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Kinetics of temperature programmed reduction of Fe_3O_4 promoted with copper: application of iso-conversional methods

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The temperature-programmed reduction of Cu/Fe_3O_4 in hydrogen was analyzed. The values of the apparent activation energy characteristic of this process were determined using the most widely known iso-conversional methods. In all cases a variation of the apparent activation energy with the degree of reduction was shown.

The values of the pre-exponential factor were evaluated assuming various kinetic models. In all cases both the apparent activation energy and pre-exponential factor depend on the degree of reduction. Their values vary according to the relationship of the *compensation effect*: $\ln A = a \cdot E + b$.

The analysis of the data suggested that the reduction of Cu/Fe_3O_4 takes place passing through three consecutive stages, in which the reduction mechanisms are different. The existence of these reduction stages was tentatively explained taking into account the possible structural changes, which accompany the increase of the reduction degree.

1. Introduction

The water-gas shift (WGS) reaction over iron-containing catalysts is one of the oldest catalytic processes in the chemical industry. Nevertheless, the search for new way of selecting highly active and economically beneficial catalysts is to prepare precursors with optimum structure and properties [1].

It is known that the active phase in WGS reaction is Fe_3O_4, usually obtained by reduction of Fe_2O_3. The impurities in iron oxide may promote or inhibit either the reducibility of Fe_2O_3 or the activity of Fe_3O_4 in WGS reaction. Although the effect of the impurities on the reducibility of Fe_3O_4 (typical redox catalyst) ought to be similar to that on the activity of this catalyst in WGS reaction sometimes there are exceptions from this rule.

Gold is a very good promoter for the reduction of hematite to magnetite. Due to the presence of gold into the structure of Fe_2O_3 the TPR maximum corresponding to reduction of magnetite to hematite decreases by more than 150 K [2]. The activity of Au/Fe_3O_4 in WGS reaction is higher than of pure Fe_2O_3 [3], but the gold has apparently no influence on the reducibility of Fe_3O_4 [2].

The presence of OH groups increases both the reducibility of Fe_2O_3 and the activity of Fe_3O_4 in WGS reaction. In case of pure hematite only the reducibility of the surface increases due to the coverage with OH groups, but in case of Au/Fe_2O_3 the all amount of hematite is reduced at a lower temperature [2].

Sulfur inhibits both reduction processes: $Fe_2O_3 \rightarrow Fe_3O_4$ and $Fe_3\ O_4 \rightarrow Fe$ [4]. The reducibility of Fe_3O_4 decreases due to the traces of sulfur, which remains into the structure of magnetite after reducing of hematite. These traces of sulfur from Fe_3O_4 inhibit also the WGS reaction.

Copper is also a promoter both for reduction of Fe_2O_3 and WGS reaction [5]. Following the procedure of Monti and Baiker [6] it was shown that the copper influences the reducibility of magnetite too. One has to notice [5] that the kinetic parameters characteristic of the reduction process $Fe_3O_4 \rightarrow Fe$ depend on the degree of reduction. According to the results of Andreini, Poels and Bliek [7] this phenomenon seems to be due to the presence of the metallic copper particles which exist into the structure of Fe_3O_4 after reduction of CuO/Fe_2O_3. They also noted that during the temperature programmed reduction of CuO the values of the apparent activation parameters vary, being correlated by a compensation effect.

This work is a first step in our attempt to find the most appropriate methods to evaluate the kinetic parameters from TPR data. The values of the apparent parameters are determined applying the most widely known iso-conversional methods reported in literature. The variations of the apparent activation energy during the reduction process are explained taking into account the presence of the metallic copper particles into the structure Fe_3O_4.

2. Experimental

The CuO/Fe_2O_3 catalyst samples were prepared by coprecipitation, in a "Contalab" laboratory reactor (Contraves AG, Switzerland) under complete control of all parameters: temperature, pH, stirrer speed, reactant feed flow rate. All chemicals used, $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and Na_2CO_3, were "analytical grade". The following conditions were employed: $T = 60°C$, pH = 8.0, stirrer speed = 250 rpm, reactant flow rate = $8\ \text{ml} \cdot \text{min}^{-1}$. The copper content of the sample was 5 wt%. After precipitation, the sample was aged for 1 hour at 60°C, filtered and washed carefully until absence of NO_3^- ions. Then, the sample was dried under vacuum at 80°C and calcined in the air at 400°C for two hours.

