Journal of Thermal Analysis, Vol. 32 (1987) 1867–1876

KINETIC DEHYDROXYLATION OF NONTRONITE, ESTIMATED FROM ISOTHERMAL AND NONISOTHERMAL THERMOGRAVIMETRY

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(Received August 11, 1986; in revised form February 6, 1987)

Dehydroxylation of an American nontronite (Manito) was followed via records of isothermal and dynamic thermogravimetry. Analysis of the isothermal weight-change curves (673–753 K) was performed with the procedure suggested by Hancock and Sharp. A fourteen-kinetic equation procedure was employed for analysis of the non-isothermal weight change in the range 623–1023 K. (A second-order decomposition equation seems to fit the dehydroxylation better under these conditions). The activation energies associated with the isothermal and nonisothermal processes are 118.8 and 136.8 kJ/mol^{-1}, respectively.

Comprehensive studies have been reported on the development of methods and equations (mainly based on the Arrhenius equation) which could describe thermal decomposition [1–11]. Numerous models have been suggested in the literature, and methods have been developed for seeking the differential equation which could represent the decomposition of solids determined under either isothermal or nonisothermal conditions [11–17]. A large set of differential equations has been reported [12, 18. 19].

In the present investigation, a typical purified nontronite deposit from the USA (Manito) was subjected to isothermal weight-change analysis, and also to dynamic thermogravimetry. The aims were to elucidate *a)* the mechanism of dehydroxylation, and *b)* the associated kinetic parameters, as determined from both techniques by the use of various methods of kinetic analysis. Moreover, an attempt was made to discover the possible dependence of these two points on the utilized technique of thermal analysis.

Experimental

An American nontronite deposit (Manito) was purified by the following technique. The crude, finely powdered deposit was thoroughly dispersed in distilled

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water ($S/L = 1/100$) using a high-speed agitator. After 24 h settling, the upper layer of the suspension was decanted off and collected. This process (agitation, settling and decantation) was repeated until the collected clay fraction was proved by X-ray and electron microscopy to be free from any contamination.

Chemical analysis of the pure form gave 40.41% SiO_2. 5.72% Al_2O_3, 29.69% Fe_2O_3, 0.61% TiO_2, 2.83% CaO, 3.62% MgO, and 16.96% loss on ignition. Its structural formula was calculated according to Kelley's method [20] and found to be

$$(Si_{6.93}Al_{1.07})(Al_{0.08}Fe_{3.83}Mg_{0.09})O_{20}(OH)_4Ca_{0.52}Mg_{0.07}$$

Isothermal weight loss curves were recorded with a thermobalance of Gebrüder Netzsch (W. Germany), at fixed temperatures of 673, 693, 713, 733 and 753 K. In each experiment, 0.5 g of the purified material was tested in the presence of air. Thermogravimetry curves were recorded on the same apparatus at a heating rate of 10 deg/min.

Results and discussions

Isothermal dehydroxylation of Manito nontronite

In every case, the sample was preheated for 1 h at 200° prior to admission to the furnace preadjusted to the desired temperature (Fig. 1).

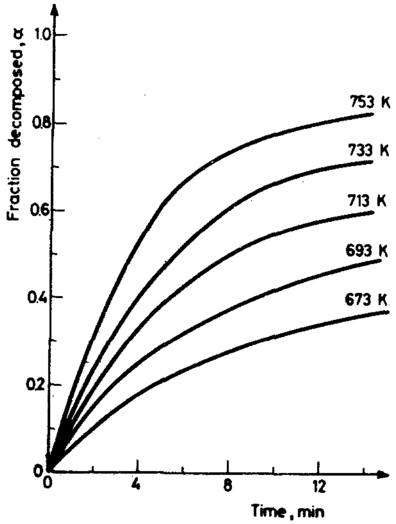

Fig. 1 Isothermal fraction dehydroxylation of Manito nontronite

a) The method of Hancock and Sharp [21]

Starting from the classical method of analysing reaction kinetics in condensed systems, these authors used the following basic equation:

$$\ln[-\ln(1-\alpha)] = \ln B + m \ln t \qquad (1)$$

as a method of comparing kinetic data on solid-state reactions. In this equation, B is a constant which depends in part on the nucleation frequency and the linear rate of grain growth, and m is a constant that can vary according to the geometry of the system. From a list of nine functions collected by Sharp et al. [12], Hancock and Sharp [21] made theoretical plots in the α range of 0.15 to 0.50. The slopes of such plots, m, were listed which are characteristic of each of these solid-state reaction equations (Table 1).

