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A KINETIC STUDY OF THE THERMAL DEGRADATION OF 3-METHYLAMINOPROPYLAMINE INSIDE $AlPO_4$-21

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Kinetics of the thermal decomposition of 3-methylaminopropylamine which was used as a structure-directing agent in the synthesis of $AlPO_4$-21 has been studied under isothermal and non-isothermal conditions. The decomposition is a single-step reaction occurring in the 573–663 K range. It is a phase-boundary-controlled process, described by the 'F2/3, R3' kinetic model. The activation energy values obtained under the non-isothermal and isothermal conditions lie in the 173–151 kJ mol^{-1} range.

Keywords: *$AlPO_4$-21, kinetic parameters, open-framework, TG, thermal decomposition*

Introduction

Synthesis of materials which exhibit desired physical and chemical properties is a great challenge in current chemistry. During the recent years much effort has been directed towards open-framework materials. One of the main reasons lies in the fact that these structures can be tailored. Several approaches can be recognized in the design of the open-framework solids. In a frequently applied method, organics (such as amines or quaternary ammonium ions) are used as structure-directing agents, which help the building units to organize themselves in an open-framework host/guest structure. This method is widely used in the synthesis of open-framework phosphates [1]. There is strong evidence that some organics have the structure-directing role in the formation of a certain type of channels. As an example, *n*-diaminopropane directs the formation of one-dimensional channel system in different aluminophosphate topologies [2, 3]. In this manner, by an appropriate choice of organics it is possible to tailor the shape, size and dimensionality of channels and cages in the networks.

The guest species typically remain in the voids of inorganic host and are held to it by hydrogen-bonding interactions. Sometimes the interactions are so strong that thermal degradation of the guest species (attempted with the aim of achieving porosity) causes the collapse of the crystal structure. Fortunately, in many cases the network remains intact after the removal of guest species, becoming ready for further applications.

Although many amines and ammonium salts have been investigated as templates for the formation of open-framework structures [1], information on their thermal degradation and the degradation kinetics is still rare. A major reason is probably the fact that the thermal degradation usually proceeds in several steps involving more than a single reaction.

In this paper we investigate kinetics of thermal degradation of 3-methylaminopropylamine (MAPA) which was used as a possible template in the synthesis of open-framework aluminophosphates ($AlPO_4$-*n*; *n* denotes a specific framework topology). Until now this amine has not been used as a structure-directing agent. Also, to our knowledge this is the first kinetic study of thermal degradation of a template species inside the porous framework.

Experimental

Materials

The reaction gel was prepared by mixing of aluminium oxide (Captal, 70 mass% Al_2O_3), orthophosphoric acid (Fluka, 85 mass% H_3PO_4), water and MAPA (Fluka, 98 mass%) using the following molar ratio: Al_2O_3:$2H_3PO_4$:2MAPA:$100H_2O$. The gel was obtained by successive additions of phosphoric acid and MAPA to the suspension of Al_2O_3 in water under vigorous stirring. Crystallization was performed hydrothermally at 160 and 190°C for 2–7 days. The white crystalline solid was filtered and washed with distilled water, then ultrasonically treated in order to remove amorphous impurities, and air-dried. The product mainly consisted of colorless plate-like crystals and careful examination under a polarizing microscope showed them to be single crystals. Elemental analysis of the crystals is consistent with the following formula: $(AlPO_4)_3\cdot H_2O\cdot 0.65MAPA$.

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Methods

The single crystal data were collected on a Nonius Kappa CCD diffractometer with MoK$_\alpha$ radiation using a transparent crystal of 0.05×0.02×0.15 mm^3 size. Unit cell parameters were determined by least-square refinement on the basis of 2941 reflections.

