

# Combined use of high resolution TGA with the isoconversion method: Kinetic analysis of the thermal dehydration of $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$

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## Abstract

In the present study was combined the use of high resolution TGA with the isoconversion method, giving us a suitable methodology for determining the stages that occur during a reaction, and providing further insights about the kinetics of the processes involved. As a model reaction was used the thermal dehydration of  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$ . The results shown that the dehydration process is controlled by internal water diffusion (intra-crystallite); with activation energy values between 43 and 36 kJ/mol. This value is consistent with a diffusion mechanism dominated by van der Waals attractions. The estimated kinetic parameters are supported with a structural analysis, that suggest lower dimensionality character for water diffusion due to the specific orientations of  $\langle 1\ 1\ 0 \rangle$  open channels in the pyrochlore framework. This would explain why the two-dimensional (D2) mechanism appears to be the most probable.

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**Keywords:** Isoconversion method; Dehydration kinetics; Hi-Res TGA; Kinetics in solids; Thermal analysis

## 1. Introduction

The majority of the heterogeneous reactions in solid state are not simple, which makes their analysis and understanding a complex and widely discordant process within the field of the kinetic, isothermal so much as non-isothermal [1–6]. In this way, isothermal and non-isothermal methods are found in the supporting and detracting literature, as well as a great variety of methods and mathematical approximations. Recently, has been published a series of papers that present and discuss the results of the ICTAC kinetic project [7–11]. Their main intention is to give a satisfactory response to the great number of arisen questions which are mainly due to the inconsistency in the results obtained upon applying one or other method and/or mathematical criteria.

On the other hand, with the aim of clarify these drawbacks, during the last years, the basic ideas of Rouquerol [12–14]

and Paulik et al. [15,16] have been used to set the bases for the development of a new conception of thermal analysis equipments, taking into account the essential experimental aspects that generate such inconsistencies. The integration of the basic elements of the thermoanalytical conventional methods, devised by these authors offer a general summary of the operation of the thermogravimetric analysis technique of high resolution (Hi-Res TGA) [17,18]. While the formal aspect has been satisfactory approached through the combination of some traditional evaluation methods of non-isothermal kinetic integral as well as differential namely isoconversion [3–11,19–21].

In the present study, the thermal dehydration of  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$  has been selected as specific example. Pyrochlore is a family of a very important model structure in which many mixed oxides crystallize. Their structure is built of two interpenetrating networks of  $\text{MO}_6$  octahedra sharing vertices and forming a three-dimensional network that results in large cavities in which water molecules accommodate.

This structure had served as a model framework to prepare superconductors, fast ion conductors and antiferromagnetic

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compounds. Pyrochlores, such as  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$ , are one of the few compounds having the anomalous phenomenon known as pressure-induced volume expansion, in which the interactions of water molecules with the open cavities play an important role [22]. Therefore, the study of water interactions in this system could be an important contribution to the understanding of its chemical behavior.

In this paper, our main objective is shown that the combined use of the model-free method with Hi-Res TGA is a suitable methodology to obtain a more realistic phenomenological analysis of any kinetic study. The results are discussed in terms of activation energy, the most probable mechanisms and their relationship with structure.

## 2. Experimental

### 2.1. Sample and methodology

The  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$  was prepared by heating at 1173 K in air, a stoichiometric mixture of  $\text{KNO}_3$ ,  $\text{WO}_3$  and  $\text{Nb}_2\text{O}_5$  (all from Merck, reagent grade), in a porcelain crucible for 12 h [23,24]. The obtained solid was characterized by X-ray diffraction using a Siemens diffractometer (Model D500) with  $\text{Cu K}\alpha$  radiation and a Ni filter. The conditions were 30 kV and 20 mA in the angular range  $10\text{--}60^\circ$  in  $2\theta$ . The diffraction patterns were compared with those included in the Joint Committee of Powder Diffraction Standards (JCPDS-ICDD 25-668) database.

Thermal analyses were made in a high-resolution thermobalance (TA Instrument, model TG-2950) using a  $\text{N}_2$  flow of 100 ml/min. The preconceived heating rates were 10, 20 and 50 K/min with instrumental resolutions of 5. Samples weight was about 66 mg in all cases.

### 3. Kinetics analysis

The experimental Hi-Res TGA data were analyzed to evaluate the activation energy and the most probable reaction mechanism. The isoconversion principle was applied in order to obtain the dependence of  $E_\alpha$  on  $\alpha$ . The methodology has been described previously [3,5,6,11]. It states that the rate at constant extent of conversion, is only a function of the temperature, and that  $f(\alpha)$  is independent of the heating rate. If the Arrhenius equation is applicable, we can write:

$$\left[ \frac{d \ln \left( \frac{d\alpha}{dt} \right)}{dT^{-1}} \right]_\alpha = - \frac{E_\alpha}{R} \quad (1)$$

where the subscript  $\alpha$  indicates the values of isoconversion,  $(\alpha_i)_1 = (\alpha_i)_2 = \dots (\alpha_i)_n$ , for each experiment and temperature. This criterion allows an estimation of  $E_\alpha$  without the assumption of any reaction model, i.e., model-free method.

