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TEMPERATURE-RESOLVED X-RAY DIFFRACTOMETRY AS A THERMOANALYTICAL METHOD

A powerful tool for determining solid state reaction kinetics

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Development and experimental setup of the time-, and temperature -resolved X-ray powder diffractometry are described. This method allows far deeper insight into solid state reactions than conventional thermoanalytical methods like differential scanning calorimetry (DSC) or thermogravimetry. As an example, the dehydration of caffeine hydrate was investigated. We found that in earlier stages the reaction is nucleation controlled, whereas for higher extent of reaction diffusion limitation becomes rate-controlling.

Keywords: caffeine hydrate, solid state reaction kinetics

Introduction

The determination of solid state reaction kinetics often leads to interpretation problems when investigated with classical thermoanalytical methods, e.g. differential scanning calorimetry (DSC) or thermogravimetry (TG). The reason lies in the comparatively non-specific parameters which are recorded, i.e. enthalpy change and mass, respectively. For more complex reactions like parallel or consecutive, the evaluation of the recorded information can be difficult and in some cases impossible. This is due to overlapping signals for the individual reaction steps.

To overcome this limitation we chose the X-ray powder diffractometry as an analytical method which provides specific information about crystalline solids. The powder diffractogram is characteristic for every crystalline substance and furthermore for its polymorphic phase. The height of a given peak is under certain circumstances (see experimental section) proportional to the molar fraction of the diffracting compound. This behaviour is used to determine concentration

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values. For mixtures an additive superposition can be assumed. For a detailed description of X-ray powder diffractometry see Ref. [1].

Some of the earliest applications of this method were the investigations of Gerard *et al.* [2] in the 1960's. More recently the method has been employed by some other groups, though typically not for non-isothermal reaction analysis of solid state reactions [3–5].

We constructed a heatable sample holder which can be used from room temperature up to 250°C. During the experiment the temperature can be controlled with a high precision. To obtain kinetic data for solid state reactions we used a constant heating rate, so that the mathematical formalism developed for non-isothermal reaction kinetics with DSC and TG could be fully applied.

As an example, we investigated the dehydration of caffeine hydrate which has been examined by Bothe and Cammenga [6, 7] by applying conventional thermoanalytical methods.

Experimental

The experimental setup is shown in Fig. 1. The sample is filled into a holder made of gilded copper which lies on a glass ceramic plate. The required sample volume is 0.3 cm^3. The heating is done with a PTFE-coated constantane-wire. Above the copper holder a plate of polystyrene foam or low-density carbon-fiber insulating material ensures good upward thermal insulation of the sample and a

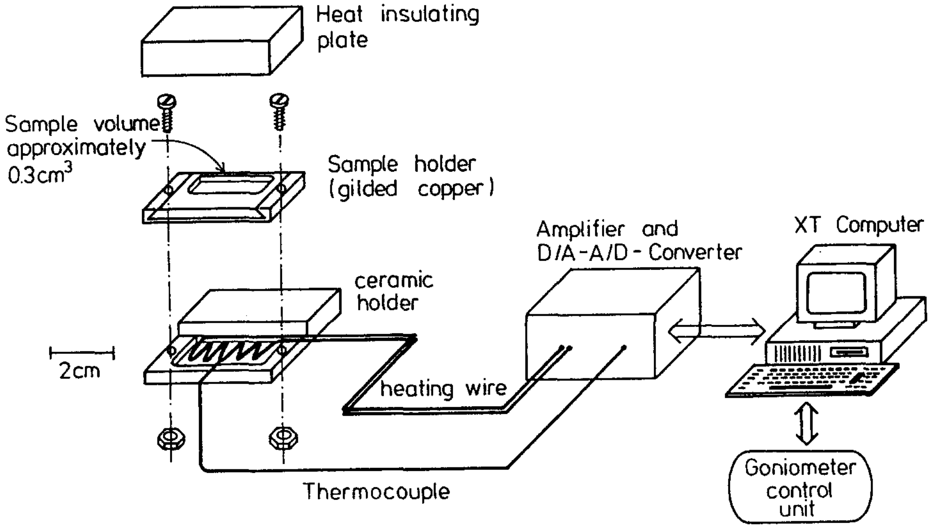

Fig. 1 The goniometer heating stage and its connection to the computer (schematic)

homogeneous temperature within the sample compartment. The temperature is measured below the copper holder beneath the sample with a Ni-CrNi thermocouple. The sample holder is connected with an IBM compatible computer via a 12-bit AD/DA extension card and a self-constructed amplifier.