Thermal decomposition was performed using a SDT Q-600 simultaneous DSC-TG instrument (TA Instruments). The samples (mass app. 6 mg) were heated in a standard alumina sample pan. All experiments were carried out under nitrogen at a flow rate of 0.1 dm^3 min^{-1}. Non-isothermal measurements were conducted at heating rates of 2, 5, 7, 10 and 15 K min^{-1}. Five experiments were done at each heating rate. Isothermal experiments were carried out at temperatures in the range of 610–650 K. A special heating program was used for isothermal measurements. The sample was isothermally heated at 573 K for 30 min to complete dehydration and then the temperature was increased at a heating rate of 20 K min^{-1} to the temperature at which the experiment was performed. Five experiments were done at each chosen temperature.

Results and discussion

The single-crystal X-ray structural analysis shows that the obtained product is AlPO$_4$-21 (Fig. 1). AlPO$_4$-21 has usually been obtained in the presence of 1,2-diaminopropane, pyrrolidine [4] and N,N',N'-tetramethyl-1,3-diaminopropane [5]. The latter decomposes under hydrothermal crystallization and the decomposition products exert the template role. Also, dimethylamine has been reported as a possible template [6].

The AlPO$_4$-21 framework is built of corrugated aluminophosphates sheets which are cross-linked by the Al–O–P chains to form a network of straight eight-membered-ring channels extending along the *c* crystallographic axis (Fig. 1). The MAPA appears to be disordered. The MAPA molecules are positioned in the eight-membered ring channels and are held within them through hydrogen bonds with the framework oxygen atoms. Each template molecule forms two such bonds, the N...O distances being 2.914 and 2.985 Å.

TG and DTG curves are shown in Fig. 2. There are two major clearly separated mass losses. The first one of about 4 mass% corresponds to dehydration which occurs up to about 300°C. Namely, in the AlPO$_4$-21 structure there are three distinct crystallographic phosphorous sites, which are all regular P(OAl)$_4$ tetrahedra and also three aluminium sites: an Al(OP)$_4$ tetrahedron [Al(1), Fig. 1] and two distorted five-coordinate Al(OP)$_3$(OH$_2$) environments [Al(2) and Al(3)]. The oxygen atom of the water molecule [O(7) in Fig. 1] bridges the two five-coordinated Al atoms. The second mass loss of about 13% corresponds to the MAPA decomposition. The MAPA decomposes in a single step over 573–663 K. This event is accompanied by a structural transformation of AlPO$_4$-21 to AlPO$_4$-25 [7].

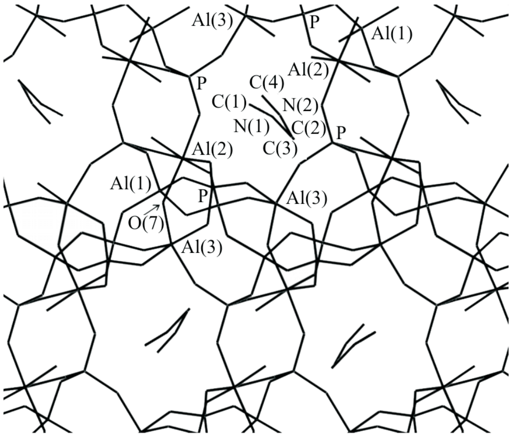

Fig. 1 The view down the *c* crystallographic axis showing MAPA inside the eight-membered-ring channels. The hydrogen atoms are omitted for clarity

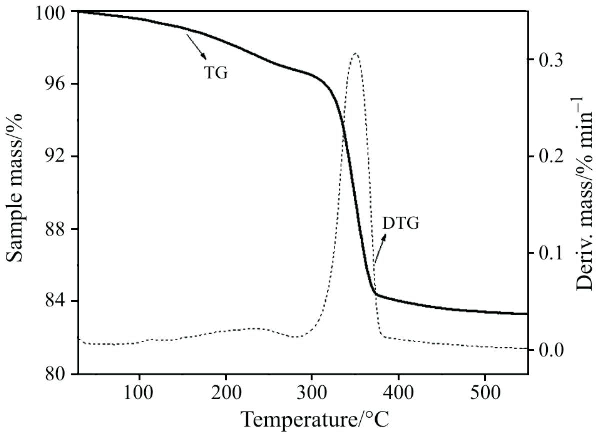

Fig. 2 TG and DTG curves for (AlPO$_4$)$_3$·H$_2$O·0.65MAPA

Thermal decomposition of MAPA in AlPO-21 has been studied in nitrogen atmosphere under non-isothermal and isothermal conditions.

