

## Isothermal decomposition kinetics of Werner-type $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] clathrates with aromatic guests

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### Abstract

Guest desorption from clathrates formed by  $\beta$ -[Ni(NCS)<sub>2</sub>(4-methylpyridine)<sub>4</sub>] host with benzene, toluene and *p*-xylene was studied under isothermal conditions within the temperature range from 6 to 30°C. Possible mechanisms of decomposition of these clathrates are discussed. In the decomposition of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-methylpyridine)<sub>4</sub>]·C<sub>6</sub>H<sub>6</sub> clathrate, guest diffusion in the solid is the rate-determining step. The activation energy of this process was found to be  $38.5 \pm 2.5$  kJ mol<sup>-1</sup>.

**Keywords:** Isothermal decomposition kinetics; Werner clathrates

### 1. Introduction

Compounds of zeolite-like  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] (where 4-MePy is 4-methylpyridine) as host (organic zeolite [1]) with a variety of guests (mainly aromatic) are best characterised in the group of Werner clathrates [1]. However, the solid–gas equilibria and clathrate decomposition kinetics of these compounds have been the subject of only a few studies. Allison and Barrer [2] investigated the sorption of gaseous guest in the  $\beta$ -phases of [M(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] (where M is Ni(II) or Co(II)). The non-isothermal dissociation of a series of Werner clathrates, accompanied by decomposition of the host lattice, has been studied [3, 4]. A paper in which isothermal desorption of *p*-xylene from the  $\beta$ -clathrate crystals was studied [5] is taken as the basis of this work.

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On being removed from their mother solutions, clathrates of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] lose guest molecules, producing metastable empty or partially filled  $\beta$ -phase [1, 6]. The remarkable kinetic stability of this clathrate phase without any guest allows investigation of the process of guest desorption separately from the destruction of host lattice, as is the case with zeolites. The loss of guest molecules is accompanied by a decrease in lattice parameters and, hence, by uncontrolled cracking of clathrate crystals [1, 6]. This phenomenon makes kinetic investigation of these substances more complex. The decomposition times for different  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] clathrates, in air at room temperature, range from one hour (methanol clathrate) to several days (*p*-xylene clathrate) [6]. X-ray data of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] clathrates were reviewed in Ref. [1], and the size and shape of the channels in the host lattice were discussed in Ref. [7].

The aim of this work was to investigate the molecular mechanism of decomposition of the  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] clathrates. Aromatic guests were chosen as the most common for this type of clathrates.

## 2. Experimental

Syntheses of the host coordination complex and the clathrate compound with benzene were carried out according to Ref. [6]. Crystals of the clathrate with *p*-xylene were prepared according to Ref. [5], and the size fraction 0.25–0.5 mm was selected for experiments. Samples of the empty  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] phase were prepared from large, well-formed crystals of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>]·C<sub>6</sub>H<sub>6</sub> clathrate, by repeated sorption and desorption of benzene.

The decomposition and formation processes were investigated using the experimental apparatus and procedure described in Ref. [8], with a Mettler AE 100 balance and an external reservoir of guests vapour. The temperature in the apparatus was maintained with an accuracy of  $\pm 0.25^\circ\text{C}$ . (This value represents the range of temperature variations during absorption/desorption experiments and is due mainly to thermal effects of the reaction studied and the cooling of the atmosphere in the apparatus during the reduction of the gas pressure. The precision of the thermostatic device used was better than  $\pm 0.05^\circ\text{C}$ .) Two plate-like sample holders of area 14 cm<sup>2</sup> were used. In a typical run, a 180–220 mg sample of empty  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] phase was saturated with benzene vapour up to a stoichiometry of 1:1, and decomposed in a flow of air. The average size of the particles was determined by sieving and weighing of fractions. The rate of air flow through the reaction vessel was kept at about 0.5 m<sup>3</sup> min<sup>-1</sup>. The thickness of the sample layer and the rate of air flow were chosen in a trial-and-error procedure so that their influence on the rate of the process could be avoided for the decomposition of the clathrate with benzene. For the toluene and *p*-xylene clathrates, samples of powder (or crystals of *p*-xylene clathrate) of mass 950–1050 mg were placed on an aluminium plate as 1–1.5 mm thick layers. Bigger samples were necessary when the changes in mass with time were very small. It was also known from pilot experiments made with benzene clathrate samples, that a bigger sample mass did not affect the activation energy determined or the shape of the decomposition curve, but did influence the measured rate of decomposition.