The oven control is done by software simulating a PID-regulator which achieves a mean absolute temperature deviation of 0.1 K or less during a typical scan. The absolute temperature accuracy is estimated to ±1 K. Typically used heating rates are 0.5–2 deg/min. The goniometer is a Philips PW 1050/81, equipped with a gas-filled proportional counter PW 1711/00 and connected to the computer by a serial interface. The X-ray tube provides CuK_α-radiation (λ=154.178 pm).

To obtain good diffractograms, the particle size of the sample must be in the range of 10–50 μm. Care must be given to avoid a preferred orientation of non-spherical crystallites (e.g. plates, needles) which may result in erroneous concentration values. Also it should be ensured by suitable experiments that the reaction is not influenced by the X-rays.

Strictly, the proportionality of peak height to concentration is only correct for constant absorption coefficient and constant density. Fortunately the influence of the release of a small mass fraction of light molecules like water can usually be neglected with respect to absorption coefficient and density.

During a measurement a selected angle range is scanned repeatedly. Typically 15–60 scans are recorded, the exact number depending on the desired angle resolution. The results can be plotted as a number of scans of intensity *vs.* goniometer angle 2θ (Fig. 2).

To extract concentration values from the diffractograms, a number of gaussians is fitted to the set of data points of each scan. Although the peak shapes do not exactly obey gaussian functions [8], they can approximated as such. This method allows us to separate overlapping peaks.

The calculated peak maxima are plotted against time and a suitable value for $\alpha=0$ or $\alpha=1$ is selected (Fig. 3). By dividing all peak maxima by this value, a number of $\alpha(T)$-values is obtained, assuming a proportionality of peak height to concentration. The estimated error in $\alpha(T)$ depends on the absolute peak height and the selected angle resolution. We estimate the standard deviation to be $\sigma_\alpha=0.03$.

The combined data set for all peaks can be evaluated with kinetic methods. Typically, 20–80 $\alpha(T)$-values are obtained. For non-isothermal scans we used the method of Kassmann [9], which is an extension of the well-known integral method of Coats and Redfern.

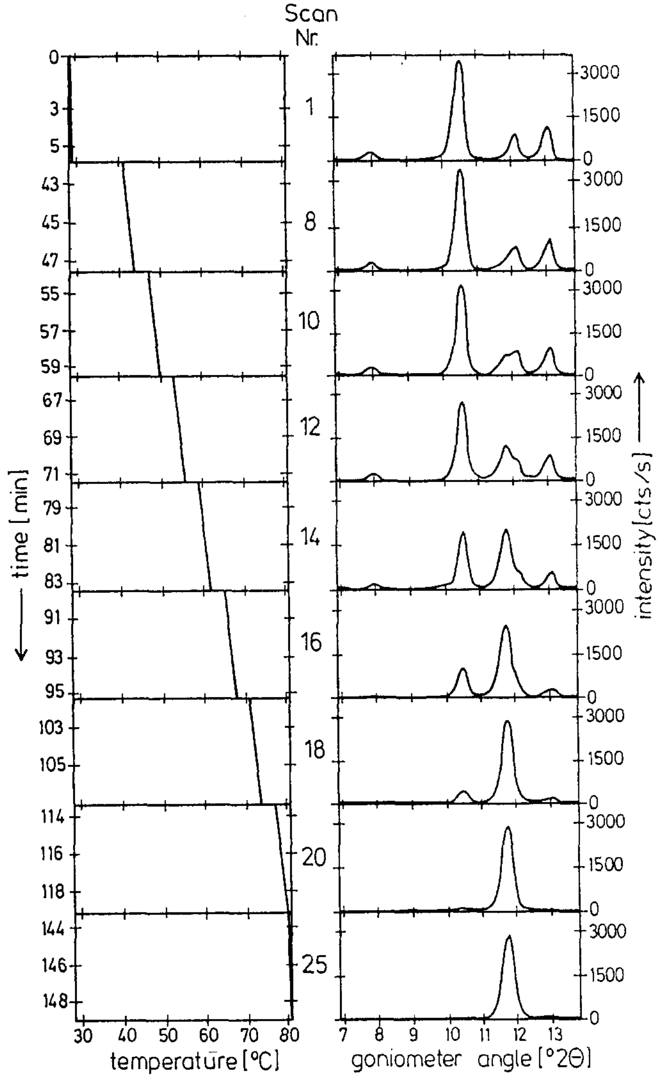

Fig. 2 Selected powder diffractograms out of a non-isothermal measurement of caffeine hydrate. An isothermal period at room temperature is followed by a heating with 0.5 deg/min to 80°C and a further annealing at this temperature . For clearity only selected scans are shown. The angular scan speed was 0.02°2θ/s