Kinetics of the reaction under non-isothermal conditions

The reaction has been studied by the interpolation method of Orfao and Martins [8] which is applicable in thermogravimetry under linear temperature programming. It is based on the Eq. (1):

$$-\log g(\alpha)=-\log\beta+[-\log I(\gamma,\theta)] \qquad (1)$$

where α is the degree of decomposition; $g(\alpha)$ – integrated form of the appropriate kinetic law; $\beta=AT_0/b$ (A – Arrhenius pre-exponential constant; T_0 – starting temperature; b – heating rate); $I(\gamma,\theta)$ is defined as follows:

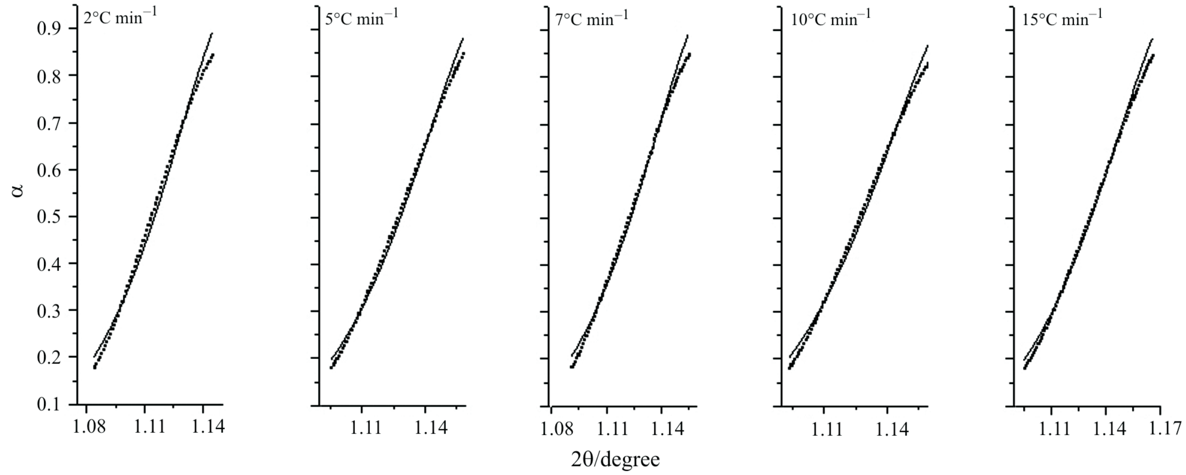

Fig. 3 Plots of the conversion degree (α) of MAPA *vs*. normalized temperature (θ) at different heating rates (··· – experimental data, — – fitted values)

$$I(\gamma,\theta)=\int_{1}^{\theta}\exp\left(-\frac{\gamma}{\theta}\right)d\theta$$

where $\gamma=E_a/RT_0$ (E_a – activation energy, R – gas constant), and $\theta=T/T_0$.

Equation (1) shows that for the correct kinetic law and the appropriate γ value a linear relationship with slope 1 is obtained when $-\log g(\alpha)$ is plotted *vs*. $[-\log I(\gamma,\theta)]$. The interpolation method starts from a normalized thermogravimetric curve α *vs*. θ and then successively determines for various kinetic functions the values of γ that yield such slope. The most satisfactory kinetic function is chosen in the end on the basis of the linear regression quality.

