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INFLUENCE OF THE EXPERIMENTAL CONDITIONS ON THE DEHYDRATION KINETICS OF K(NbW)$O_6.H_2O$

INFLUENCIA DE LAS CONDICIONES EXPERIMENTALES SOBRE LA CINETICA DE DESHIDRATACION DEL K(NbW)$O_6.H_2O$

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Abstract

The influence of the experimental conditions on the calculated kinetic parameters of the thermal dehydration of K(NbW)O_6 H_2O were studied using quasi-isothermal (Q-TGA) and high resolution (TGA Hi-Res) thermogravimetric techniques. The dependence of $(Ea)_\alpha$ shows the importance of the partial pressure of the gaseous product (P_{H2O}) in the vicinity of the reactant. The results show the limited validity of kinetic data calculated from experiments carried out under arbitrary chosen conditions, although the experimental conditions are strictly controlled.

Keywords: isoconversion method; dehydration kinetics; high resolution thermogravimetry, quasi-isothermal thermogravimetry, influence of experimental conditions.

Resumen

Se utilizaron las técnicas de análisis térmico, quasi-isotérmico (Q-TGA) y termogravimetría de alta resolución (TGA Hi-Res), para demostrar la influencia de las condiciones experimentales sobre los parámetros cinéticos calculados, usando como modelo de reacción la deshidratación del K(NbW)O_6 H_2O. La dependencia de $(Ea)_\alpha$ muestra la influencia de la presión parcial del producto gaseoso (P_{H2O}) en la vecindad del sólido residual. Se demuestra la validez limitada de los datos cinéticos calculados en experimentos realizados bajo condiciones de reacción arbitrarias, aún cuando los parámetros experimentales son estrictamente controlados.

Palabras claves: método de isoconversión, cinética de deshidratación, termogravimetría de alta resolución, termogravimetría cuasi-isotérmica, influencia de las condiciones experimentales.

1. Introduction

Solid state kinetic data have increasingly become useful in the formulation and characterization of materials and technological processes (Valor *et al*., 2002, Torres-García *et al*., 2001, Torres-García *et al.,* 2001). External stimuli, such as thermal activation by thermogravimetry (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA), can activate solid state reactions (Brown *et al*., 1980). By using these methods it is possible to take numerous data from a single experiment and simplify the estimation of the kinetic parameters. However, the reliability of these parameters is extremely low, because the above mentioned techniques are not chemically specific in the detection of the reactions. Furthermore data analysis is complicated and prone to error because of the extent of reaction dependence upon temperature (Arii and Fujii, 1997). The under- and/or over-estimation by these kinetic methods may result from an incomplete understanding of the kinetics of the solid state reactions.

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It has often been reported that kinetic parameters of heterogeneous solid state reactions, i.e. activation energy, E, pre-exponential factor, A, and the function of the reaction extent, $f(\alpha)$, depend on the experimental conditions and it is difficult to accept them as intrinsic constants of the analyzed reaction (Roduit *et al.*, 1996). Many papers have illustrated this problem and have presented the influence of the sample weight, the atmosphere, the gas flow, or the crystallite size (Arii and Fujii, 1997; Roduit *et al.,* 1996; Bordère *et al.*, 1996; Vyazovkin *et al.*, 1997) on the course of the kinetic curve for heterogeneous reactions. There you could find empirical relationships between, e.g., the sample mass and the activation energy in the form of polynomial expressions assuming that the mechanism of the process remains unchanged under different conditions.

This simple assumption is not always true, as shown by Roduit *et al.,* (1996) and Criado *et al.,* (1986) in their researches on $CaCO_3$ decomposition under different atmospheres. These authors have demonstrated that not only E and A, but also the shape of the thermogravimetric (TGA) and differential thermal analysis (DTA) curves vary, indicating a change in the form of the $f(\alpha)$ function dependent on the kinetic models of the heterogeneous reactions.

The present paper shows the influence of the experimental conditions using high resolution thermogravimetric (Hi-Res TGA) and quasi-isothermal thermogravimetric (Q-TGA) analysis on the kinetic parameters of the thermal dehydration of $K(NbW)O_6.H_2O$.

2. Experimental

2.1. Materials

The pyroclore $K(NbW)O_6\ H_2O$ was prepared from a stoichiometric mixture of KNO_3, WO_3 and Nb_2O_5 (all of them from Merck, reagent grade) by heating at 900 °C for 12 h in air (Jerez *et al.*, 1987). The resulting material was a white microcrystalline solid.

2.2. Apparatus

A high resolution thermobalance (TA Instruments, mod. TG-2950) and derivatographs (MOM Budapest) of the type Paulik-Paulik, namely Q-1500 D were employed. The conditions for the Hi-Res TGA analysis was as follows: flow of N_2 (100 ml/min); heating rates of 10 and 20 °C/min with a resolution of 5; weight of sample was about 66 mg. While, the Q-TGA experimental conditions were as follows: a labyrinth crucible was used and the programmed transformation rate between 0.04 and 0.1 mg/min with an static air atmosphere. Sample weight was about 300 mg.