### 3. Results and discussion

#### 3.1. Theoretical introduction

Theoretical examination and experimental observations of the process of guest evaporation from the  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] clathrate crystals in Ref. [5] indicated to us that there are two most probable rate-determining steps in this reaction:

- (i) Release of the guest molecules from the cavity in preparation for diffusion (the change of orientation to allow the guest molecule to penetrate the three-dimensional system of channels), or
- (ii) Diffusion of the guest molecule through the solid to the crystal surface.

The possibility of surface desorption as the rate-determining step has been excluded, based on experimental observations.

Let us discuss both possibilities, assuming that crystals are of approximately spherical shape and do not crack during desorption of the guest. No universal law of decomposition is expected in the first case because different possible variants of molecular reorientation may occur (monomolecular, collective, etc.). One simple variant was considered in Ref. [5]. Systems with a diffusive rate-determining step may be divided into two groups: stoichiometric systems, where guest molecules occupy 100% of the possible positions, and non-stoichiometric systems with guest vacancies. These situations, and different possible ways of decomposition caused by different arrangements of the guest molecules in the host lattice, are shown in Fig. 1.

Diffusion in non-stoichiometric systems is exactly analogous to diffusion of molecules in zeolites, comprehensively reviewed by Barrer [9, 10]. In the simplest situation,

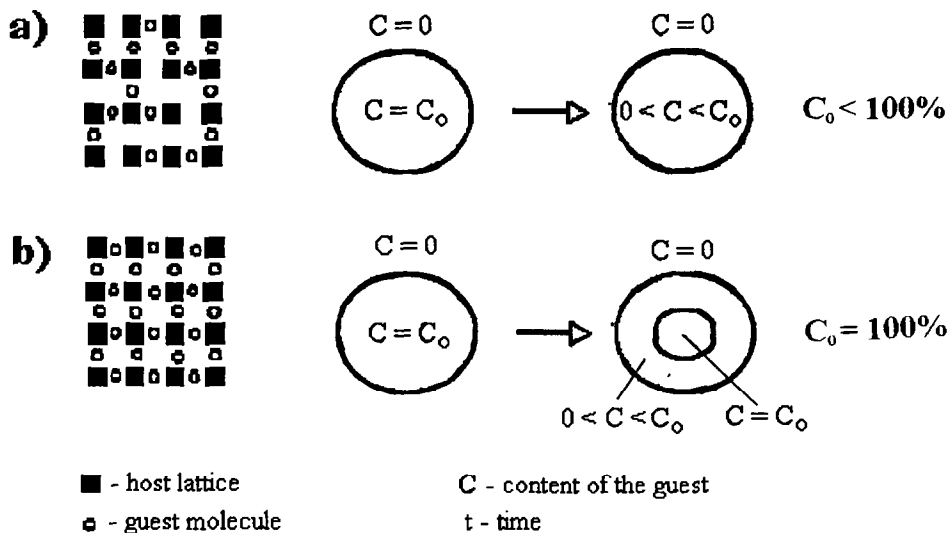


Fig. 1. Different decomposition pathways for: (a) clathrates with less than 100% occupation of guest positions; (b) clathrates with 100% occupation of guest positions.

when the diffusion coefficient is a constant, the following equations may be obtained [9] (mechanism 1)

$$\alpha^2 = \frac{36D}{\pi r^2} t \quad (1)$$

for small  $t$ , and

$$\ln \left( \frac{\pi^2}{6} (1 - \alpha) \right) = - \frac{D \pi^2}{r^2} t \quad (2)$$

for large  $t$ .

Here  $D$  is the diffusion coefficient,  $t$  the time,  $\alpha$  the degree of transformation, and  $r$  the radius of the particles. Our preliminary experiments have shown that the characteristic time of half-transformation for guest desorption from the  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] lattice (at temperatures 10–30°C) is less than 10 min for most of the guests studied. Comparison of this value with possible values of diffusion coefficients (data of this work) according to Ref. [9] leads to the conclusion that 10 min is a small time, hence Eq. (1) should be valid in the experiments performed.