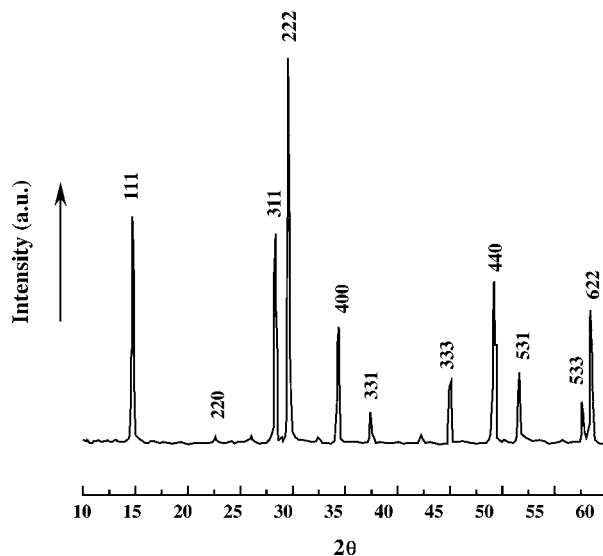


Fig. 1. X-ray powder diffraction pattern of  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$ , under ambient conditions.

## 4. Results and discussion

The experimental room temperature X-ray diffraction pattern of  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$  is shown in Fig. 1. According to Fig. 1, the microcrystalline solid obtained shows a monophasic pyrochlore-type structure. This material spontaneously re-hydrates in air at ambient temperature leading to the compound formulated as  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$ . These results are in agreement with those previously cited in the literature [23].

The results obtained for different heating rates using Hi-Res TGA for  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$  are shown in Fig. 2. It can be observed that the sample is continuously dehydrated between room temperature and 393 K. The total weight loss (about 3.9%) corresponds to a monohydrate (expected

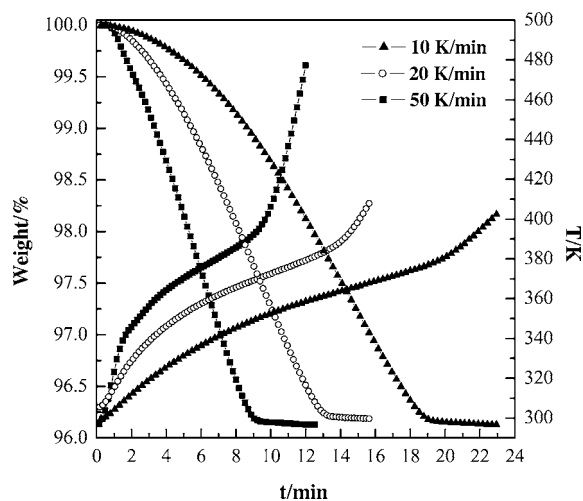


Fig. 2. Hi-Res TGA characteristic curves of the dehydration of  $\text{KNbWO}_6 \cdot \text{H}_2\text{O}$ : heating rate programmed at 10, 20 and 50 K/min.

value 4.1%). The partial weight loss corresponding to this stage is approximately equivalent to the evolution of a water molecule (according to the crystal structure [23,24]). A small fraction of this water could be removed under the  $N_2$  flow during the experimental setting for running the TGA experiment. This could explain the difference observed between the experimental and the expected weight loss.

As could be seen in Fig. 2, there were no constant temperature plateaus under the used experimental conditions. This behavior can be related with the nature of the process in the residual solid. When a loss of weight is detected in Hi-Res TGA technique, the heating rate slows in response to the increasing rate of mass loss and the system tries to keep it at the lowest value until the end of the loss of weight. Under these conditions, and with a rapid and efficient removal of decomposition products, is possible to obtain well-controlled experimental conditions which reduce the gradients of temperature and pressure in the direct vicinity of the residual solid. This concept summarizes the essential difference with conventional techniques. If the  $T$  versus  $t$ -curve is a consequence of nature of the process studied, then its profile contains kinetic information about the dehydration reaction. Probably, the dependence on the water vapor pressure during the dehydration of  $KNbWO_6 \cdot H_2O$  is more complex than in the case of others hydrates, for example,  $CuSO_4 \cdot 5H_2O$  or  $CaC_2O_4 \cdot H_2O$ , where the dehydration process shows an isothermal behavior and constant  $d\alpha/dt$  dependence, under similar experiments conditions, using Hi-Res TGA [25].

