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HYDROGEN TEMPERATURE PROGRAMMED REDUCTION BASED ON WATER ANALYSIS
Application to vanadium pentoxide

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Abstract

Profiles of temperature programmed reduction (TPR) of V_2O_5 under H_2 have been studied through water analysis. This new approach enhances the sensitivity of the method. The influence of experimental parameters on the temperature corresponding to the maximum reduction rate, T_m, has been studied. The hydrogen concentration and heating rate are the two major factors that influence T_m. In our method, the amount of solid and the flow rate are also important factors in monitoring of profile distortions attributed to water condensation at the outlet of the reactor. An approach of the mechanism of reduction of V_2O_5 has been carried out. The best kinetic model which describes the reduction process is the Avrami-Erofeev tridimensional nucleation model.

Keywords: heterogeneous catalysis, temperature programmed reduction, V_2O_5, water analysis

Introduction

In the field of heterogeneous catalysis, thermal analysis is often used as a tool to investigate changes of surface and/or bulk reactivity of solids in different gas atmospheres as a result of variation in composition, preparation method or preliminary treatment. Different techniques can be used as the temperature programmed reduction (TPR) which has gained increasing importance during the last decade [1–8]. Usually the rate of reduction is continuously measured by monitoring the composition of the reducing gas at the outlet of the reactor. Some studies have been devoted to V_2O_5 reduction [1, 2, 9–11]. The experiments have been performed under partial pressure of hydrogen to observe oxide intermediates. Under such conditions, the reduction process occurs in a temperature interval where melting processes take place [10,12–15] and can change the course of the reaction. The new approach based on the analysis of

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the reduction product (H_2O) has been applied in our laboratory to enhance the sensitivity of the method which allows to perform TPR experiments under atmospheric pressure of hydrogen. The present paper describes the effect of the experimental parameters on the TPR profiles of V_2O_5 obtained by thermal conductivity detection of H_2O. A mechanism for V_2O_5 reduction under an atmospheric pressure of hydrogen is proposed.

Theoretical background

The rate of a heterogeneous reduction process can be expressed by the following relation:

$$r = \frac{d\alpha}{dt} = k(T)f(\alpha)\varphi(C) \tag{1}$$

where α is the degree of reduction, t is the time, C is the concentration of the reducing gas ($mol \cdot cm^{-3}$), $k(T)$ is the rate constant, $f(\alpha)$ is a function that accounts for the dependence on the degree of reduction and $\varphi(C)$ is a function that accounts for the dependence of the rate upon the reducing gas concentration.

Taking into account a linear temperature program (β ($deg \cdot s^{-1}$) and considering that the temperature dependence of the rate constant obeys the Arrhenius law, the following relation is obtained:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha)\varphi(C) \tag{2}$$

where A is the preexponential factor (s^{-1}), E is the activation energy ($J \cdot mol^{-1}$) and R is the gas constant (8.31434 $J \cdot mol^{-1} \cdot K^{-1}$).

A characteristic experimental TPR profile obtained for V_2O_5 is shown in Fig. 1.

From this profile, the following data are obtained:

i) the temperature of maximum reduction rate, T_m(K),

ii) the profile area that allows to determine the extent of reduction of the solid,

iii) the maximum amplitude of the peak N_m(mV),

iv) the width at half N_m, B(K) and

v) the temperature at half B, T_m^* (K).

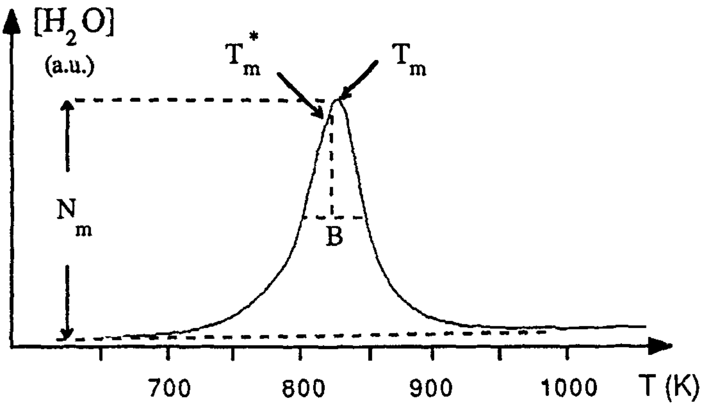

Fig. 1 TPR profile of V_2O_5 under hydrogen; m = 0.050 g, $F(H_2)$ = 0.833 cm^3·s^{-1},β = 0.116 deg·s^{-1}