The TPR measurements were performed using a versatile apparatus described for the first time, in detail, in [8] and schematically, quite recently, in [4]. The following conditions were used: hydrogen-argon mixture (10% H_2) at a flow rate of $24\ \text{ml} \cdot \text{min}^{-1}$, sample mass 0.01 g, in agreement with the recommendations of Monti and Baiker [6]. There were recorded three different TPR curves, the heating rates having the following values: 5, 10 and $15\ \text{K} \cdot \text{min}^{-1}$.

3. The iso-conversional methods used to evaluate the apparent activation energy

The kinetic analysis of the experimental data is based on the rate equation:

$$\beta \frac{d\alpha}{dT} = A f(\alpha) \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α is the degree of conversion, $T =$ the temperature, $\beta =$ the linear heating rate ($\beta = \frac{dT}{dt} =$ const.), $A =$ the pre-exponential factor, $E =$ the apparent activation energy, $f(\alpha) =$ the differential function of conversion and $R =$ the gas constant.

Forms of $f(\alpha)$ suggested in the literature for a wide variety of situations, including the decomposition of solids and the reduction of metal oxides, can be found in [9].

The dependence of the apparent activation energy on α was evaluated by means of the following iso-conversional methods: Friedman method [10] (FR method); Flynn-Wall-Ozawa method [11, 12] (FWO method); Kissinger-Akahira-Sunose method [13] (KAS method); Li-Tang method [14–16] (LT method) and Vyazovkin and Dollimore nonlinear procedure [17] (NL-INT method). These methods are known to allow for model-independent estimates of apparent activation energy.

The differential iso-conversional method suggested by Friedman [10] (FR method) is based on Equation 1 that leads to:

$$\ln \beta \frac{d\alpha}{dT} = \ln A + \ln f(\alpha) - \frac{E}{RT} \tag{2}$$

For $\alpha =$ const., the plot $\ln(\beta \frac{d\alpha}{dT})$ vs. $(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope allows to evaluate the apparent activation energy.

The iso-conversional integral method suggested independently by Flynn and Wall [11] and Ozawa [12] uses Doyle's approximation [18] of the temperature integral. This method is based on the equation:

$$\ln \beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT} \tag{3}$$

where $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$.

Thus, for $\alpha =$ const., the plot $\ln \beta$ vs. $(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope allows to evaluate the apparent activation energy. For $x \equiv \frac{E}{RT} < 20$, Doyle's approximation leads to errors higher than 10%. In order to correct these errors, we shall use the method suggested by Flynn [19].

The KAS iso-conversional integral method [13] is based on the Coats-Redfern approximation [20] of the temperature integral. It was shown that:

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{Eg(\alpha)} - \frac{E}{RT} \tag{4}$$

Thus, for $\alpha =$ const., the plot $\ln \frac{\beta}{T^2}$ vs. $(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope can be used to evaluate the apparent activation energy.

The method suggested by Li and Tang [14–16] is based on the following equation that results from Equation 1 by taking the logarithm, multiplying by $d\alpha$ and integrating:

$$\int_{\alpha_0}^{\alpha} \left(\ln \beta \frac{d\alpha}{dT}\right) d\alpha = -\frac{E}{R} \int_{\alpha_0}^{\alpha} \left(\frac{1}{T}\right) d\alpha + G(\alpha, \alpha_0) \tag{5}$$

where $G(\alpha, \alpha_0) = (\alpha - \alpha_0) \ln A + \int_{\alpha_0}^{\alpha} (\ln f(\alpha)) d\alpha$.

The plot of $I_2 \equiv \int_{\alpha_0}^{\alpha} (\ln \beta \frac{d\alpha}{dT}) d\alpha$ vs. $I_1 \equiv \int_{\alpha_0}^{\alpha} (\frac{1}{T}) d\alpha$, at a given α, for a set of β, should be a straight line whose slope is $(-\frac{E}{R})$.

