Activation Energies of the Reduction of Bulk and Supported Vanadium Pentoxide

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Three methods to evaluate apparent activation energies for reduction from temperature-programmed reduction (TPR) measurements are discussed. Application of the well known method of Gentry results in values of the experimental activation energy, E_e, which are dependent on the heating rate in the region 8–15 K min^{-1}. Two new approaches are described: the reference method and the curve-fitting method.

Application of a curve-fitting method, by integration of an appropriate nucleation equation, results in an activation energy for the growth of nuclei, E_a, of 60 ± 3 kJ mol^{-1} for both bulk and supported V_2O_5.

In the reference method, the onset of a single TPR peak of a sample under investigation is compared to the onset of the TPR peak of a reference sample with a known value of E_e. Activation energies obtained by the reference method are in good agreement for almost all heating rates applied (8–20 K min^{-1}). Agreement with the activation energy obtained by Gentry's method exists only in a limited region of heating rates.

Bosch *et al.*[1] found a very high activation energy for the reduction of bulk V_2O_5 (*ca.* 200 kJ mol^{-1}). This value was obtained from temperature-programmed reduction (TPR) experiments carried out at different heating rates and determining the related shift of the maximum of a TPR peak. There are reasons to suspect such high values; in this paper the existing methods to determine activation energies from TPR experiments will be discussed and some new approaches will be suggested.

An impressive theoretical background has been developed for the derivation of kinetic parameters from TGA or DSC experiments.[2,3] In general, assumptions concerning the form of the kinetic expression have to be made so that the reaction rate equation can be handled. Kissinger,[2] however, has developed a method to determine the activation energy of a reaction without the knowledge of the complete reaction-rate equation. This method is based on the measurement of the conversion of any chemical or physical reaction as a function of the temperature at a constant heating rate β. This approach leads to the general equation:

$$\ln T_m^2/\beta = E_e/RT_m + C \qquad (1)$$

where T_m is the temperature at the maximum reaction rate, E_e is the activation energy of the empirical rate equation, R is the gas constant and C is a constant. Such an approach could be applied to TPR methods since most TPR systems measure the rate of reduction by monitoring the change of gas concentration as a function of temperature, producing reduction profiles with peaks corresponding to maxima for the rate processes. Gentry *et al.*[4] successfully applied the method of Kissinger to results obtained from the reduction of Cu^{2+} ions situated within the pores of zeolites. They derived eqn (1) for the case of reduction in hydrogen-containing gases. The application of this equation has since then often been referred to as the Gentry method.

In this paper, TPR results for unsupported and supported V_2O_5 are presented and attempts to evaluate relevant kinetic parameters from these are reported. In the

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following, three different methods which can be used to determine activation energies from TPR peaks will be discussed: (1) the Gentry method, (2) a so-called reference method, and (3) a curve-fitting method. The method of Gentry[4] is the accepted method; the other two approaches are new and represent an attempt (i) to obtain more self-consistent results for the reduction of vanadium pentoxide than those obtained by the method of Gentry, and (ii) to decrease the number of experiments necessary for the calculation of activation energies from TPR data.

Theoretical Background

The Gentry Method

The Gentry equation is based on a single power-rate equation. The reduction rate, dr_T, at a certain temperature, T, in a small slice of the bed of oxide particles of weight dG is expressed as:

$$dr_T = k_o [H_2]^p [O_l]^q \exp(-E_e/RT) dG \qquad (2)$$

where $[H_2]$ is the concentration of hydrogen, $[O_l]$ is the concentration of lattice oxygen, p, q are the reaction orders; index e refers to the temperature dependence of an empirical rate equation and k_o is a pre-exponential factor. Integration of (2) can be carried out by a summation of all the elements dG and this results in the equation:

$$r_T = k_o [H_2]^p [O_l]^q \exp(-E_e/RT) G. \qquad (3)$$

Such a treatment is allowed if the following requirements are fulfilled:

(*a*) the hydrogen concentration does not influence the reaction rate (*i.e.* $p = 0$) or the hydrogen conversion is sufficiently low to allow one to assume a constant concentration throughout the reactor;

(*b*) no temperature gradient exists across the reactor;

(*c*) the concentration of lattice oxygen is constant throughout the bed.