A peculiarity of stoichiometric clathrates is that guest molecules inside the crystal may diffuse only when the adjacent neighbouring cage is vacant (Fig. 1(b)). The situation where a molecule could jump over a neighbouring molecule in the channel is improbable, because of the great displacement of host molecules which would be necessary. In such a case, diffusion may be described by the Ginstling–Brounshtein equation [11] (mechanism 2)

$$1 - \frac{2\alpha}{3} - (1 - \alpha)^{2/3} = \frac{2D}{r^2} t \quad (3)$$

The diffusion coefficient is assumed to be constant for both equations given earlier. This is not always the case for zeolites [9]. Correlation between the diffusion coefficient and the content of the guest molecules in the host lattice has to be more characteristic for the  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] host than for zeolites because of the strong dependence between guest content and lattice parameters of clathrates [1]. In this case one may obtain kinetic information by the methods discussed in Ref. [10].

### 3.2. Preliminary experimental data

Our observations of sorption of guests by the empty  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] phase have shown that these are much more rapid processes than the decomposition of the resulting clathrates. From estimates of the changes in size of particles before sorption, after sorption and after guest desorption from thin layers of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] powder, we might conclude that, after 3–4 sorption–desorption cycles, an average particle undergoes only small changes in size during desorption of the guest (but strong cracking of particles of the sample occur during sorption, and the average size of the particles decreases significantly). The shape of the particles, from microscopic observations, may be regarded as approximately spherical (the equilibrium crystal form is a distorted octahedron).

When benzene is used as a guest, an average particle size of 0.15–0.1 mm may be obtained, depending on the rate of sorption and decomposition (controlled by the temperature and effective pressure of the guest). The corresponding values for toluene and *p*-xylene are a bit smaller.

The great dependence of decomposition rate upon the residual pressure of the guest vapour was detected for all the clathrates tested. To clarify this, isotherms for benzene– $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] were studied (Fig. 2). The shape of the isotherms and the stoichiometry of the resultant clathrates will be discussed elsewhere and only the conclusions which are important for this work will be formulated here: (i) The rectangular shape of the isotherms shows a strong influence of low guest pressures on the intracrystalline gradient of the guest concentration. (ii) Isotherms with *p*-xylene and toluene should be expected to be more rectangular in shape because of the greater heat of clathrate formation for both these guests [1].

The sorption of benzene reached equilibrium after 5–15 min. The data in Table 1 show that *p*-xylene and toluene reach equilibrium more slowly in comparison with benzene.

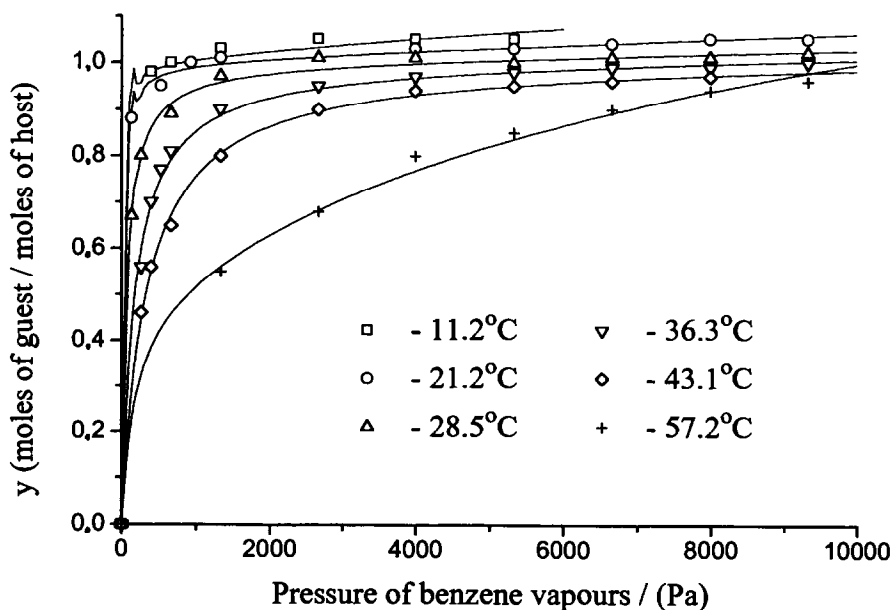


Fig. 2. Isotherms of benzene in the  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] host.

Table 1  
Saturation of an empty  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] phase by gaseous guests

Guest	$T/^\circ\text{C}$	Pressure of guest vapour/Pa	Particle size/mm	Degree of saturation $y^a$ /mol	Time of host–guest contact/min
<i>p</i> -Xylene	27.1	800	0.1–0.14	0.73	30
Toluene	19.3	1333	0.1–0.14	0.53	30
Toluene	19.3	2400	0.09–0.14	0.61	30
Toluene	33.8	2000	0.1–0.14	0.93	30
Benzene	6–25	1333–6665	0.1–0.14	1–1.1	5–10

<sup>a</sup> [Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>]  $\times$   $y$ G (G is guest).