Determination of the activation energy

The classical method used in this work is based on the variation of β which provokes changes in T_m and N_m values. At T_m, the reduction rate is maximum:

$$\left(\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\right)_{T=T_m} = 0 \tag{3}$$

By assuming the following assumptions:

i) H_2 conversion is low enough to consider H_2 concentration as constant throughout the reactor,

ii) the reduction process follows first order kinetic with respect to H_2,

iii) the reduction mechanism and the concentration of lattice oxygen in the sample are independent of the heating rate and

(iv) $(\mathrm{d}f(\alpha)/\mathrm{d}\alpha)_{T=T_m}$ is not equal to zero, the differentiation of Eq. (2) leads to the well known equation [5, 16–18]:

$$\ln\frac{T_m^2C}{\beta} = \frac{E}{RT_m} + \ln\frac{E}{AR} + \text{constant} \tag{4}$$

At a given temperature, the peak amplitude N is proportional to the reduction rate and is defined from Eq. (2) by:

$$N \approx \frac{A}{\beta}\mathrm{e}^{-\frac{E}{RT}}f(\alpha)\varphi(C) \tag{5}$$

At T_m and taking logarithms

$$\ln N_m = -\frac{E}{RT_m} + \ln f(\alpha)C + \ln \text{constant} \tag{6}$$

Experimentally, the activation energy is obtained from the slope of the linear equations $\ln(T_m^2/\beta)$ *vs.* $1/T_m$ and $\ln(N_m)$ *vs.* $1/T_m$.

Calculation of TPR profile

From the experimental values of E, T_m and β, theoretical TPR profiles can be calculated according to different kinetic models and compare to the experimental ones. This mechanistic approach of heterogeneous process by non-linear thermal analysis has been extensively studied [19–24]. In this work, the integration method was used [22]. According to this method, Eq. (2) can be rewritten as follows:

$$\frac{d\alpha}{f(\alpha)} = \frac{A'}{\beta} e^{-\frac{E}{RT}} dT \tag{7}$$

with

$$A' = A\varphi(C) = AC \tag{8}$$

Integration of this equation gives the function $g(\alpha)$:

$$g(\alpha) = \frac{A'E}{R\beta} p(x) \tag{9}$$

where

$$x = \frac{E}{RT} \text{ and } p(x) = \frac{e^{-x}}{x} - \int_x^{\infty} \frac{e^{-x}}{x} dx \tag{10}$$

To resolve *p(x)*, the following approximation reported by Sestak *et al.* [22] was used:

$$p(x) = \frac{e^{-x}}{x}\left(\frac{674.567 + 57.412x - 6.055x^2 - x^3}{1699.066 + 841.655x + 49.313x^2 - 8.02x^3 - x^4}\right) \tag{11}$$

$$\text{with } 9<x<174 \tag{12}$$

A' is determined from the following set of equations:

$$-A'\frac{\mathrm{d}f(\alpha)}{\mathrm{d}\alpha}=\mathrm{e}^{\ln\left(\frac{\beta \mathrm{E}}{\mathrm{RT}_{\mathrm{m}}^{2}}\right)+\frac{\mathrm{E}}{\mathrm{RT}_{\mathrm{m}}}} \tag{13a}$$

$$g(\alpha)=\frac{A'E}{R\beta}p(x) \tag{13b}$$

The value *A'* allows to calculate α for different temperatures from Eq. (9). Eq. (2) can be resolved and plotting $\mathrm{d}\alpha/\mathrm{d}T$ *vs.* *f(T)* allows to obtain the theoretical TPR profile for the reduction model selected. Our interpretation concerning the results of kinetic studies of solid decomposition is mostly based on the traditional concept of nucleation and nuclei growth. Table 1 reports the functions $f(\alpha)$ and $g(\alpha)$ for common reduction models described in the literature [19, 22–25].