By definition:

$$r_T = \phi_v ([H_2]_{in} - [H_2]_{out}) = -G \, d[O_l]/dt \qquad (4)$$

where $\phi_v =$ volume flow rate. The reduction rate is proportional to the rate of hydrogen consumption, a quantity which is plotted in all TPR spectra. When the temperature is increased, there is an increase in the exponential term of eqn (3); however, this increase is compensated by the consumption of oxygen from the lattice which causes a decrease in $[O_l]$. In the early stages of a reduction peak, the former factor predominates, but the reduction rate falls to zero in the later stages, due to the predominance of the latter factor. The reduction rate thus always exhibits a maximum during the complete reduction. At the peak maximum:

$$\frac{dr_T}{dT} = \frac{dr_T}{dt} = 0 \qquad (5)$$

where $t =$ time. The heating rate β can be expressed as:

$$\frac{dT}{dt} = \beta. \qquad (6)$$

When the temperature is increased linearly with time, differentiation of eqn (3) with respect to time, followed by substitution of eqn (4) into (6) leads to:

$$\ln T_m^2/\beta = E_e/RT_m + \ln \frac{E_e}{Rk_o q} - p \ln [H_2]_m - (q-1) \ln [O_l]_m. \qquad (7)$$

The subscript m in this equation refers to the maximum of the TPR peak. Comparison of eqn (7) with eqn (1) throws light on the meaning of the constant C used therein. In

addition to the three assumptions mentioned above, one must also make the following assumption:

(*d*) the concentrations of hydrogen and lattice oxygen present in the sample at the temperature corresponding to the maximum of the TPR peak are not influenced significantly by changes in the heating rate.

Two of these four assumptions, (*a*) and (*b*), have been justified experimentally. The influence on the rate, if any, of the hydrogen concentration is probably not significant [assumption (*a*)], as will be shown from results presented in fig. 1 and 3 (later). Assumption (*b*) is justified by the results of the experiments described in the work of Bosch *et al.*[1]

The concentration of lattice oxygen present at T_m, however, could be different at different heating rates, since the height of the peak at its maximum temperature T_m increases considerably with heating rate and also because the TPR peaks are not symmetrical [assumption (*d*)]. There are two reasons to look for another approach: (i) the application of eqn (1) to calculate the apparent activation energy of reduction from the change in T_m as a function of heating rate involves assumptions (*a*)–(*d*), while (*c*) and (*d*) have not been justified experimentally; (ii) the application of eqn (1) uses the data on the position of the maximum of the peaks for a whole series of experiments at different heating rates.

In the following two sections, two new approaches are suggested and attempts are then made using these to calculate the kinetic parameters from the data of a single peak.

Reference Method

The basic idea of the reference method is to compare a TPR peak of a certain sample with that of a reference sample for which the activation energy for reduction is known. Application of eqn (3) to both samples leads to the following rate expressions:

$$r_r = k_{or} f_r(\alpha_i) \exp(-E_r/RT_r) \tag{8}$$

$$r_s = k_{os} f_s(\alpha_i) \exp(-E_e/RT_s) \tag{9}$$

where the subscript r refers to the reference sample, the subscript s to the sample under investigation and $f(\alpha_i)$ is a function which expresses the influence of all the parameters involved (the hydrogen partial pressure and the concentration of the lattice oxygen) upon the reaction rate. T_s and T_m are temperatures which must be chosen in such a way that both samples are compared at the same reduction rate (and hence at equal partial pressures of hydrogen) and at the same conversion of the solid-state reaction, so that the values of $f(\alpha_i)$ are the same in both eqn (8) and (9). These requirements are only fulfilled at that temperature at which the reduction begins. Under these conditions $r_r = r_s$, and, because the influence of all values of α_i is similar in both cases, eqn (8) and (9) can be combined to give:

$$E_e = \left(R \ln \frac{k_{os}}{k_{or}} + \frac{E_r}{T_r} \right) T_s. \tag{10}$$

Here, k_{os} and k_{or} represent the number of active sites. It therefore seems reasonable to assume that the pre-exponential factor is proportional to the number of V=O surface groups present in (010) planes. Miyamoto *et al.*[5] have shown that the surface area exposed by the (010) planes for bulk V_2O_5 occupies *ca.* 50% of the total surface area. Assuming that a monolayer of V_2O_5 supported on TiO_2 exposes only (010) phases, the ratio k_{os}/k_{or} thus would amount to 2 for TiO_2 with an area of $10 \text{ m}^2 \text{ g}^{-1}$ when compared with bulk V_2O_5. The value of E_s can thus be estimated using this reasonable estimate of the ratio k_{os}/k_{or}. It must be noted, however, that E_s is not very sensitive to this ratio: four times as high a value would result in an increase of only 3 kJ mol^{-1} in the value of E_s.