The FR, FWO, KAS and LT methods are linear ones. The nonlinear procedure suggested by Vyazovkin [17] is based on the following condition of minimum that is obtained from the integral form of Equation 1:

$$\sum_{i}^{n} \sum_{j \neq i}^{n} \left[\frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \right] = \min \qquad (6)$$

where $I(E, T) = \frac{E}{R} p(x)$ ($p(x)$ is the temperature integral and n is the number of the heating rates for which the $\alpha = \alpha(T)$ curves were determined). To evaluate the value of E, for a given value of α, a range of E with a given step is considered. After computing the expression (6) for the whole range, one chooses the value of E_α that corresponds to the minimum value, S_{min}, of the expression (6).

Unlike the FWO and KAS integral methods, Vyazovkin integral method permits the use of more exact approximations of the temperature integral. In this paper we will use the 4th rational expression of Senum and Yang [21].

Obviously, the different methods applied to the same non-isothermal data should lead to the same value for the activation energy. However, it was pointed out [16, 22–24] that when E changes with α, the FWO, KAS and NL-INT integral iso-conversional methods lead to close values of E, but which differ substantially from the values of E obtained using the differential iso-conversional method suggested by Friedman. These differences could be due to the approximation of the temperature integral that were used in the derivations of the relations that ground FWO, KAS and NL-INT methods. On the other hand, some important differences were noted between E_{FR} and E_{LT} values, although both these methods do not use the approximation of the temperature integral. Therefore, we think that the existence of significant differences between E_{FR} and E calculated using all of integral iso-conversional methods are due to the way in which the relations that form the basis of the integral methods are derived. In these derivations, it was considered that the activation parameters do not depend on α. Obviously, if $E = E(\alpha)$ and $A = A(\alpha)$, these derivations are not correct. Consequently, if E depends on α, the FR method, which uses directly the equation of the reaction rate, is recommended. Another method, which is a modification of NL-INT method (modified non-linear integral method (MNL-INT)) and that leads to E values close to E_{FR} values, was recently suggested by Vyazovkin [25]. In this method the constancy of E_α is assumed only for a small interval $\Delta\alpha$ and the integral I(E,T) with the limits $T_{\alpha-\Delta\alpha}$ and T_α ($t_{\alpha-\Delta\alpha}$ and t_α in [25]) is evaluated numerically for non-isothermal data by using trapezoidal rule.

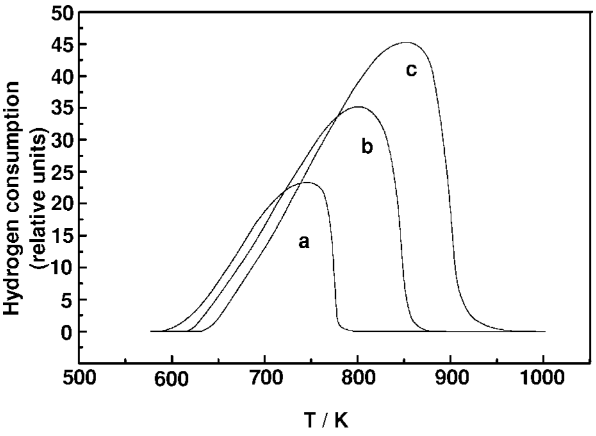

Figure 1 The experimental TPR curves obtained with the three heating rates: (a) 5 K · min^{-1}, (b) 10 K · min^{-1} and (c) 15 K · min^{-1}.