The decomposition of MAPA has been studied at five different heating rates: 2, 5, 7, 10 and 15 K min^{-1}. In all cases the interpolation method showed that the experimental data can be fitted to more than one kinetic model. Thus it is practically impossible to select the proper model on the basis of the non-isothermal measurements alone. Following the usual practice in such cases [9] we also studied the MAPA decomposition under isothermal conditions. These studies (next section) showed that the reaction follows the two-thirds order kinetics (kinetic model F2/3, R3). Therefore, we now present the detailed results of the kinetic analysis of the non-isothermal measurements by the interpolation method only for the F2/3, R3 model.

Table 1 lists the activation energy (E_a) and the Arrhenius pre-exponential constant (A) obtained at different heating rates, together with the reaction rate constant k calculated at 643 K from these E_a and A values, and the correlation coefficient r^2 of the linear regression. Figure 3 shows the part of the TG curves in the region of the MAPA decomposition. The experimental points considered in the kinetic analysis are shown as well as the lines corresponding to the γ and β values from which the results in the Table 1 have been calculated.

Table 1 The activation energy (E_a) and the Arrhenius pre-exponential constant (A) obtained at different heating rates (b). The reaction rate constant k is calculated at 643 K* from these E_a and A values; r^2 is the correlation coefficient of the linear regression

b/ °C min^{-1}	E_a/ kJ mol^{-1}	A/ min^{-1}	k/ min^{-1}	r^2
2	173	$2.59\cdot10^{13}$	0.200	0.990
5	174	$2.42\cdot10^{13}$	0.188	0.995
7	170	$1.24\cdot10^{13}$	0.177	0.993
10	160	$1.98\cdot10^{12}$	0.180	0.993
15	159	$1.48\cdot10^{12}$	0.187	0.995

*This is an arbitrarily chosen value lying within the MAPA decomposition temperature range.

The data in Table 1 show the compensation effect (CE), i.e. the following relationship between the activation energy and the Arrhenius pre-exponential constant [10–12]:

$$\ln A=c+E_a/RT_{is}$$

where T_{is} – isokinetic temperature and c – constant. The plot of $\ln A$ *vs*. E_a for the data in Table 1 gives a straight line; from the slope of the line the value T_{is}=631 K is obtained. The CE is quite often found for heterogenous reactions [13]. It has been a source of continuous debate [14, 15] in which the reality of this effect had been sometimes doubted. However, recent work has shown [10] that CE can be a real phenomenon.

Kinetics of the reaction under isothermal conditions

The measurements have been performed in the 618–648 K temperature range. It has been found that the data obtained can be satisfactorily treated only by the kinetic model F2/3, R3.

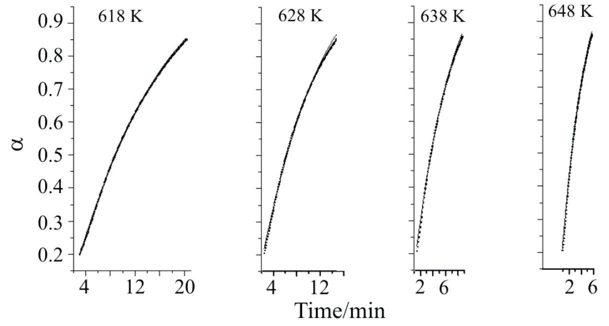

Fig. 4 Plots of the conversion degree (α) of MAPA *vs.* time for several temperatures (··· – experimental data, — – plots of Eq. (2) using the obtained parameter *k*)

The equation describing the model F2/3, R3 in the integrated form has been used to calculate the rate constant *k*:

$$\alpha=1-(1-kt/3)^3 \tag{2}$$

where t – time.

Equation (2) has been fitted to the experimental data in the α range α=0.15–0.90 using a non-linear regression procedure. The estimated values of *k*, together with their confidence intervals (at a level of confidence of 95%) are given in Table 2 (the correlation coefficients of the non-linear regression were r^2=0.999 in all cases). Figure 4 shows the experimental data for the isothermal MAPA decomposition and the plots of Eq. (2) with the obtained parameter *k* for several temperatures.