In a previous study on the thermo-kinetic behavior of the dehydration of  $KNbWO_6 \cdot H_2O$ , Jerez et al. [24] concluded that the process occurred via two-dimensional diffusion having activation energy of 82 kJ/mol. However, a detailed analysis of their results, it can be seen that the four diffusive mechanisms were equivalent, as well as the  $F$  and  $R$  models, under conditions of dynamic heating rate [ $dT/dt = \text{constant}$ ]. In all cases, the correlation coefficients were about 0.99. These results clearly indicate that it is not possible to conclude unequivocally which model describes satisfactorily the most probable reaction mechanism.

This problem has been extensively discussed in the literature and an alternative model-free method has been proposed [3,5–11]. Then, we performed an isoconversion analysis in order to find the dependence of  $E_\alpha$  with  $\alpha$  for the different stages observed in the  $dT/dt$  versus  $t$ -curves. The results are summarized in Fig. 3. From these results, it was possible to analyze the dehydration of  $KNbWO_6 \cdot H_2O$ . At  $T < 353$  K, the activation energy decreases from about 86 kJ/mol (at low conversion) to nearly 43 kJ/mol at  $\alpha = 0.15$  conversion. At  $\alpha > 0.15$ ,  $E_\alpha$  is essentially constant, 43–36 kJ/mol, as  $\alpha$  changes from 0.15 to 0.97. This suggests that the natures of the interaction sites, during the dehydration process are energetically equivalent. Vyazovkin and Linert [3,6] have shown that the decreasing dependence of  $E_\alpha$  on  $\alpha$  is typical

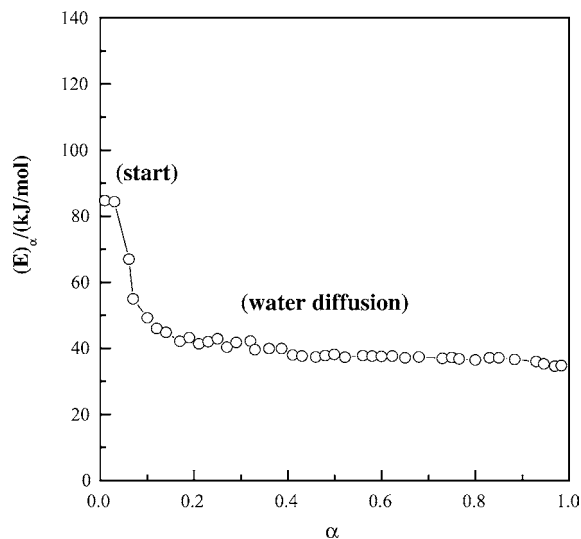


Fig. 3. Dependence of the  $E_\alpha$  on  $\alpha$  for dehydration of the  $KNbWO_6 \cdot H_2O$ .

for a kinetic scheme corresponding to reversible reactions. Such prediction agrees with the reversible character of the dehydration process in this compound, as previously reported [24]. Furthermore, this small value of  $E_\alpha$  in this stage is an indirect evidence suggesting that it is a diffusion-controlled process [26].

In our opinion, the change in the activation energy during the first stage, from about 86 to nearly 43 kJ/mol, can be interpreted as the energy necessary to break the interaction of the  $H_2O$  molecules with potassium ions.

#### 4.1. Structural considerations

A detailed analysis in terms of activation energy, the most probable mechanisms and their relationship with structure, helps to understand the material behavior during the dehydration process. The ideal pyrochlore structure is cubic with space group  $Fd\bar{3}m$ , with eight formula units per unit cell. In  $KNbWO_6 \cdot H_2O$ , Nb and W are randomly distributed in 16c positions, while oxygen is in 48f sites [23,27]. The structure may be conveniently thought as a framework composed by corner-shared  $[MO_6]$  octahedra. The  $MO_6$  framework form one-dimensional interconnected channels along  $(1\ 1\ 0)$  directions (see Fig. 4), with K and water molecules occupying 32e sites alternately along the channels [28]. Potassium is eight-coordinate with six equatorial lattice oxygens in a chair configuration, while water molecules locates in its axial coordination sphere (Fig. 4d); one at K–OH<sub>2</sub> bond distance of 2.86 Å and the other at 2.28 Å [22]. The larger bond distance is near to the distance between water molecules in pure water, which implies that there is a minimum energy barrier for water diffusion necessary to overcome van der Waals interactions that are typically in the range of 20–40 kJ/mol [29]. The shorter K–OH<sub>2</sub> distance is slightly larger than the characteristic K–O distance expected for potassium hydroxide