Experimentally, the commonly used analysis method is based on the variation of hydrogen concentration. Hence the variation must be high enough to be detected and low enough to assume $[H_2]$ as constant. In order to avoid high distortion in the TPR profiles and to ensure a good resolution, Baiker *et al.* [17] and Malet *et al.* [26] have respectively defined *M* and *P* criteria as follows:

$$M=\frac{S_o}{F[C]_i} \tag{14}$$

$$P=\frac{\beta S_o}{F[C]_i} \tag{15}$$

where S_o is the initial amount of reducible species(mol), *F* is the total flow rate ($\mathrm{cm^3 \cdot s^{-1}}$) and $[C]_i$ is the initial hydrogen concentration ($\mathrm{mol \cdot cm^{-3}}$). According to Baiker *et al.* [17], *M* should have a value in the range 55–140 s for $0.1<\beta<0.3$ $\mathrm{deg \cdot s^{-1}}$ to maintain an optimal resolution. If *M* is lower than 55 s, the variation of hydrogen concentration is too small to be detected and if *M* is higher than 140 s, the hydrogen consumption is too important to consider $[H_2]$ as a constant whereas according to Malet *et al.* [26], *P* values should be kept as low as possible with the upper limit of 20 K.

Experimental

V_2O_5 (7.2 $\mathrm{m^2 \cdot g^{-1}}$) was purchased from Merck. It was calcined at 753 K in air for 12 h before use. Hydrogen and nitrogen (99.99%) were purchased from

Air Liquide. The TPR apparatus elaborated is similar to the one previously described by Robertson *et al.* [27]. The reducing gas was first passed through the reference of an IGC 120 MB Intersmat katharometer, then through the reactor, then through the second arm of the detector and finally through a six valve port connected to a conventional GC equipped with a katharometer detector and a Porapak T (L = 1.5 m, φ = 0.31 cm, 80–100 mesh) for analyzing H_2 (carrier gas flow rate $F(N_2)$ = 0.2 $cm^3 \cdot s^{-1}$, T(column) = 323 K). The reactor consisted in a 6 mm quartz glass U tube. The rate of water production was monitored by a CR4A Shimadzu integrator.

Results and discussion

TPR profile of H_2O production

We have checked that the TPR profile of H_2O production corresponds to the hydrogen consumption analysed by GC (Fig. 2).

This comparison has been done with a gas feed of 2.5% H_2 to be able to measure hydrogen consumption. Therefore water desorption step is not the limiting step and the analysis of the reaction product can be used in this TPR study.

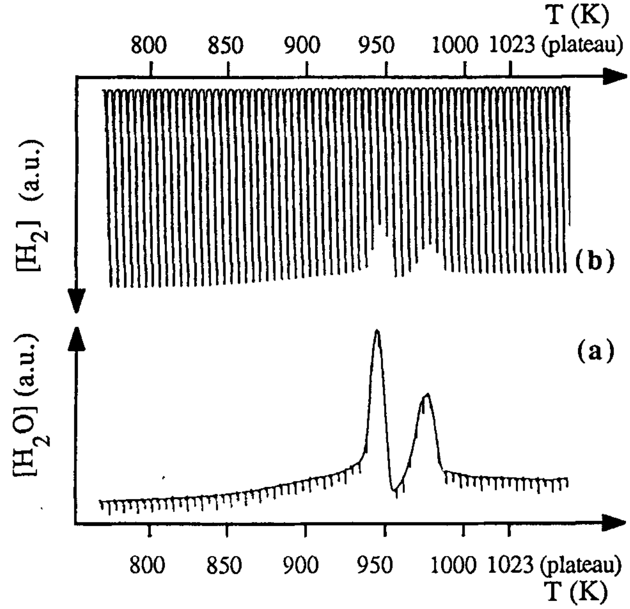

Fig. 2 (a) water and (b) hydrogen analysis for TPR profiles of V_2O_5 under 2.5% H_2; m = 0.014 g, $F(H_2)$ = 0.35 $cm^3 \cdot s^{-1}$, β = 0.116 $deg \cdot s^{-1}$