### 3.3. Decomposition of the benzene clathrate

The kinetics of thermal decomposition of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] $\cdot$ C<sub>6</sub>H<sub>6</sub> were studied in terms of isothermal mass changes between 6 and 30°C. The  $\alpha$ - $t$  curves are shown in Fig. 3. The mechanism of the decomposition process was determined by testing the linearity of  $f(\alpha)$ - $t$  plots for different expressions of  $f(\alpha)$  [12] and by the reduced-time method [13] ( $t/t_{0.5}$  and  $t/t_{0.9}$ , where  $t_x$  is the time when reaction achieves

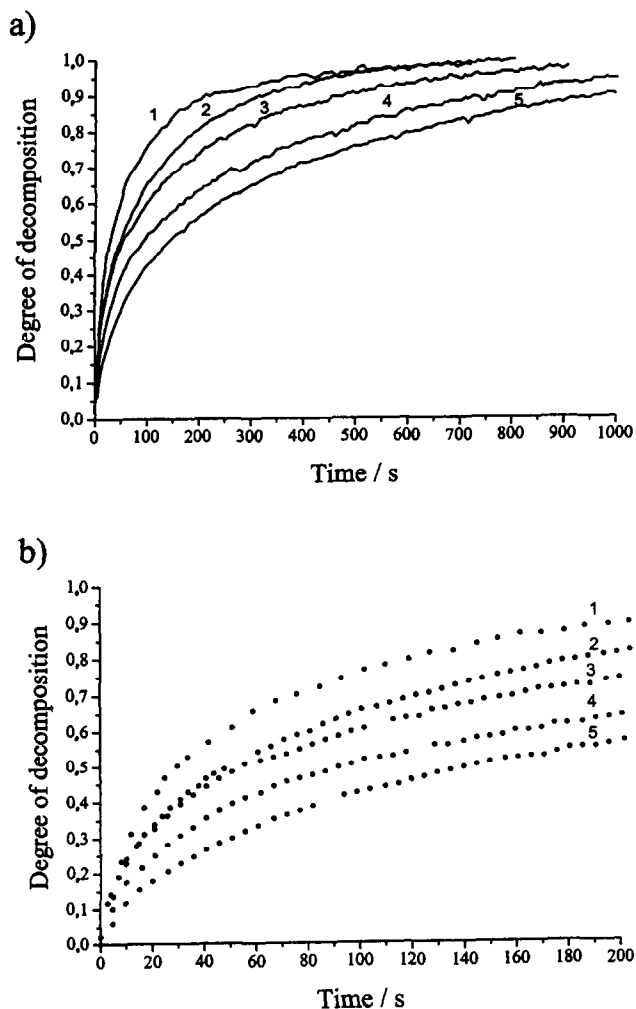


Fig. 3. Isothermal decomposition curves of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] clathrate with benzene at (1) 30.3°C, (2) 25.2°C, (3) 20.2°C, (4) 14.8°C, (5) 6.0°C.

the degree of transformation  $\alpha$ ). Both methods gave similar results. The best fit for the first stage of guest desorption ( $\alpha=0-0.6$ ) was obtained using Eq. (3). Results of least-squares calculations for different  $f(\alpha)$  are given in Table 2. Taking into account that the experimental samples were stoichiometric, one may conclude that decomposition of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>]·C<sub>6</sub>H<sub>6</sub> clathrate, at this stage, takes place according to mechanism 2. All data are summarised in Table 3. Diffusion coefficients were calculated from Eq. (3) for  $\alpha=0-0.6$ . Computer modelling of guest desorption from an ensemble of spherical particles, according to mechanism 2, using calculated diffusion coefficients and an experimentally determined distribution of particle sizes, showed that the influence of actual differences in particle sizes on the rate of decomposition is insignificant. The activation energy for this process, calculated from the Arrhenius plot is  $38.5 \pm 2.5$  kJ mol<sup>-1</sup>, and the pre-exponential factor of the diffusion coefficient is  $3.2(\pm 2.1) \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup>. In the late stages, reaction proceeds more slowly than would result from mechanism 2. This may be a consequence of a decrease in the diffusion coefficient, caused by a shifting of guest molecules to other positions in the channels, but no attempts were made to check this hypothesis. Experiments with a decomposi-