The Hi-Res TGA technique incorporates basic elements of the conventional techniques and the ideas set by Roquerol (1997) and Paulik´s (1986), Paulik´s (1987). In this technique, when no loss of mass occurs, it is possible to have a high heating rate (for example, 50 °C/min), but when a loss is detected the heating rate is reduced towards zero, and kept low until the mass again becomes nearly constant (Haines, 1995). The Hi-Res TGA techniques have the advantage of higher resolution of thermal events without requiring long experimental times.

On the other hand, the Q-TGA techniques of the Paulik´s (1986), controlled their system in such a way as to keep the rate of the mass loss constant, and to confine the reaction gases so that they were lost at constant atmospheric pressure. The disadvantage of this technique is the long time taken for each experiment (it could be several hours). Both techniques, Q-TGA and Hi-Res TGA, maintain a constant reaction rate, and control the pressure of the evolved species in the reaction environment, allowing for strict experimental conditions of reaction.

2.3. Procedure

The kinetic analysis of the isokinetic data was done as reported by Brown *et al.,* (1980) and Vyazovkin (2000). The general equation of the reaction rate is given by:

$$\frac{d\alpha}{dt} = A\,exp^{-Ea/_{RT}} f(\alpha) \qquad (1)$$

where A is the pre-exponential factor, Ea is the apparent activation energy, R is the gas constant, T is the absolute temperature and f(α) is a function depending on the kinetic model, while α can be defined as:

$$\alpha = \frac{Wo - W}{Wo - Wf} \qquad (2)$$

where W_0, W and W_f are the initial, actual and final sample masses, respectively. Eq. (1) at two decomposition rates for isoconversion $\alpha_1=\alpha_2$, with the corresponding temperatures, allows to an independent calculation of $(Ea)_\alpha$ of the equation (Torres-García *et al.*, 2001):

$$Ea_\alpha = R\ln\left[\frac{\left(d\alpha/_{dt}\right)_2}{\left(d\alpha/_{dt}\right)_1}\right]\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^{-1} \qquad (3)$$

where $(d\alpha/dt)_1$ and $(d\alpha/dt)_2$ are the two decomposition rates corresponding to the temperatures T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the Q-TGA and Fig. 2 Hi-Res TGA characteristic curves of the dehydration of $K(NbW)O_6.H_2O$. It can be observed that the sample is continuously dehydrated between room temperature and 120 °C.

This behavior suggests that the water molecules are weakly bonded. This kind of material spontaneously rehydrates in air (Jerez *et al.*, 1987).

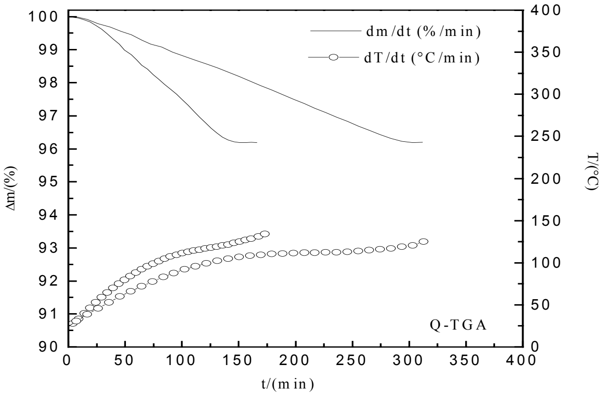

Fig. 1. Q-TGA of the dehydration of $K(NbW)O_6.H_2O$.

By using conventional thermogravimetric analysis (TGA) and the controlled-rate thermal analysis (CRTA), Jerez *et al.*, (1987) concluded that the process occurs following a kinetic law of two-dimensional diffusion. The diffusion kinetic model is consistent with their proposed structural model, i.e., the water molecules occupy defined lattice position from which they can diffuse outside the material without substantial changes in the structure (Jerez *et al.*, 1987).

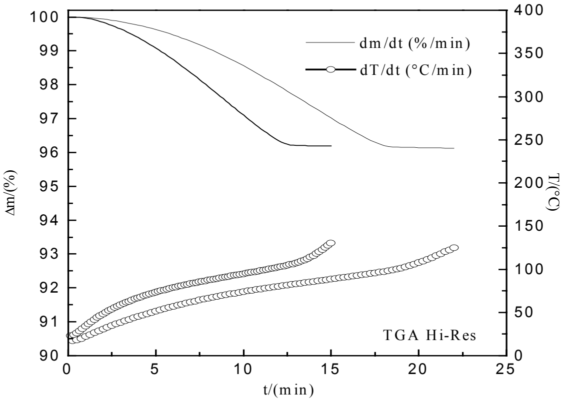

Fig. 2. Hi-Res TGA of the dehydration of $K(NbW)O_6.H_2O$.