Table 1 $f(\alpha)$ and $g(\alpha)$ functions, A' and B values for different reduction models using $E=83$ kJ·mol^{-1}, $\beta = 0.1166$ deg·s^{-1} and $T_m=829$ K

Reduction model	$f(\alpha)$	$g(\alpha)$	A'/ s^{-1}	B / K
Three-dimensional nucleation according to Avrami-Erofeev	$(1-\alpha)(-\ln(1-\alpha))^{2/3}$	$(-3\ln(1-\alpha))^{1/3}$	456	48
Two-dimensional nucleation according to Avrami-Erofeev	$(1-\alpha)(-2\ln(1-\alpha))^{1/2}$	$(-2\ln(1-\alpha))^{1/2}$	40	278
Two-dimensional phase boundary	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$	140	105
Three-dimensional phase boundary	$3(1-\alpha)^{1/3}$	$1-(1-\alpha)^{1/3}$	107	120
Unimolecular decay according to Mampel	$1-\alpha$	$-\ln(1-\alpha)$	272	153
Three-dimensional diffusion according to Jander	$3/2(1-\alpha)^{1/3}((1-\alpha)^{-1/3}-1)^{-1}$	$(1-(1-\alpha)^{1/3})^2$	27	153
Experimental value				52

Influence of operating variables on T_m

The parameters which may govern the resolution of TPR profiles such as hydrogen concentration, heating rate, sample mass and flow rate have been studied.

In the range of hydrogen concentration 35.3–99.99% (14.4–40.89 10^{-6} mol·cm^{-3}) the TPR profile shows only one peak (Fig. 1). The quantitative analysis of the profile area gives an amount of H_2O corresponding to the reduction of V_2O_5 to V_2O_3 in agreement with previous works [28]. Decreasing H_2 concentration initiates the splitting of the main peak and for H_2 concentration below 5%, the profile is constituted of two peaks (Fig. 2) and the final stoichiometry product is V_4O_7. At such concentration values, TPR measurements are performed in a temperature range where melting processes can occur [21–25]. For conditions where one peak was observed, the decrease of hydrogen concentration shifts T_m towards higher temperatures (Fig. 3a) in agreement with Eq. (2). The extrapolation of the curve at zero abscissa gives a T_m value of 948 K that means V_2O_5 can loose oxygen spontaneously above 948 K.

An opposite behaviour is observed for β variation (Fig. 3b). When β increases from 0.070 to 0.150 deg·s^{-1}, T_m is moved by 75 K to the higher temperatures.

The effect of the amount of sample and of the total flow rate on T_m are quite insignificant for data respectively inferior to 0.080 g and superior to 0.555 cm^3·s^{-1} (Figs 3c and 3d). When the amount of sample increases and the flow rate decreases, T_m shifted towards the higher temperature and asymmetrical profiles are observed which have led us to introduce a new parameter, T_m^* (Fig. 1) which remains approximately at the same value. The difference between T_m and T_m^* points out the asymmetry of the peak observed. This effect is also observed in Fig. 3e which represents T_m and T_m^* *vs.* δ (the contact time) defined as the ratio m/F_m (s); m is the amount of sample (g) and F_m is the weight flow rate of hydrogen (g·s^{-1}). For $\delta \leq 1000$ s, $T_m = T_m^*$ but for higher values, the resulting profiles are asymmetrical, even flat at the peak maximum for the high value of amount of sample and for weak values of flow rate. This result suggests that the concentration limit of water has been attained in the gas phase.