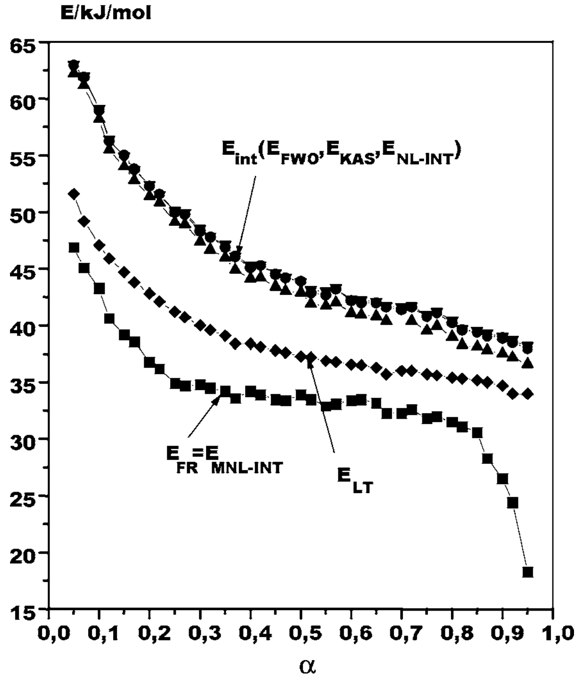

Figure 2 Curves showing the change of the values of the apparent activation energy evaluated by means of various isoconversional methods with the conversion degree.

4. Results and discussions

Starting from the experimental TPR curves—see Fig. 1—both α and $\frac{d\alpha}{dt}$, as functions of temperature, were computed. Using these curves and applying the above mentioned iso-conversional methods, the curves E vs. α shown in Fig. 2 were obtained. The correlation coefficients of the linear regressions corresponding to the methods FR, FWO, KAS and LT were higher than 0.993. For nonlinear methods (NL-INT and MNL-INT) $e = 2 - \frac{S_{\text{min}}}{n(n-1)} \geq 0.994$ (one may prove that e could be a measure of the accuracy of the apparent activation energy evaluation by nonlinear procedures). The results obtained by means of FWO method were corrected according to the procedure suggested by Flynn [22] (four iterations). From Fig. 2 one can notice the similar shape of the curves E vs. α corresponding to the integral methods. The common curve, corresponding to FR and MNL-INT methods, is different, especially in the range for $\alpha > 0.8$. For a given value of α, the E value depends on the applied iso-conversional method ($E_{\text{FWO}} \approx E_{\text{KAS}} \approx E_{\text{NL-INT}} > E_{\text{LT}} > E_{\text{FR}} \equiv E_{\text{MNL-INT}}$). The relations who ground the methods of E evaluation can explain the lower value of $E_{\text{FR}} \equiv E_{\text{MNL-INT}}$ with respect to all other E values. FR method uses the point values of the overall reaction rate and MNL-INT method uses a small range of α, while the integral iso-conversional methods use integrals which describe the history of the system in the range $0 \div \alpha$ This is why one expects that for a decrease of E with α, E_{FR} is lower than E evaluated by integral iso-conversional methods (E_{int}) and for an increase of E with α, $E_{\mathrm{FR}}(\equiv E_{\mathrm{MNL\text{-}INT}}) > E_{\mathrm{int}}$. According to the discussion made in the previous section of this paper, if E depends on α, the FR method or MNL-INT is recommended.

The analysis of the curve $E_{\mathrm{FR}}(\equiv E_{\mathrm{MNL\text{-}INT}})$ vs. α (Fig. 2) shows three distinct regions, namely: an initial range $0 < \alpha \leq 0.30$ where $E_{\mathrm{FR}}(\equiv E_{\mathrm{MNL\text{-}INT}})$ decreases relatively fast with α (from 46.9 $\mathrm{kJ \cdot mol^{-1}}$ to 34.8 $\mathrm{kJ \cdot mol^{-1}}$); a second range where E_{FR} ($\equiv E_{\mathrm{MNL-INT}}$) is practically constant, $0.30 \leq \alpha \leq 0.80$, and a final range, $0.80 \leq \alpha \leq 0.95$, where $E_{\mathrm{FR}}(\equiv E_{\mathrm{MNL\text{-}INT}})$ decreases relatively fast with α. The existence of these three ranges suggests three steps of Fe_3O_4 reduction.

The dependence $E = E(\alpha)$ suggests the existence of the relation of the compensation effect according to which:

$$\ln A = aE + b \tag{7}$$

where a and b are constant parameters. Such a relation was verified previously for many non-isothermal decompositions [26–29] as well as for the temperature-programmed reduction of copper oxide [7].