Results

Caffeine (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione) forms a stable 4/5-hydrate which crystallizes from aqueous solutions in long, white needles (diameter ca. 0.1 mm). Its stability point is 51.5°C. Dehydration leads to the low-temperature phase β-caffeine, which can reversibly be transformed into the high-temperature phase α-caffeine at 140°C [6, 7].

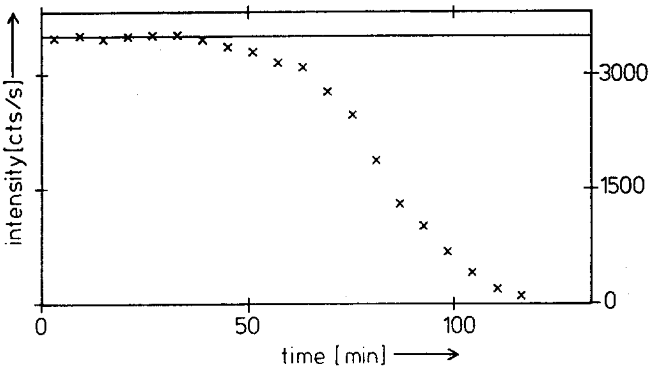

Fig. 3 Calculated intensity of the caffeine hydrate peak at 10.5°2θ *vs.* time. The line denotes the selected maximum intensity for α=0

Caffeine is a technical product which is commercially used in pharmaceuticals, beverages and food. The knowledge of the phase relations is of special interest in the decaffeination process of coffee beans with liquified or supercritical gases.

Bothe and Cammnga investigated the dehydration of caffeine hydrate with thermogravimetry, DSC and microscopic methods. From isothermal and non-isothermal experiments they found a dehydration kinetics in the range of 20°–73°C obeying a contracting volume mechanism *R*3:

$$R_3(\alpha) = 3 \cdot [1 - (1 - \alpha)^{1/3}] = k_{R3} \cdot t \tag{1}$$

This was also supported by microscopic examination of partly dehydrated crystals, which showed a topochemical reaction starting at the crystal surface. The activation energy was found to 94±3 kJ/mol.

Before carrying out experiments the hydrate was thoroughly ground. Microscopic examination revealed irregular, roughly spherical particles with a particle size of 10–50 μm. All experiments were carried out with specimens taken from the same mortared sample to avoid errors due to variations in particle shape and size distribution.

In isothermal experiments we found a distinct kink in a plot of $\ln(-\ln(1-\alpha))$ *vs.* $\ln(t)$ at an extent of reaction of ca. $\alpha=0.6$. For $\alpha < 0.6$ the slope was about 1.5, for $\alpha > 0.6$ about 0.7–0.8. This is in all probability due to a change in the reaction mechanism from a nucleation-controlled to a diffusion-controlled reaction [10].

Similar kinks were found in kinetic plots for different mechanisms and, of course less distinct, in non-isothermal runs. The slope of the nucleation period suggests an $A1$-Mechanism according to Avrami-Erofeev:

$$A1\,(\alpha) = 3/2 \cdot [-\ln(1-\alpha)]^{2/3} = k_{A1} \cdot t \qquad (2)$$

For the deceleration period the reaction seems to obey a three-dimensional diffusion law (Jander equation):

$$D3\,(\alpha) = 3/2 \cdot [1-(1-\alpha)^{1/3}]^2 = k_{D3} \cdot t \qquad (3)$$

The fitting for a $D3$-mechanism is better than for two-dimensional ($D2$) or one-dimensional ($D1$) mechanism, but the differences are rather small, so that these alternative mechanisms cannot be completely ruled out. In the following, a $D3$-mechanism is assumed, as it is also corroborated by the findings of Bothe and Cammenga.