Table 2  
The best least-squares linear approximations of  $f(\alpha)-t$  plots

No.	$T/^\circ\text{C}$	Correlation coefficients for different $f(\alpha)$ <sup>a</sup>		
		A	B	C
1	30.3	0.9986	0.9984	0.9984
2	25.2	0.9996	0.9959	0.9981
3	24.3	0.9996	0.9983	0.9994
4	20.2	0.9981	0.9946	0.9935
5	16.3	0.9993	0.9986	0.9975
6	14.8	0.9968	0.9902	0.9957
7	6.0	0.9997	0.9981	0.9972

<sup>a</sup> A,  $f(\alpha) = 1 - 2\alpha/3 - (1 - \alpha)^{2/3}$  (D4); B,  $f(\alpha) = \alpha^2$  (D1); C,  $f(\alpha) = (1 - \alpha)^{-1}$ .

Table 3  
Kinetic data for decomposition of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] clathrate with benzene

No.	$T/^\circ\text{C}$	$\langle r \rangle/\text{mm}^a$	$t_{0.5}/\text{s}$	$y/\text{mol}^b$	$D \times 10^{12} \text{ c}$
1	30.3	0.114	30	1.05	7.85(5)
2	25.2	0.122	50	0.99	5.39(1)
3 <sup>d</sup>	24.3	0.101	35	1.07	5.39(3)
4	20.2	0.121	56	1.06	4.46(2)
5	14.8	0.127	94	1.00	2.94(1)
6	6.0	0.130	145	1.00	2.07(1)

<sup>a</sup> Average radius of particles in the sample.

<sup>b</sup> In [Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] ×  $y$ G (G is guest).

<sup>c</sup> Calculated from Eq. (3).

<sup>d</sup> Not included in Fig. 1.

tion of 100%, or less than 100% filling of guest positions in the sample, were carried out to investigate the suggestion that there are different decomposition pathways for stoichiometric and non-stoichiometric clathrates. The results of these experiments (Fig. 4) confirm our suggestion.

Two factors, which undoubtedly change the rate of decomposition, should finally be discussed: thermal equilibrium between the sample and the thermostat, and microcracks in the host particles. Thermal equilibrium presents problems in all similar apparatus [13]. In our experiments, thermal contact between thermostatted walls and the sample was improved by using a dynamic atmosphere (with pressure about 1400 Pa) in the apparatus. A thermocouple placed 5–10 mm distance from the sample did not show significant variations in temperature. In addition, temperature variations in different experiments over small ranges of temperature have to be equal due to standard experimental conditions. (Variations of temperature in the apparatus are caused by the heat of reaction. If the mass of the sample and the conditions of heat transfer remain unchangeable, and the rate of reaction changes slightly, temperature variations have to be equal.) Only the absolute value of  $D$ , but not the activation energy, may change in this case. A decrease in the diffusion coefficient caused by cooling of the sample during decomposition cannot be estimated experimentally, or by calculations, but experiments with samples of different mass and shape (hence different conditions of heat transfer) showed that the order of magnitude of  $D$  does not change. Microscopic

