in this way a form very close to that of Friedman.

Taking into account this simplification suggested by Eq. (2) we may understand that in the Friedman's form the pre-exponential factor, *A*', is not really a constant. It contains inside the hydrogen concentration into reaction space, c_{r} and as we mentioned above, around the maximum of the TPR profile, it may decrease very much. In the frame of Friedman's method the pre-exponential factor is considered constant, its decrease is not taken into account and, consequently, it is reflected, of course, in a fluctuation of the activation energy. Consequently, because in the case of the A_3 TPR experiment we have the largest fluctuations of the hydrogen concentration into the reaction space, we have the most erroneous values of the activation energy.

To prove this we generated four triplets of TPR curves in which the quantity of the oxide that is reduced during the experiment increases from 42 up to 630 μmol, the other characteristics being the same like those of the A_1 process of Table 1.

In the Table 2 one may see the main characeristics of these TPR numeric experiments. Here we may note that for a given quantity of the oxide increasing the heating rate the relative hydrogen consumption at the maximum becomes higher and higher. We may also note that having a certain heating rate increasing the quantity of the oxide reduced during the TPR experiment the relative hydrogen consumption at the maximum becomes higher and higher too.

A significant case is the fourth of the Table 2, when the quantity of the oxide reduced during the TPR experiment, *q*=630 μmol. We note that the volume of the hydrogen consumed during the TPR experiment is 15 cm^3, that represents a significant percentage of the hydrogen volume that passes through the reactor during the TPR process, especially when the heating rate is large. We also note that the hydrogen volume that passes through reactor is smaller and smaller when the heating rate is larger and larger: V_{H} decreases from 108 down to 40.8 cm^3 when β increases from 5 up to 15 K min^{-1}. Consequently, V_{NHC} represents a significant percentage, larger and larger, of V_{H} when the heating rate increases. According to this the maximum relative hydrogen consumption increases from 36.6% up to 93.6% when the heating rate increases from 5 up to 15 K min^{-1}. This means that in all these three cases the hydrogen concentration in the reaction space has very large fluctuations; when β=15 K min^{-1} the hydrogen concentration into the reaction space decreases down to only 6.7% of the entering value when the reaction rate reaches its maximum. Under these conditions it is obvious that the value of A' – Eq. (2) – has very large fluctuations and, consequently, the values of the activation energy, *E vs.* α, determined by Friedman's method, have large fluctuations too.

Table 2 The main characteristics of the TPR profiles simulated with *E*=71 kJ mol^{-1}, *A*=6·10^4 m^3 mol^{-1} s^{-1}, *m*=0.0, *n*=1.3 and increasing quantities of the MeO type oxide, *q*, which have to be reduced during the TPR experiments.

q/ 10^{-6} mol	V_{NHC}/ 10^{-6} m^3	β/ K min^{-1}	Δ*T*/ K	V_{H}/ 10^{-6} m^3	δ*C*/ %
42	1	5	214	107.3	2.5
		10	231	57.7	4.6
		15	241	40.2	6.7
210	5	5	215	107.5	12.4
		10	231	57.9	22.9
		15	242	40.3	32.7
420	10	5	215	107.7	24.6
		10	232	58.1	45.1
		15	243	40.6	63.8
630	15	5	215	108.0	36.6
		10	233	58.4	66.6
		15	245	40.8	93.6

In Fig. 3 we present the values of the activation energy as a function of the reduction degree, determined both by applying Friedman's method and Eq. (1) to the four TPR triplets. According to those presented above we note that indeed increasing the quantity of the oxide that is reduced during the TPR experiment the errors of the activation energies deter-

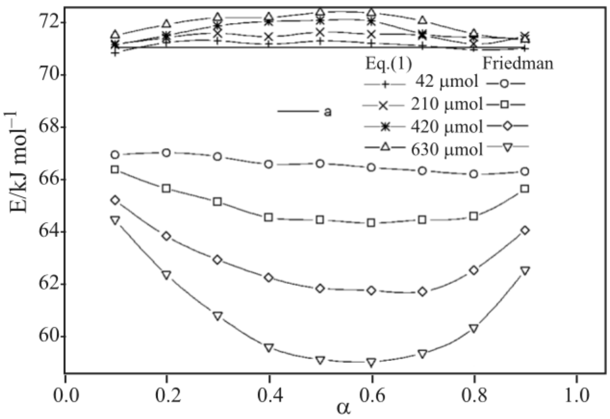

Fig. 3 The values of the activation energies, *E*, *vs.* the degree of reduction, α, determined both by Eq. (1) – b, c, d, e – and Friedman's method – f, g, h, i, for a series of TPR profiles simulated with *E*=71 kJ mol^{-1}, *A*=6·10^4 m^3 mol^{-1} s^{-1}, *m*=0.0, *n*=1.3 and different amounts of the oxide that has to be reduced during the experiments. Curve a (unmarked line): the value of the activation energy used in simulations

mined by Friedman's method also increase. The fluctuations of the values of the activation energy – *E vs.* α – are also larger and larger when the amount of the oxide becomes larger and larger.

In our opinion the errors of the activation energies determined by Friedman's method are due to the simplification of the reaction rate equation to a first order one. Proceeding in this way the fluctuations of the hydrogen concentration (when the degree of reduction varies) are automatically reflected into the determined values of *E vs.* α. The Friedman's method gives good results only when the recommendation of Monti and Baiker [5] is taken into account and consequently the hydrogen consumption is low.

We can note in Fig. 3 that applying Eq. (1) we obtained good results: values of the activation energy very close to that used in simulations, with small fluctuations, below 1.5%. This accuracy is due, of course, to the fact that δc (together with all the other experimental parameters) appears into the Eq. (1).

Conclusions

It can be concluded that analyzing TPR data by Friedman's method one obtaines erroneous results not only due to its sensitivity to the noise of the experimental measurements. The main reason is that it neglects the experimental parameters which influence the position and shape of the TPR profile, the fluctuations of the hydrogen concentration into the reaction space being automatically reflected into the values of the activation energy determined by this method.

Friedman's method can be used to determine the activation parameters from TPR data only the request of Monti and Baker [5] regarding the correlation between the mass of the oxide, the flow rate and the hydrogen concentration into reducing mixture is taken into account.

To determine kinetic parameters from TPR data we recommend to use specific methods like that given by Eq. (1), that gives good results even when the experimental conditions are extreme. The accuracy of this method [25] is good because it takes into account the experimental parameters which influence the position and shape of the TPR profile. Like in case of any non-isothermal experiment, TPR data have always to be analyzed using at least three curves obtained by three different heating rates.

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