A typical plot of selected scans of a non-isothermal experiment is shown in Fig. 2 (heating rate 0.5 deg/min). It can easily be seen that four reactant peaks are slowly vanishing and one product peak is growing. Figure 3 shows the calculated intensity for the hydrate peak at 10.5°2θ and the calculated maximum for α=0.

From non-isothermal measurements with different heating rates we obtained the following kinetic parameters:

$A1$:	$\log(k_o \cdot s)=8.8$ [4]	$E_A=76$ kJ/mol [3]
$D3$:	$\log(k_o \cdot s)=13.2$ [9]	$E_A=111$ kJ/mol [6]

The plot of calculated and measured $\alpha(T)$-values *vs.* temperature and of its first derivative with respect to time is shown in Fig. 4 (heating rate 0.5 deg/min). It can be seen that the data points are well-represented by the two mechanisms. In isothermal scans the change of the mechanism is even more obvious.

It seems, as if in the early stages of the reaction nucleation is rate-determining, whereas for higher extent of reaction diffusion through the thickening product layer becomes the slowest step.

It should be pointed out that a fit over the whole α-range to a $R3$-mechanism gives an apparent activation energy of 90–110 kJ/mol. It can therefore be concluded that the agreement to the results of Bothe and Cammenga is good, but that the situation is more complicated than suggested there.

Similar results were obtained by thermogravimetry and DSC. There was no different behaviour of a previously irradiated sample, so an influence of irradia-

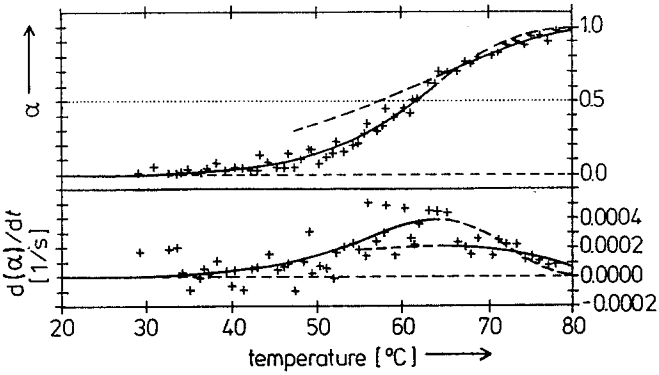

Fig. 4 Measured and calculated extents of reaction and the first derivative with respect to time for the measurement of Fig. 2 *vs.* temperature. For $\alpha<0.6$ the solid line denotes the calculated *A*1-mechanism, for $\alpha>0.6$ the calculated *D*3-mechanism. The dashed lines show the extrapolated values for these mechanisms beyond the range of application, respectively

tion on the reaction can probably be excluded. No intermediate sub-hydrates could be detected.

After dehydration the low-temperature from β-caffeine is formed. The intermediate formation of α-caffeine cannot be excluded due to very similar diffractograms of the two phases, but any intermediate concentration should be well below 10%.

Conclusions

It has been shown that the method of time- and temperature-resolved X-ray powder diffractometry can be successfully applied in non-isothermal reaction kinetics. The method provides deeper insights into the reaction than thermogravimetry or DSC. The dehydration kinetics of caffeine hydrate was investigated, and earlier results were confirmed and extended. The results can be interpreted as a nucleation period obeying an *A*1-mechanism up to an extent of reaction of ca. 0.6, followed by a three-dimensional diffusion mechanism *D*3. In the near future we plan to apply the new method to polymorphic phase transformations and reactions in the solid state, especially of organic solids.

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Zusammenfassung — Entwicklung und Aufbau der Zeit- und Temperaturaufgelösten Röntgenpulverdiffractometrie werden beschrieben. Die Methode ermöglicht weit tiefere Einblicke in das Reaktionsgeschehen bei Reaktionen fester Stoffe als die üblichen thermoanalitischen Methoden wie Dynamische Differenz-Kalorimetrie (DDK/DSC) und Thermogravimetrie. Als Beispiel wurde die Dehydration von Coffeinhydrat untersucht. Dabei wurde festgestellt, daß zu Beginn der Reaktion offenbar Keimbildungsvorgänge Geschwindigkeitsbestimmend sind, während bei höheren Umsatzgraden zunehmend Diffusionshemmung eintritt.