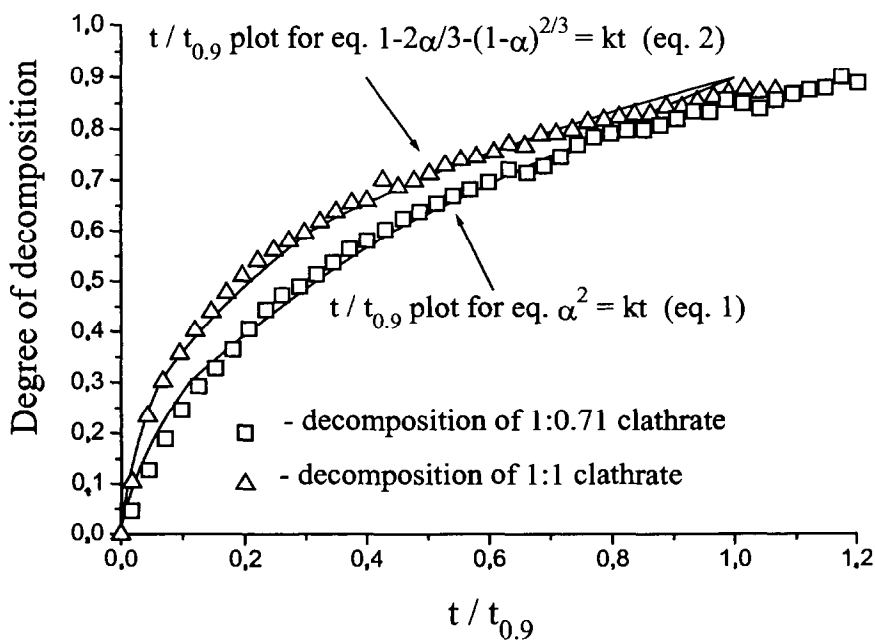


Fig. 4.  $t/t_{0.9}$  tests for decomposition of stoichiometric and non-stoichiometric clathrates at 20.1°C;  $t_{0.9}$  = 375 s for  $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4] \cdot 0.71\text{C}_6\text{H}_6$  and 400 s for  $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4] \cdot 1.00\text{C}_6\text{H}_6$  clathrates.



observations were used to check the existence of micro-cracks in particles of clathrate after guest desorption. The main parts of the particles remain transparent and hence are most probably uncracked.

### 3.4. Decomposition of the toluene and *p*-xylene clathrates

Some  $\alpha$ - $t$  decomposition curves of toluene and *p*-xylene clathrates are given in Fig. 5. Strong cracking of crystals of clathrate with *p*-xylene was observed under experimental

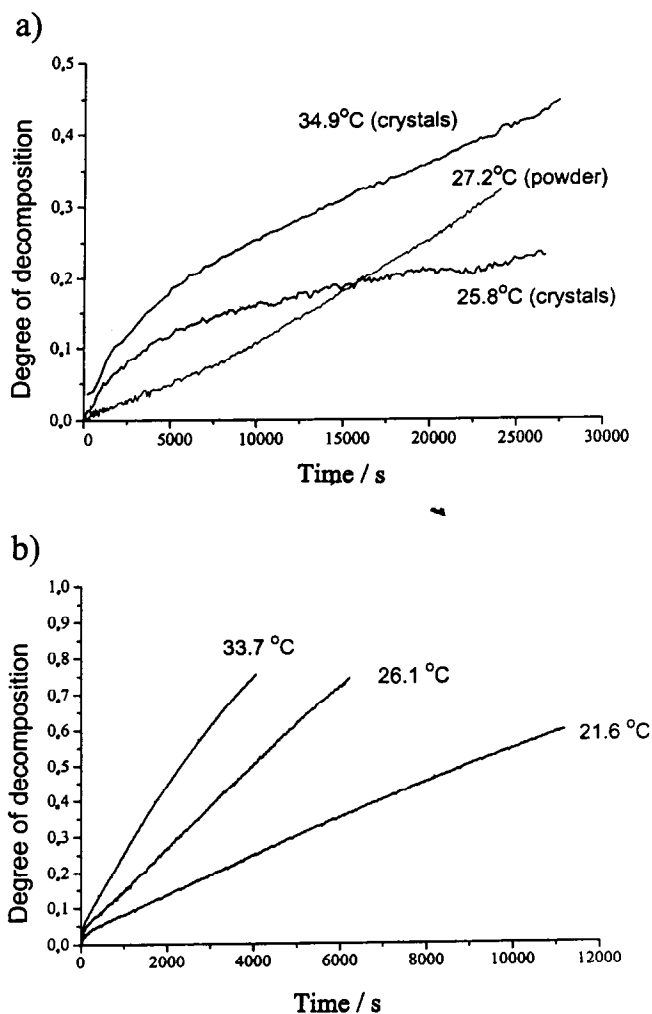


Fig. 5. Isothermal decomposition curves of  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>] clathrate with (a) *p*-xylene and (b) toluene.

conditions. Activation energies were estimated to be more than  $82.1 \text{ kJ mol}^{-1}$  for toluene clathrate, and  $96.8 \text{ kJ mol}^{-1}$  for *p*-xylene clathrate. The shape of the decomposition curves obtained cannot be described with certainty by the equations discussed in this article. It may be caused by a variable *D* for diffusion of toluene and *p*-xylene molecules in the host's channels, or by a non-diffusive rate-determining stage. The second variant is supported by the value of the activation energy, which is much greater than for the benzene clathrate. To prove which of the two options is the correct one, further studies (and new ideas) are necessary.

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