The plot of ln*k* *vs.* 1/*T* (Fig. 5) is a straight line (correlation coefficient of the fit is r^2=0.988). The activation energy calculated from the slope is E_a=151 kJ mol^{-1} (95% confidence interval: 138–164 kJ mol^{-1}). The Arrhenius pre-exponential constant calculated from the intercept is A=3.68·10^{11} min^{-1} (95% confidence interval: 3.01·10^{10}–4.50·10^{12} min^{-1}).

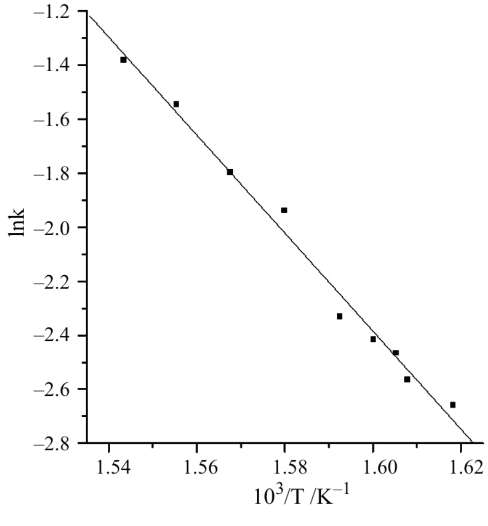

Fig. 5 Plot of ln*k* *vs.* inverse temperature for the isothermal MAPA decomposition

Dependence of the activation energy on the degree of conversion

The dependence of E_a upon α for both non-isothermal and isothermal conditions has been examined in order to obtain the definite proof that the thermal decomposition of MAPA can indeed be described as a single-step kinetic process. If E_a does not depend upon α, the kinetic process is simple and can be described by a unique 'kinetic triplet' [*E*, *A*, *f*(α)] [13, 16–18]. However, if E_a significantly changes with α, the process is complex (multi-step reaction).

In accord with the recommendations of the 'ICTAC 2000 Project' [19], the variation of E_a with α has been studied by the model-free isoconversional method of Friedman [20]. The non-isothermal data have been analysed using the following form of the Friedman's expression:

$$\ln\left(b\frac{d\alpha}{dT}\right)=\ln A+\ln f(\alpha)-\frac{E_a}{RT}$$

for α=const., and using various heating rates (*b*), the plot of ln[*b*(dα/d*T*)] *vs.* 1/*T* should be linear and from the slope of the straight line the value of E_a can be obtained. The results are shown in Table 3.

For the isothermal data the alternative form of the Friedman's expression has been used:

$$\ln\left(\frac{d\alpha}{dt}\right)=\ln A+\ln f(\alpha)-\frac{E_a}{RT}$$

for α=const., the plot of ln(dα/d*t*) *vs.* 1/*T* should be linear and the slope of the straight line leads to the value of E_a. The results are shown in Table 4.

It is seen from Tables 3 and 4 that the value of E_a varies with the extent of conversion by no more than ~6 and ~7% for non-isothermal and isothermal data, respectively. These comparatively small variations seem to justify the assumption that the thermal decomposition of MAPA can be interpreted in terms of a single-step reaction mechanism.

Table 2 Values of *k* and their confidence intervals (at a level of confidence of 95%)

Temperature/K	*k*/min^{-1}	Confidence interval for *k*
618	0.0702	0.0701–0.0703
622	0.0771	0.0769–0.0773
623	0.0851	0.0849–0.0853
625	0.0894	0.0891–0.0897
628	0.0975	0.0971–0.0978
633	0.144	0.1442–0.1448
638	0.166	0.165–0.167
643	0.214	0.213–0.215
648	0.252	0.251–0.253

Table 3 The activation energy (E_a/kJ mol^{-1}) obtained by Friedman's method for the non-isothermal data

α	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85
E_a	164	160	158	158	157	157	155	155	156	157	157	159	159	161

Table 4 The activation energy (E_a/kJ mol^{-1}) obtained by Friedman's method for the isothermal data

α	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85
E_a	155	158	160	160	159	160	158	158	157	158	157	156	155	150

Conclusions

In order to obtain porous materials, thermal decomposition of the template species that remains occluded inside the porous matrix after crystallization is a mandatory step. In spite of the importance of this process there is a lack of the relevant kinetic information. This lack is partly due to the fact that kinetic analysis in many cases is rather unfeasible because of the multistep character of the decomposition.