In order to check relation (7), the results obtained by means of FR method are going to be used. From the intercept of the curve $\ln(\beta \frac{d\alpha}{dT})$ vs. $(1/T)$, for a given value of α, one can obtain $\ln A$, by supposing a certain analytical form of $f(\alpha)$. The corresponding kinetic models are listed in Table I.

The most difficult task in such a procedure is to unify the entire range of the degree of reductions. This means to find a conversion function that allows to determine the values of the ln A which depend linearly on E in the whole range of α, from 0.05 up to 0.95, according to only one compensation effect equation.

In case of our TPR data it was not possible to do such an unification. As an example one shows in Fig. 3 the plot $\ln A$ vs. E for the cases B1, SB0.3 and SB0.5 (see Table I). As one can easily see these plots exhibit two growing linear portions, one for $0.05 \leq \alpha \leq 0.30$ and another for $0.80 \leq \alpha \leq 0.95$. In the transition portion between them, only the plot corresponding to the SB0.3 model is a linear one. For the other models, in this range of $\alpha - 0.30 \leq \alpha \leq 0.80$—the dependence of $\ln A$ on E does not present the necessary monotony—see the B1 plot in Fig. 3.

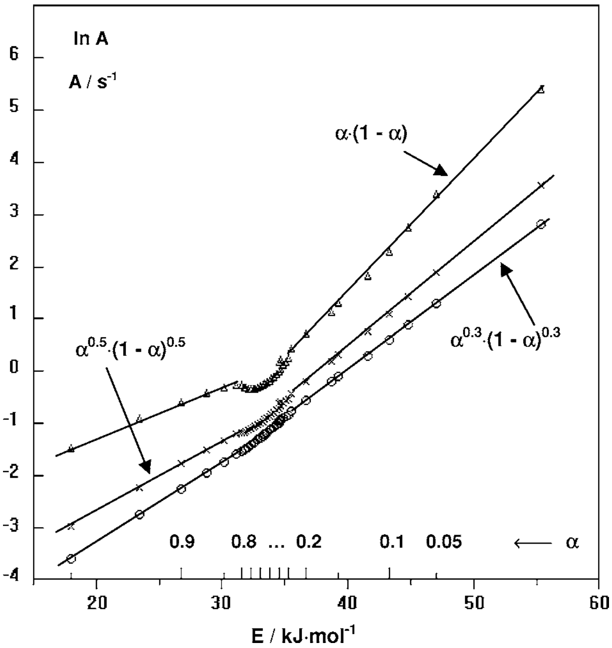

Figure 3 The curves $\ln A$ vs. E for the differential conversion functions: $f(\alpha) = \alpha(1-\alpha)$, $f(\alpha) = \alpha^{0.3}(1-\alpha)^{0.3}$ and $f(\alpha) = \alpha^{0.5}(1-\alpha)^{0.5}$.

We have to mention that similar results were obtained for the all tested models, except D2, D3 and A0.5. The compensation effect parameters, a and b, for the two mentioned linear portions are presented in Table II.

We will suppose that the most probable differential conversion function that describes the first stage of the reduction process is that corresponding to the closest to unity correlation coefficient of the straight line $\ln A = aE + b$ (CE relationship). This method to find the conversion function was suggested by Tanaka and Koga [30]. As shown in Table II, for the first reduction process, the values of r corresponding to SB0.3 and SB0.5 are very close. Neglecting other arguments and taking into account only the suggestion of Tanaka and Koga, we could conclude that $f(\alpha) = \alpha^{0.3}(1-\alpha)^{0.3}$ is the best conversion function that describe the reduction process in the first stage. Analyzing the data presented in Table II one may note that the all values of r, corresponding to the range $0.05 \leq \alpha \leq 0.30$, are larger than 0.99 and, consequently, it is difficult to eliminate any of the tested mechanisms and to choose the best kinetic model taking into consideration only the