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Curve-fitting

In the Gentry and reference methods discussed earlier, only a single point of a complete TPR peak is used to calculate the activation energy, E_a. This has the advantage that an exact rate equation is not necessary (because the reduction mechanism is mostly not known). Furthermore, with these methods the *peak-form* is not taken into account.

Only Monti and Baiker[6] and Arnoldy[7] have carried out calculations, in which the peak-form is taken into account. Monti and Baiker evaluated quantitatively the TPR data for nickel oxide, applying the analytical procedure of Kissinger,[2,8] assuming first-order kinetics. They used the following rate equation:

$$r = k_o [H_2]^m [O_1]^q \exp(-E_e/RT) \tag{11}$$

where $m = q = 1$ and E_e is the experimental activation energy of reduction. A computer program was used to estimate values of k_o and E_e to give the best fit of the theoretical curve to the measured TPR peak. This analysis of peak shapes and the estimate of the kinetic parameters (k_o and E_e) has the advantage that only one accurately measured peak is needed. Arnoldy[7] used the Gentry method to determine the activation energy (E_e) for reduction of Fe_2O_3. With the value of E_e thus obtained, he tried several reduction models to find the best fit of all the experimental data.

In the Results section it will be shown that approaches based on the Gentry method failed to work for bulk (fig. 1) and supported (fig. 2) vanadium oxides. Therefore we tried to develop a new curve-fitting method which uses only the complete data of just a single TPR peak. The basic idea of the method put forward in this section is to evaluate the theoretical rate of reduction from an appropriate nucleation model, based on a proposed reduction mechanism, which will be presented in the Discussion section and to find the best values of the unknown parameters to fit these calculated rates with the observed reduction rates. To describe the reduction process of vanadium oxide mechanism, several nucleation models (including Jander diffusion equations) were examined, but only the Avrami–Erofeev equation gave satisfactory results. The activation energy E_a of the growth of nuclei is one of the parameters used for fitting, contrary to Arnoldy's approach. Furthermore, we use the data of the complete reduction peak.

The data of the complete peak-form must be available for the estimation of E_a. The procedure involves a minimalization, by choosing a suitable value of E_a, of the following function:

$$\int_{peak} [r_T(\text{experimental}) - r_T(\text{theoretical})]^2 \, dT. \tag{12}$$

Theoretical Reduction Rate

According to Avrami–Erofeev, the unobstructed conversion for two-dimensional nucleation can be written as:[9-11]

$$\alpha_E = A_2[-\exp(-k_f t) + 1 - k_f t + (k_f t)^2/2] \tag{13}$$

and
$$A_2 = C_0(k_g/k_f)^2 \tag{14}$$

with α_E = conversion which would occur with completely unobstructed nucleation, k_f = rate constant for the formation of nuclei, k_g = rate constant for the growth of nuclei, C_i = constants for $i = 0, 1, 2, \dots$. When $k_f t \gg 1$, then only the last term in eqn (13) is important; it can therefore be rewritten as:

$$\alpha_E = C_1 k_g^2 t^2. \tag{15}$$

When two nuclei approach one another, unobstructed growth is no longer possible. When the nuclei become larger with time, a number of potential nuclei also become
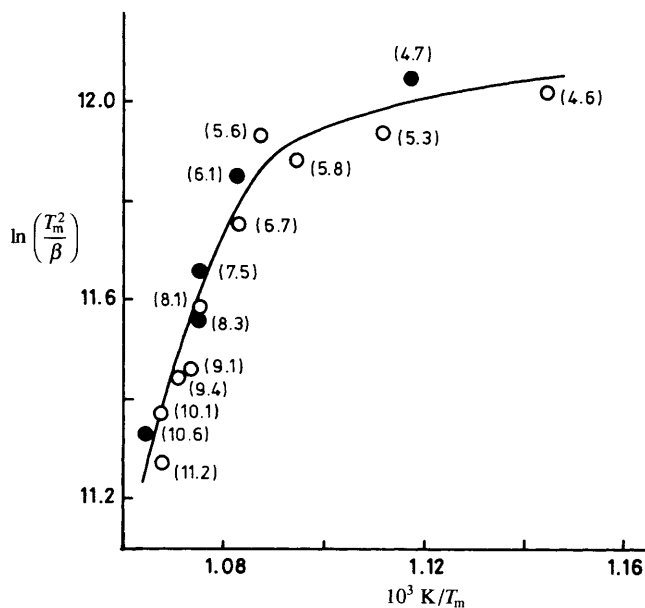
Fig. 1. Gentry plot for bulk V_2O_5. $\bigcirc$, 10^{-2} dm³ min⁻¹; $\bullet$, 2×10^{-2} dm⁻³ min⁻¹. Numbers in parenthesis indicate heating rates (K min⁻¹).
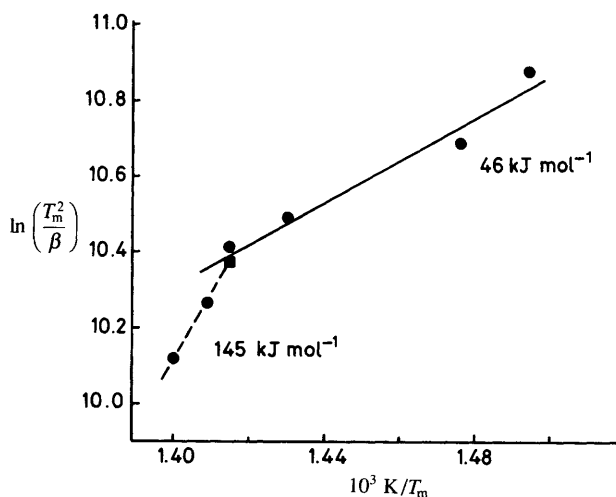
Fig. 2. Gentry plot for V_2O_5/TiO_2(rutile). T_m = maximum temperature on TPR peak, β = heating rate. $\bullet$, experiments with 10^{-2} dm³ min⁻¹; $\blacksquare$, experiment with 2×10^{-2} dm³ min⁻¹.

included in the product phase. The real conversion α is related to α_E, with the following boundary conditions: (1) when $\alpha = 0$ then $d\alpha/dt = d\alpha_E/dt$; (2) when $\alpha = 1$ then $d\alpha/dt = 0$ and $d\alpha_E/dt$ has a finite value. The most common relation, valid under conditions when the nuclei are randomly distributed, is:

$$\frac{d\alpha}{dt} = (1-\alpha)^m \frac{d\alpha_E}{dt}. \qquad (16)$$

The constant m can have non-integral values, because the two conditions are still valid in that case. Substitution of eqn (15) in eqn (16) gives the theoretical rate equation for the case of two-dimensional nucleation; in this case, *e.g.* for supported V_2O_5:

$$r_{T,2} = \frac{d\alpha}{dt} = C_2(1-\alpha)^m \left(\frac{T-T_S}{\beta}\right) \exp(-2E_a/RT) \tag{17}$$

where T_S = starting temperature, and β = heating rate.

A procedure which is analogous to the above, can also be followed for three-dimensional nucleation. This leads to the following equation:

$$r_{T,3} = \frac{d\alpha}{dt} = C_3(1-\alpha)^m \left(\frac{T-T_S}{\beta}\right)^2 \exp(-3E_a/RT). \tag{18}$$

Experimental Reduction Rate

The experimental reduction rate, r_T, at a certain temperature may be obtained from mass balances for the hydrogen and inert gas, respectively:

$$\text{H}_2: \quad \phi_o x_o = \phi x_T + r_T \tag{19}$$

$$\text{inert}: \quad \phi_o(1-x_o) = \phi(1-x_T) \tag{20}$$

where x is the mole fraction of hydrogen, and the subscript o refers to the feed and represents the molar flow rate. From these equations, by elimination of ϕ, the rate r_T at any temperature T can be calculated from:

$$r_T = \phi_o \frac{x_o - x_T}{1 - x_T}. \tag{21}$$

If the values of m and E_a are known, the theoretical rate ($r_{T,2}$ or $r_{T,3}$) for the cases of two-dimensional, or three-dimensional nucleation, respectively, can be calculated from one of the following two equations:

$$r_{T,2} = r_{m,2} \left(\frac{1-\alpha}{1-\alpha_m}\right)^m \left(\frac{T-T_S}{T_m-T_S}\right) \exp\left[2E_a/R\left(\frac{1}{T_m}-\frac{1}{T}\right)\right] \tag{22}$$

$$r_{T,3} = r_{m,3} \left(\frac{1-\alpha}{1-\alpha_m}\right)^m \left(\frac{T-T_S}{T_m-T_S}\right)^2 \exp\left[3E_a/R\left(\frac{1}{T_m}-\frac{1}{T}\right)\right] \tag{23}$$

where $r_{m,2}$ and $r_{m,3}$ refer to, respectively, the reduction rates at the temperature of the peak maximum for two-dimensional and three-dimensional nucleation. These values are calculated from eqn (21) with the observed value of x_T at T_m. The other parameters are determined experimentally. The concentration of lattice oxygen may be calculated as the ratio of the amount of oxygen still present for reduction to the amount of oxygen originally available to be reduced from V_2O_5 to V_2O_4. The latter quantity is calculated from the known amount of V_2O_5 present in the reactor and the amount left at any temperature is calculated from the total amount of hydrogen consumed up to that temperature.