Determination of M and P parameters

The value of the parameter M, 19.7 s, has been determined from Eq. (15) with the following standard conditions: $[H_2] = 40.89\ 10^{-6}$mol·cm^{-3}, β = 0.116 deg·s^{-1}, m = 0.050 g, F = 0.833 cm^3·s^{-1}. M is lower than 55 s which

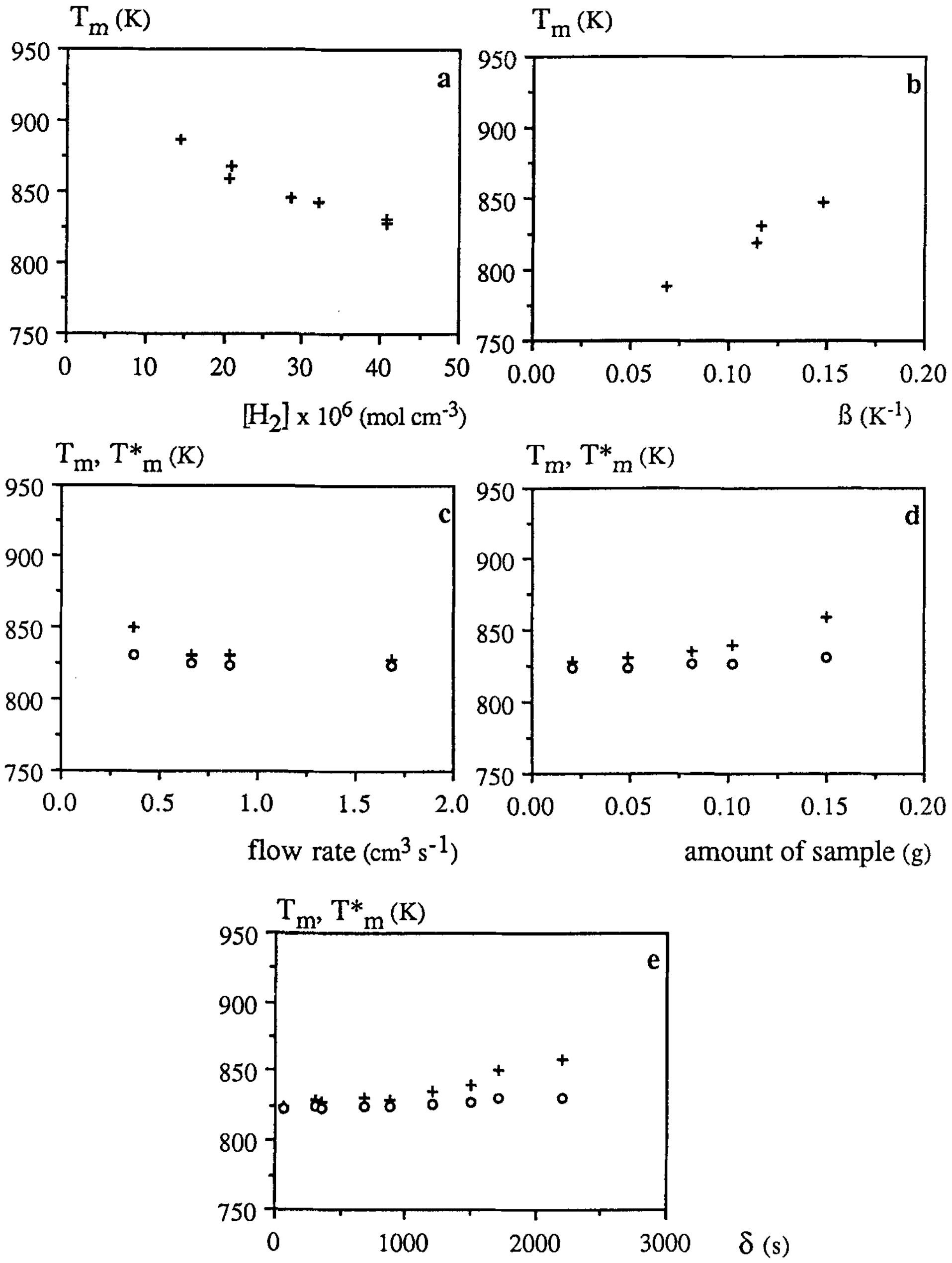

Fig. 3 Effect of operating variables on T_m (+) and T^*_m (o) in TPR of V_2O_5; (a) $[H_2]$, (b) β, (c) F, (d) m, (e) δ; $m = 0.050$ g, $F(H_2) = 0.833$ cm^{3}s^{-1}, $[H_2] = 40.89\ 10^{-6}$ mol·cm^{-3}, $\beta = 0.116$ deg·s^{-1}

means that the variation of hydrogen concentration should be too small to be detected [10]. By using the analysis of water production, this problem is avoided and the hydrogen concentration can be better considered as constant. Our *P* value (2.3 K) is also much lower than 20 K, showing experimental standard conditions for good resolution.