TABLE I Algebric expressions for $f(\alpha)$ functions used for $\ln A$ evaluation

Mechanism	Symbol	$f(\alpha)$
Phase boundary controled reaction (contracting area, i.e., bidimensional shape)	R2	$(1-\alpha)^{1/2}$
Phase boundary controled reaction (contracting volume, i.e., tridimensional shape)	R3	$(1-\alpha)^{2/3}$
Reaction order	Fn	$(1-\alpha)^n$ $n = 0, 0.1, 0.2, 0.3, 0.4, 1$
One-dimensional diffusion (parabolic law)	D1	$\frac{1}{2\alpha}$
Two-dimensional diffusion (bidimensional particle shape)	D2	$\frac{1}{-\ln(1-\alpha)}$
Three-dimensional diffusion (tridimensional particle shape) Jander equation	D3	$\frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$
Random nucleation and growth of nuclei (Avrami-Eforeev equation)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$ $n = 0.5; 2; 3; 4$
Prout-Tompkins	B1	$\alpha(1-\alpha)$
Sestak-Berggren[a]; $m = n = 0.3$; $p = 0$	SB0.3	$\alpha^{0.3}(1-\alpha)^{0.3}$
Sestak-Berggren[a]; $m = n = 0.5$; $p = 0$	SB0.5	$\alpha^{0.5}(1-\alpha)^{0.5}$

[a] $f(\alpha) = \alpha^n(1-\alpha)^m[-\ln(1-\alpha)]^p$.

TABLE II The compensation effect parameters obtained for various expressions of $f(\alpha)$

	$0.05 \le \alpha \le 0.30$			$0.80 \le \alpha \le 0.95$		
Mechanism	a (mol · kJ^{-1})	$-b(A/\mathrm{s}^{-1})$	r	a (mol · kJ^{-1})	$-b$ (A/s^{-1})	r
F0	0.146	6.450	0.99973	0.180	7.782	0.99992
F0.1	0.143	6.342	0.99972	0.170	7.287	0.99999
F0.2	0.141	6.235	0.99969	0.159	6.792	0.99997
F0.3	0.139	6.128	0.99962	0.149	6.297	0.99982
F0.4	0.137	6.021	0.99953	0.139	5.803	0.99947
R2	0.134	5.913	0.99940	0.129	5.308	0.99885
R3	0.131	5.734	0.99911	0.112	4.483	0.99679
F1	0.123	5.377	0.99816	0.078	2.833	0.98281
D1	0.297	9.089	0.99893	0.192	7.285	0.99933
A2	0.195	7.996	0.99967	0.100	4.518	0.99599
A3	0.219	9.044	0.99951	0.108	5.254	0.99777
A4	0.231	9.653	0.99940	0.111	5.706	0.99838
B1	0.256	8.709	0.99893	0.090	3.029	0.99376
SB0.3	0.179	7.128	0.99996	0.153	6.356	0.99994
SB0.5	0.201	7.579	0.99976	0.135	5.406	0.99976

r is the correlation coefficient of the linear regression $\ln A$ vs. E.

criterion of Tanaka and Koga. We decided that indeed $f(\alpha) = \alpha^{0.3}(1-\alpha)^{0.3}$ is the best conversion function because according to Sestak, Satava and Wendlandt [31], in case of a system that contains metallic particles the reduction processes take place mainly along the border between the oxide and metallic particles.

In case of the third range, $0.80 \le \alpha \le 0.95$, the highest values of r correspond to the F0.1 and F0.2 models. These models are specific to the reduction of the metallic oxides which do not have metallic particles into their composition for any values of α, like in case of reduction of Fe_2O_3 to Fe_3O_4. In our case, when $\alpha \in [0.80, 0.95]$ the main part of Fe_3O_4 is reduced to metallic iron. Observing that for the SB0.3 model the value of r is very close to those discussed above, our conclusion is the same: $f(\alpha) = \alpha^{0.3}(1-\alpha)^{0.3}$ is the best conversion function that describe the reduction process in this third range.