All data of the complete TPR profile are now available for the estimation of E_a. The procedure will now be given. Curve-fitting of the complete peak involves a non-squares method to calculate the values of the unknowns E_a and m, in such a way that the calculated peak coincides as well as possible with the experimentally determined one. The following function must be minimized by choosing a suitable combination of m and E_a:

$$\int \{r_T[\text{eqn (21)}] - r_T[\text{eqn (22) or (23)}]\}^2 \, dT. \tag{24}$$

Table 1. Reduction data of the first peak of the TPR spectrum of bulk V_2O_5

heating rate /K min^{-1}	sample weight/mg	T_s^a/K	T_m^b/K
4.6	14.8	853	873
5.6	16.2	898	920
6.7	14.6	907 ⎫	924
8.3	10.3	907 ⎪	932
9.4	9.7	902 ⎬ 905 ± 2	934
10.1	10.7	904 ⎪	936
11.2	9.9	905 ⎭	936

^{a} T_s = starting temperature of reduction; ^{b} T_m = temperature of the peak maximum.

In this study, the minimum of this function was calculated using a Simplex method, as modified by Nelder and Mead.[12] This is a rigid, but not very rapid, method which is very suitable for least-squares methods, involving scattered data points.

In summary, three different methods to determine the activation energy of reduction are described: (1) shift of T_m with heating rate [eqn (7)], (2) comparison of the peak position with that of a reference peak [eqn (10)], (3) curve-fitting of a single peak [eqn (24)].

The results of the application of these methods will be discussed in the following sections.

Experimental

The TPR apparatus used was described previously.[1] The H_2 concentration of the reduction gas was 9 vol % in argon. This gas was premixed using gases of technical purity; the mixture contained 800 ppm of water. Flow rates of 10^{-2} and 2×10^{-2} dm^3 min^{-1} were used.

Bulk V_2O_5 was supplied by Merck (proanalysis). The V_2O_5/TiO_2 sample was prepared by adsorption of vanadyl acetylacetonate $VO(acac)_2$ on TiO_2.[13,14] The sample thus prepared contained 0.83 wt % V and had a specific surface area of 10 m^2 g^{-1}.