The kinetic analysis of the thermal decomposition of MAPA, which is immobilized as the template species inside the aluminophosphate framework, has shown that the decomposition occurs as a single step process. The decomposition is a phase-boundary-controlled reaction, i.e. the reaction controlled by the movement of an interface at constant velocity, the nucleation occurring practically instantaneously. The F2/3, R3 kinetic model implies a sphere reacting from its surface inward.

The activation energy values obtained for the F2/3, R3 model under the non-isothermal and isothermal conditions thus lie in the 173–151 kJ mol^{-1} range, i.e. they vary by about 14%. These variations are comparable to those encountered in the kinetic analyses combining non-isothermal and isothermal measurements [8, 21, 22].

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References

1 N. Rajic and V. Kaucic, Molecular sieves: Aluminophosphates, in Encyclopedia of Catalysis, Vol. 5, Ed. I. T. Horvath, John Wiley & Sons, Inc., Hoboken 2003, p. 188.
2 A. F. Ojo and L. B. McCusker, Zeolites, 11 (1991) 460.
3 A. K. Sinha, S. Sainkar and S. Sivasanker, Microporous Mesoporous Mater., 31 (1999) 321.
4 J. B. Parise and C. S. Day, Acta Cryst., C41 (1985) 515.
5 J. M. Bennett, J. M. Cohen, G. Artioli, J. J. Pluth and J. V. Smith, Inorg. Chem., 24 (1985) 188.
6 Z. Liu, W. Xu, G. Yang and R. Xu, Microporous Mesoporous Mater., 22 (1998) 33.
7 R. Jelinek, B. F. Chmelka, Y. Wu, P. J. Grandinetti, A. Pines, P. J. Barrie and K. Klinowski, J. Am. Chem. Soc., 113 (1991) 4097.
8 J. J. M. Orfao and F. G. Martins, Thermochim. Acta, 390 (2002) 195.
9 R. M. Mahfouz, M. A. S. Monshi and N. M. Abd El-Salam, Thermochim. Acta, 383 (2002) 95.
10 T. Vlase, G. Vlase, A. Chiriac and N. Doca, J. Therm. Anal. Cal., 80 (2005) 87.
11 T. Vlase, G. Vlase and N. Doca, J. Therm. Anal. Cal., 80 (2005) 207.
12 T. Vlase, G. Vlase, N. Doca and C. Bolcu, J. Therm. Anal. Cal., 80 (2005) 59.
13 P. Budrugeac, C. Popescu and E. Segal, J. Therm. Anal. Cal., 64 (2001) 821.
14 G. Pokol and G. Várhegyi, CRC Critical Reviews in Analytical Chemistry, 19 (1988) 65.
15 A. Corma, F. L. Copis, I. B. Monton and S. Waller, J. Catal., 142 (1993) 97.
16 P. Budrugeac, Polym. Degrad. Stab., 89 (2005) 265.
17 T. Vlase, G. Vlase and N. Doca, J. Therm. Anal. Cal., 80 (2005) 425.
18 P. Budrugeac, D. Homentcovschi and E. Segal, J. Therm. Anal. Cal., 63 (2001) 457.
19 M. E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H. L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H. O. Desseyn, C.-R. Li, T. B. Tang, B. Roduit, J. Malek and T. Mitsuhashi, Thermochim. Acta, 355 (2000) 125.
20 H. L. Friedman, J. Polym. Sci., 6C (1965) 183.
21 J. Guo and A.C. Lua, J. Therm. Anal. Cal., 59 (2000) 763.
22 E. Tomaszewicz and M. Kotfica, J. Therm. Anal. Cal., 77 (2004) 25.

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