The activation energy obtained was 82.41 kJ/mol with the differential method proposed by Jerez *et al.,* (1987) and 58.25 kJ/mol employing the temperature-jump method proposed by Rouquerol (Bordère *et al.*, 1996).

Fig. 1 and 2, Q-TGA and Hi-Res TGA characteristic curves for the dehydration of $K(NbW)O_6.H_2O$. Q-TGA constant reaction rate to dm/dt=0.045 and 0.10 mg/min; Hi-Res TGA: programmed heating rate were dT/dt=10 and 20 °C/min. The rate of the temperature increase is subordinated to the changes in the control property. Fig. 3 shows the results analyzed by using each ratio of different decomposition rates according to Eq. (2). These results reveal that the dependence of the activation energy $(Ea)_\alpha$ on conversion rate (α) helps not only to disclose the complexity of a process, but also to identify its kinetic scheme.

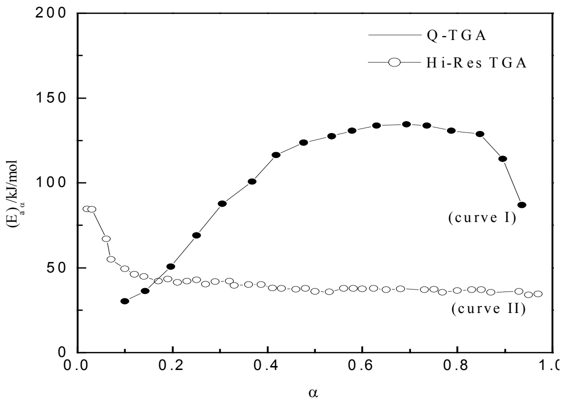

Fig. 3. Variation of measured $(Ea)_\alpha$ values with the transformation rate (α) during the dehydration process of the $K(NbW)O_6.H_2O$, under different experimental conditions.

The curves obtained in this paper (Fig. 3), reveal a typical dependence for competitive (curve I) and reversible reactions (curve II) according to Vyazovskin and Wight (1997). These types of dependencies have been observed for other thermal processes, for example, the thermal decomposition of polypropylene by using conventional (TGA) (Vyazovkin *et al.*, 1992). Such behavior was interpreted as a competition between pyrolysis and oxidation taking place in the presence of oxygen. An example of such reversible reaction can be the dehydration of crystal hydrates, such as calcium oxalate monohydrate (Vyazovkin and Wight, 1997), which displays these type of dependencies of $(Ea)_\alpha$ on α (Fig. 3, curve II). In our opinion, the essential differences observed in the dependence $(Ea)_\alpha$ against α in this paper, as in that by Jerez *et al.,* (1987) as well, is associated to the experimental conditions, specifically to the atmosphere around the samples, which suggests that this process is dependent of the partial pressure of the gaseous product (P_{H2O}). Frequently the rate parameters ($d\alpha/dt$, E and A), measured for dehydration, are sensible to the availability of water vapor in the vicinity of the reactant (Brown *et al.*, 1980). This is one of the fundamental factors for the apparent variation in kinetic data, sometimes found between different reports concerning the some reaction. The decrement, as well as the constant value of the $(Ea)_\alpha$ against α (around 44 kJ/mol) in the Hi-Res TGA experiments demonstrate the importance of the continuous flow of nitrogen to guarantee a slow water vapor pressure (P_{H2O}) and then favor the direct reaction. On the other hand, $(Ea)_\alpha$ against α curve obtained from the Q-TGA, shows an increase of the activation energy with the transformation rate, characteristic of a competitive reaction, with a maximum around 135 kJ/mol. The high water vapor pressure generated during the dehydration process of the $K(NbW)O_6.H_2O$ limits the exit of the water and justifies the increase of the activation energy, competing the direct and inverse reactions, due to the reversible character of the process (Jerez *et al.*, 1987). This complication can be ignored under experimental conditions of vacuum or a strong flow of inert gas through the sample. Then, when the influence of the reverse reaction has been effectively eliminated, the characteristic profile is as in curve II.

Conclusions

This paper shows the great influence of the experimental conditions on the calculated kinetics parameters and the limited validity of kinetic data calculated from experiments carried out under arbitrary chosen conditions. The profile of the $(Ea)_\alpha$ on α curves shows that the dehydration kinetic of the $K(NbW)O_6$ H_2O is sensible to the influence of water vapor in the vicinity of the reactant. The combined use of the high resolutions techniques, as Q-TGA and TGA Hi-Res, with the isoconversion method gives us a powerful tool to determinate the stages taking place during a reaction and providing us with further insights about the kinetics of the processes involved.

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