Results

Application to Bulk V_2O_5

Method of Gentry

The method of Gentry was applied to bulk V_2O_5. The TPR profile of bulk V_2O_5 consists of several peaks; the calculation of the activation energy is here only applied to the first peak which corresponds to the reduction of V_2O_5 to V_6O_{13}. The apparent activation energy for the reduction for bulk V_2O_5 was estimated to be *ca.* 200 kJ mol^{-1}.[1] This value, however, was an estimated average for heating rates between 5 and 10 K min^{-1}. It was stated[1] that deviations from the best straight line occurred beyond these limits. The relevant Gentry plot, in which $\ln(T_m^2/\beta)$ is plotted against $10^3/T_m$, is given in fig. 1. The numbers given beside each point in this figure indicate the heating rate (K min^{-1}). From the slope, it can be calculated that the apparent activation energy increases from 20 kJ mol^{-1} at heating rates between 4 and 5 K min^{-1}, through a value of 133 kJ mol^{-1} at a heating rate of 7 K min^{-1}, to a value as high as 370 kJ mol^{-1} at the highest heating rates.
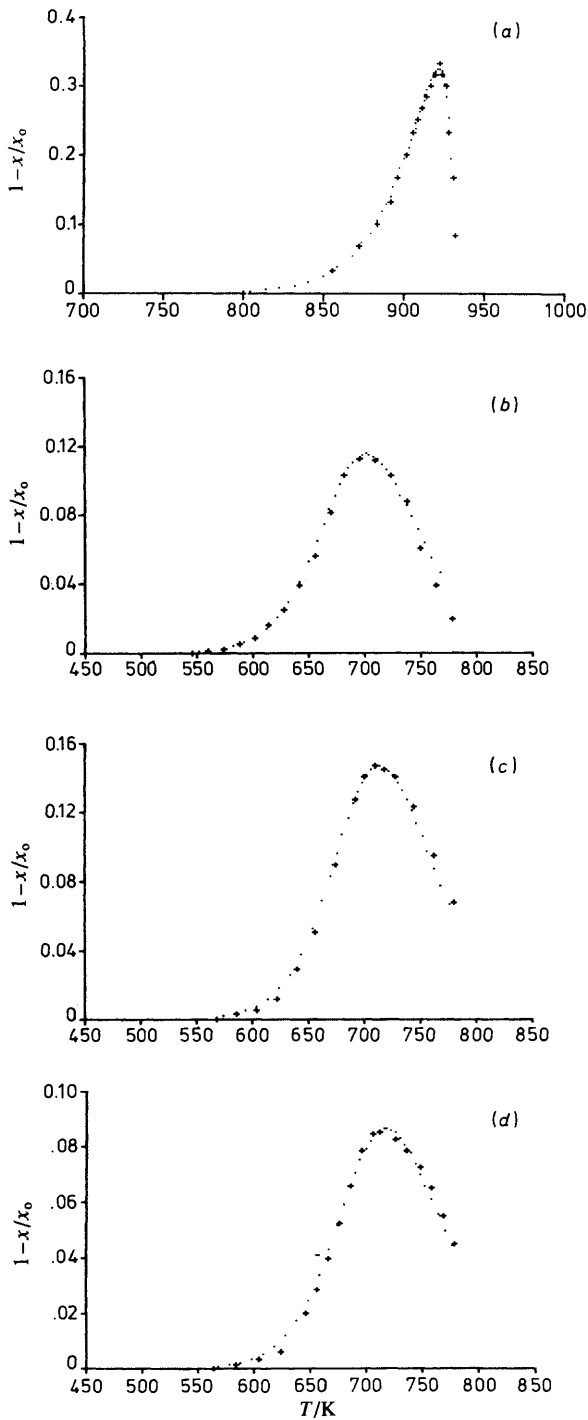
Fig. 3. Curve-fitting of TPR peaks. $+ + +$, observed; $\cdots\cdots$, calculated. $x =$ mole fraction of H_2; subscript o refers to the feed. (a) V_2O_5, $\beta = 6.7$ K min^{-1}, $E = 61$ kJ mol^{-1}, $m = 0.19$; (b) V_2O_5/TiO_2, $\beta = 13.6$ K min^{-1}, $E = 58$ kJ mol^{-1}, $m = 2.1$; (c) V_2O_5/TiO_2, $\beta = 17.6$ K min^{-1}, $E = 58$ kJ mol^{-1}, $m = 2$; (d) V_2O_5/TiO_2, $\beta = 20.4$ K min^{-1}, $E = 60$ kJ mol^{-1}, $m = 2.2$.

Table 2. Summary of the calculation of the activation energy[a] of the reduction of V_2O_5/TiO_2, using different methods

	shift of T_m		calculations from single peak			
	Gentry equation [eqn (7)]		reference method [eqn (10)]		curve-fitting [eqn (24)]	
heating rate /K min^{-1}	$E_e/2$, lower heating rate	$E_e/2$, higher heating rate	T_s/K	$E_e/2$	E_a	m order in nuclei growth
8.4			—	—	—	—
10.4			568	69	—	—
13.6	23		560	68	58	2.1
15.3			—	—	—	—
15.4		73	—	—	—	—
17.6			577	70	58	2
20.4			583	70	60	2.2
overall	23	73		69 ± 4	59 ± 2	

E_e = experimental energy of activation in an emperical rate equation; E_a = energy of activation of nuclei growth according to Avrami–Erofeev. [a] Energies in kJ mol^{-1}.

Reference Method

Analysis of TPR data using eqn (10) requires a knowledge of the temperatures required to give constant rates of reduction. The temperature at which the reduction starts fulfills this requirement. Table 1 lists the temperatures for the start of the reduction, T_s, and the temperatures of the peak maxima, T_m, as a function of the heating rate. When the heating rate is increased from 6.7 to 11.2 K min^{-1}, the peak maximum shifts 12 K to higher temperatures, whereas the temperature of the start of the reduction remains virtually constant at 905 ± 2 K. An average value of 214 kJ mol^{-1} is calculated using eqn (10). This value and the onset of the reduction peak (905 K) for bulk V_2O_5 are taken as the reference values E_r and T_r in the section on supported V_2O_5.

Curve-fitting

In fig. 3(a), the experimental curve and the optimized curve were found to coincide best with a value of $E_a = 61$ kJ mol^{-1} and of $m = 0.19$. The value of the activation energy is considerably lower than those obtained by the Gentry and reference methods. These differences will be discussed in a later section.