For the second range, $0.30 \le \alpha \le 0.80$, as one may be noticed in Fig. 3, only the SB0.3 can be applied. The values of the compensation effect parameters, a and b, are 0.193 mol/kJ and, respectively, -7.66258 the correlation coefficient being large enough, 0.99934.

As we mentioned above it was not possible to unify the whole range of α by only one compensation effect equation. The curves $\ln A$ vs. E show identical ranges with the three ranges of E_{FR} vs. α. Only in case of the SB03 model it was possible to determine a good compensation effect equation for every of these three ranges, the corresponding iso-kinetic temperatures being respectively 668 K, 623 K and 788 K. Consequently, one may say that the compensation effect seems to confirm the existence of the three steps of Cu/Fe_3O_4 suggested by the curve E vs. α.

In the following we propose a possible reduction mechanism for Cu/Fe_3O_4. According to the phenomenology involved in the reduction of Cu/Fe_3O_4 the above reported results could be explained considering that during the reduction two different parallel mechanisms take place. These two reduction mechanisms could be distinguished by the adsorption place of the hydrogen molecules. One involves the adsorption of the hydrogen on the active sites, which we shall name σ_1, located in the border region between the metallic copper particles and magnetite; the other involves the active sites, named σ_2, located on the proper surface of magnetite, far from the metallic particles.

Because in case of the first mechanism the copper particles probably dissociate the hydrogen, this process is characterized by a higher reaction rate than that of the second process. Very probably the apparent activation energy characteristic to the second process is larger than that characteristic to the first one.

We may imagine that at the beginning of the reduction process, when α is very close to zero, the number of the σ_2 active sites is larger than the number of the σ_1 active sites. Consequently, at low values of the reduction degree the hydrogen consumption could be mainly due to reduction by the second mechanism. Due to this reason the apparent activation energy is the one which characterize the second mechanism. Increasing the reduction degree the first mechanism becomes more and more noticeable; consequently the apparent activation energy decreases down to that characteristic to the second mechanism. Taking into account the results presented in Fig. 2, this happens when $\alpha \approx 0.3$. For values of α in the range $0.3 \div 0.8$ the apparent activation energy is almost constant. At $\alpha \approx 0.8$, when the main part of the sample consists of metallic particles (iron and copper), the hydrogen dissociation probably becomes very fast and consequently the activation energy decreases.

The low value of the Sestak-Berggren exponent, $\lambda = 0.3$, suggests a diffusion process, the hydrogen penetrating into the bulk of the oxide particles. This would mean that during the reduction of Fe_3O_4 the oxygen is removed not only from the surface of the oxide particles: it is also removed from the deeper crystallographic layers.

Starting from this observation another interpretation of the TPR experimental data could be developed, considering that the reduction mechanism depends on the reduction degree. This will be shown in a following work.

The above explanation is a consequence of the accepted fact that magnetite is directly reduced to metallic iron. This image could be different if we consider that this reduction involves two stages: Fe_3O_4 → FeO and FeO → metallic iron. To choose between the two possible mechanisms it is necessary to have supplementary structural information.

5. Conclusions

We mentioned at the beginning of this work that in case of CuO both apparent kinetic parameters depend on the degree of reduction [7], being evidenced 3 stages of the reduction process. The metallic copper particles, which appear during the reduction, seem to determine this evolution of the CuO reduction process. Taking into account these facts as well as that in case of pure Fe_3O_4 no variation of the apparent activation energy has been noted [3, 4] one may say that the metallic copper particles influence the reduction process of Fe_3O_4. They seem to determine a fast increase of the sizes of the metallic particles that is accompanied by a strong decrease of the apparent activation energy of reduction when the reduction degree increases up to 0.3. Probably, starting with $\alpha \cong 0.3$ the reduction becomes a self-catalytic one. According to our interpretation the reported results could be explained considering that this way of reduction acts just from the beginning of the reduction.

The all three reduction steps are very well fitted by the SB0.3 model: $f(\alpha) = \alpha^{0.3}(1-\alpha)^{0.3}$. Because the compensation coefficients corresponding to the all three stages are different one may conclude that the three reduction stages cannot be unified by only one kinetic model.

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