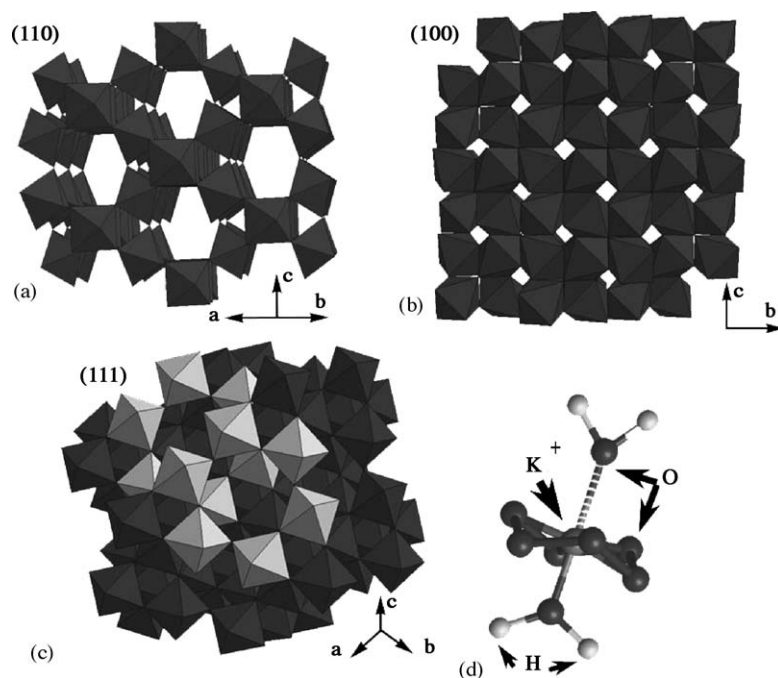


Fig. 4. Schematic representation of  $[MO_6]$  ( $M = W, Nb$ ) octahedra framework in cubic  $KNbWO_6 \cdot H_2O$ , showing the  $\langle 110 \rangle$  channels. Potassium and water were omitted for more clarity. (a), (b) and (c) are the  $\langle 110 \rangle$ ,  $\langle 100 \rangle$  and  $\langle 111 \rangle$  projections, respectively. Light gray polyhedrons in (c) highlights bottleneck-like sites in which water and K are distributed along channels. (d) Schematic representation of the coordination sphere around  $K^+$  ion in  $KNbWO_6 \cdot H_2O$ .

[30], it implies more energy than larger bond to achieve the activate state for diffusion (usually higher than 60 kJ/mol).

From a structural point of view, it is expected that elemental diffusion path has essentially a three-dimensional character (i.e., D3 mechanism). However, this is valid if crystallites faces are related with channel direction, but this is not the actual case for isometric crystals like cubic pyrochlore, in which the most common surfaces are the  $\{111\}$ .

Following the structure characteristics, diffusion seems to be reduced due to lower channels density along  $\langle 111 \rangle$  and  $\langle 100 \rangle$  directions (Fig. 4b and c). Channels are clearly directed toward the specific directions  $\langle 110 \rangle$ , suggesting a lower dimensionality character for water diffusion. It explains why the two-dimensional (D2) mechanism appears to be the most probable; it can be seen as result of pseudo-two-dimensional mechanism.

Taking into account these considerations and analyzing the results obtained by the isoconversion method, it can be recognized that the most probable reaction mechanism is the intra-crystallite diffusion kinetic model. It should corresponds to WET 1 class of dehydration process according to the classification scheme proposed by Galwey [31] for solid-state dehydrations (water evolution type, WET) based on structural criteria.

The differences between our results and those reported by Jerez and co-workers suggests that the fitting of different  $f(\alpha)$  used in the literature, in much cases, is not the proper way to determine the kinetic reaction. It is a fact that the goodness-of-fit are usually so close to each other that discriminating between them is usually not possible. It appears that only

mechanism-free schemes can help in determining some of the global parameters, in particular  $E_{obs}$ .

## 5. Conclusions

Dehydration of the  $KNbWO_6 \cdot H_2O$  is controlled by internal water diffusion (intra-crystallite); with activation energy values between 36 and 43 kJ/mol. These values are near to the energy barrier for water diffusion necessary to overcome van der Waals interactions that are typically in the range of 20–40 kJ/mol (close to the latent heat for water evaporation).

The structural considerations show channels are clearly directed toward the specific directions  $\langle 110 \rangle$ , suggesting a lower dimensionality character for water diffusion. It explains why the two-dimensional (D2) mechanism appears to be the most probable; it can be seen as result of pseudo-two-dimensional mechanism.

The combined use of the isoconversion method with high resolution TGA is a powerful tool for determining the stages occurring during decomposition reactions and obtaining insights about them. This is possible because Hi-Res TGA allows a strict control of the experimental conditions and reduces the gradients of temperature and pressure in the bulk of residual solid.

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