Application to Supported V_2O_5

Method of Gentry

TPR experiments have been carried out with the supported V_2O_5 using different heating rates. The Gentry plot of $\ln(T_m^2/\beta)$ *vs.* $1/T_m$ is shown in fig. 2. At lower heating rates of 8.4–15.4 K min^{-1}, a value of 46 kJ mol^{-1} was calculated from the slope; at higher heating rates of 15.3–20.4 K min^{-1}, a value of 145 kJ mol^{-1} was calculated.

Reference Method

From the temperatures T_s at which the reduction starts and application of eqn (10) (using $E_r = 214$ kJ mol^{-1} and $T_r = 905$ K), an average value of 138 ± 3 kJ mol^{-1} was calculated for the activation energy.

Curve-fitting

Adjustment of the values of E_a and m in eqn (22) was carried out so that the best fit occurred between the calculated and experimental peaks. The results are given in fig. 3(b)–(d) and the optimal values of both parameters are given in table 2 (see next section). The overall E_a is 59 kJ mol^{-1}.

Discussion

Reduction Mechanism

The reduction of bulk V_2O_5 probably proceeds in a number of distinct, successive reduction steps:[1]

$$V_2O_5 \rightarrow 1/3V_6O_{13} \rightarrow 2VO_2 \rightarrow V_2O_3. \qquad (25)$$
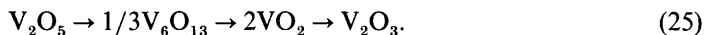
Vanadium oxide has the possibility of forming oxides of mixed valency, the ratio of these depending on the proportion of shared corners (V^{5+}) relative to shared edges (V^{4+}).[15] Andersson[16–18] found that the bond length of V^{5+}=O in V_2O_5 is 1.585 Å, while the bond length of V^{5+}=O in V_6O_{13} appeared to be 1.685 Å and 1.674 Å. He calculated the corresponding bond strengths with an empirical expression derived for vanadium oxides.[17] From these results, he concluded that the presence of reduced V^{4+}–OH sites adjacent to V^{5+} sites with V=O bonds, weaken these bonds.

As a consequence of this, these 'excited' V^{5+}=O sites, adjacent to V^{4+}–OH sites, are easier to reduce. A V^{4+} site can be considered as a nucleus, from where reduction proceeds. This is an autocatalytic nucleus formation mechanism. This self-catalysed formation of weaker V=O bonds at V^{5+} sites under the influence of adjacent V^{4+} sites during the TPR is considered as the rate-determining step. This led to the idea of describing the mechanism, presented above, with a commonly used nucleation model. Different models were applied (*e.g.* Jander diffusion models), but only the Avrami–Erofeev nucleation model turned out to be reasonable.

Bulk V_2O_5

Using the region with heating rates of 15–20 K min^{-1}, the experimental activation energies calculated from Gentry's method are in agreement with those calculated from the reference method using heating rates of 6–11 K min^{-1}. However the values obtained are quite high. The result of the application of the curve-fitting method to the first reduction peak of bulk V_2O_5 resulted in a considerably lower value of the activation energy, 61 kJ mol^{-1}. Comparison of the theoretical rate equation derived for three-dimensional nuclei growth [eqn (18)] and the rate equations for the Gentry and reference method [eqn (3) and (9), respectively], lead to the suggestion, that the experimental activation energies from the latter methods, must be divided by 3 to compare to E_a for nuclei growth. Doing so, an E_a of 71 kJ mol^{-1} for these methods is obtained. The agreement with the value of 61 kJ mol^{-1} for bulk and 59 kJ mol^{-1} for supported V_2O_5 (see table 2) obtained by curve-fitting is reasonable, taking into account that the value of the starting temperature cannot be estimated very accurately and that the slope in Gentry's plot (fig. 1) depends on the region which is used.