Kinetic approach of the reduction mechanism

The activation energy has been calculated from the slope of the linear equations $\ln(T_m^2/\beta)$ *vs.* $1/T_m$ and $\ln(N_m)$ *vs.* $1/T_m$ and found for the reduction of V_2O_5 to V_2O_3 an activation energy of 83±5 $kJ \cdot mol^{-1}$ under hydrogen atmosphere. From the application of the integration method, *A*' values have been calculated (Table 1), theoretical profiles have been plotted and so *B* values have been measured for the six kinetic models mentioned in Table 1. Therefore the experimental profile has been retraced in terms of $d\alpha/dT$ *vs.* $1/T$. The comparison of *B* values (Table 1) suggests that the three-dimensional nucleation model according to Avrami-Erofeev is the most appropriate to describe the reduction of V_2O_5 to V_2O_3 under hydrogen atmosphere. The comparison of the theoretical profile of this model with the experimental one (Fig. 4) confirms this hypothesis.

Therefore, under atmospheric pressure of hydrogen, it is most likely that the reduction of V_2O_5 proceeds with three-dimensional nucleation according to Avrami-Erofeev. The same model was proposed by Bosch *et al.* [11] for the reduction of V_2O_5 under 9% H_2.

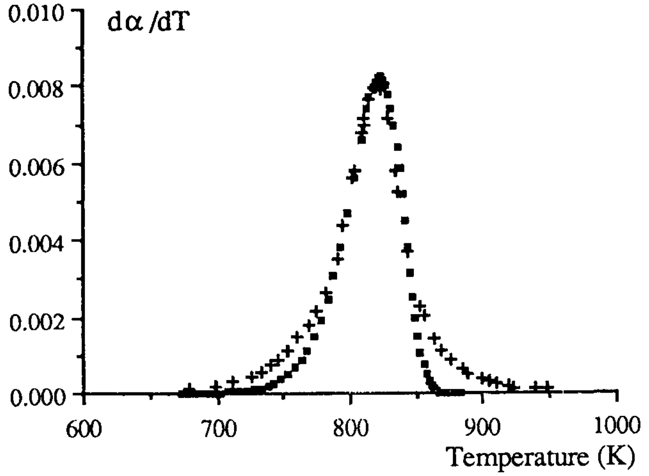

Fig. 4 Comparison of the experimental (+) and theoretical profile corresponding to the three-dimensional nucleation model according to Avrami-Erofeev (•)

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Zusammenfassung — Über eine Wasseranalyse wurde der Verlauf der temperaturprogrammierten Reduktion (TPR) von V_2O_5 in Wasserstoff untersucht. Diese neue Art steigert die Empfindlichkeit der Methode. Es wurde der Einfluß der Versuchsparameter auf die Temperatur der maximalen Reduktionsgeschwindigkeit T_m untersucht. Wasserstoffkonzentration und Aufheizgeschwindigkeit sind diejenigen beiden Parameter, welche T_m am meisten beeinflussen. In unserem Verfahren sind die Feststoffmenge und die Strömungsgeschwindigkeit ebenfalls wichtige Faktoren bei der Beobachtung der Profiländerungen im Zusammenhang mit der Kondensation von Wasser am Außenmantel des Reaktors. Es wurde ein Versuch zur Beschreibung des Mechanismus der Reduktion von V_2O_5 unternommen. Das beste reaktionskinetische Modell zur Beschreibung des Reduktionsprozesses ist das dreidimensionale Keimbildungsmodell von Avrami-Erofeev.