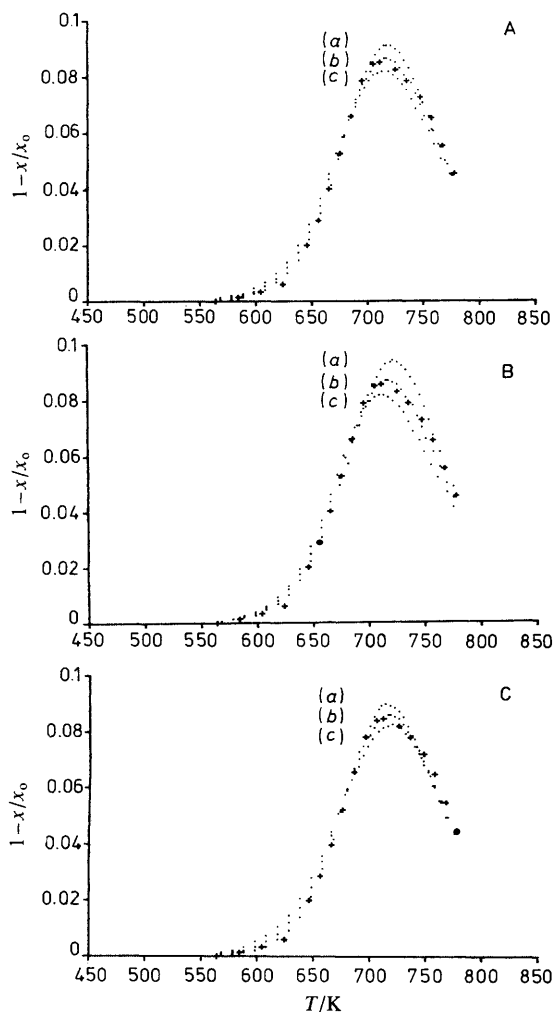These results indicate that the activation energy calculated by the curve-fitting method

Fig. 4. Sensitivity analysis [data fig. 3(*d*)]. + + +, observed; · · · ·, calculated. x = mole fraction of H_2; subscript o refers to the feed. A, $m = 2.2$, $E_a = 63$ (0.10), $E_b = 60$ (0.050), $E_c = 56$ kJ mol^{-1} (0.1). B, $E = 60$ kJ mol^{-1}, $m_a = 2.0$ (0.14), $m_b = 2.2$ (0.050), $m_c = 2.4$ (0.12). C (*a*) $E = 56$, $m = 2.0$ (0.059); (*b*) $E = 60$, $m = 2.2$ (0.050); (*c*) $E = 64$, $m = 2.4$ (0.059). Numbers in parenthesis denote the variance $\times 10^6$ in concentration.

for both bulk and supported V_2O_5 are comparable (61 and 59 kJ mol^{-1}, respectively). Similar values are obtained using the Gentry method or the reference method, provided an appropriate region of heating rates is chosen.

Supported V_2O_5

The reduction of a monolayer catalyst is probably a chemically controlled process. Simon *et al.*[19] showed with thermogravimetry that an increase of the heating rate resulted in a lowering of the activation energy. Applying Gentry's method, the opposite is found for the reduction of both unsupported and supported V_2O_5. Neither of the two single-peak approaches, the reference method nor the curve-fitting method, reveals a dependency on the heating rate.

Just like above, the values of the obtained experimental activation energies with the Gentry and reference method [eqn (3) and (9), respectively] can be divided, in this case, by 2, to compare to the E_a for two-dimensional nuclei growth in eqn (17). For higher heating rates the E_a from Gentry's method results in 73 kJ mol^{-1}, while the E_a from the reference method becomes 69 kJ mol^{-1}.

The deviation found in E_a using Gentry's method at lower heating rates for supported V_2O_5 (accepting 60–70 kJ mol^{-1} to be a reasonable estimate of the value of activation energy) could be caused by differences in the concentration of lattice oxygen at the peak maximum for the different heating rates: the higher the heating rate, the higher is the oxygen conversion at the peak maximum. This effect is taken into account using the curve-fitting method, while in the Gentry method the concentration of lattice oxygen at the peak maximum is assumed to be independent of the heating rate.

Accuracy of the Calculations

Finally, it is interesting to look at the influence of the evaluated parameters, E_a and m, on the calculated TPR peak. Fig. 4 shows calculated TPR-peaks for a number of values of E_a and m. For the sake of clarity, these values are chosen in such a way that differences in the calculated TPR-peaks are sufficiently large to be shown. Fig. 4C demonstrates the compensation of a higher value of E_a by a higher value of m.

Conclusions

The activation energy for the reduction of a supported catalyst can be calculated from the analysis of a single TPR experiment, provided a reasonable reduction model is available. This approach saves a lot of time compared with the method of Gentry.

Once the kinetic parameters of a certain sample are known, a series of similar samples can be screened very rapidly by measuring the temperature of the onset of reduction (reference method).

The values of the activation energy of nuclei growth obtained for both bulk V_2O_5 and V_2O_5/TiO_2 applying the curve-fitting method is 60 ± 3 kJ mol^{-1}.

It is suggested that experimental activation energies using empirical rate equations have to be divided by 3 and 2 in case of, respectively, three- and two-dimensional nuclei growth.

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