Table 1 General solid-state reaction rate equations

Method No.	Notation	$g(\alpha)$	Mechanism	m
1		α	Power law	
2	D_1	α^2		0.62
3		$\alpha^{1/3}$		
4	R_2	$1-(1-\alpha)^{1/2}$	Contracting geometry	1.11
5	R_3	$1-(1-\alpha)^{1/3}$		1.07
6	F_1	$-\ln(1-\alpha)$	Erofeev–Avrami	1.00
7		$[-\ln(1-\alpha)]^{1/1.5}$		
8	A_2	$[-\ln(1-\alpha)]^{1/2}$		2.00
9	A_3	$[-\ln(1-\alpha)]^{1/3}$		3.00
10	D_2	$\alpha+(1-\alpha)\ln(1-\alpha)$	Diffusion controlled, 2D	0.57
11	D_4	$1-2\alpha/3-(1-\alpha)^{2/3}$	Diffusion controlled, 3D	0.57
12	D_3	$[1-(1-\alpha)^{1/3}]^2$	Jänder	0.54
13		$(1-\alpha)^{-1}-1$	Second order	
14		$(1-\alpha)^{-1/2}-1$	One & a half order	

Accordingly, a plot of any isothermal weight-change data in the form of $\ln[-\ln(1-\alpha)]$ *vs.* $\ln t$, in the range $0.15 \leqslant \alpha \leqslant 0.50$, would approximate to a straight line. From the slope, m of this line, it is readily possible to distinguish between the various models of the solid-state equation. The most appropriate would then be plotted as $f(\alpha)$ *vs.* t over a wider range of α.

The prescribed plots were tried for the five decomposition temperatures (Fig. 2). The slope of each was evaluated in the range $0.15 \leqslant \alpha \leqslant 0.50$, and the obtained mean value of m was found to be 0.86 ± 0.02. This value is actually different from any value predicted by the commonly used theoretical equations. This case could

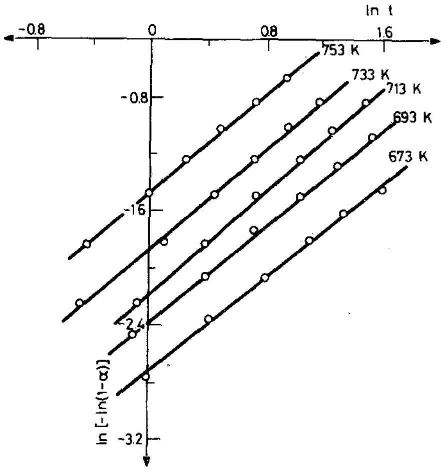

Fig. 2 Linear plots of Hancock and Sharp's equation for isothermal decomposition of nontronite

therefore represent a complicated decomposition process in which more than one model is involved during the course of the reaction.

b) The method of Austin and Rickett [22]

An alternative equation was suggested by the same authors [21], namely that of Austin and Rickett:

$$\ln [\alpha/(1-\alpha)] = \ln k + n \ln t \tag{2}$$

The plot of the left hand side *vs.* ln (time) is linear, with a slope n if this equation applies. The least squares straight line fit was applied in this case, and very satisfactory straight lines were obtained (correlation coefficients $r \geqslant 0.9973$). From the evaluated intercepts, $\ln k$, the activation energy of dehydroxylation was evaluated from the Arrhenius relationship of $\ln k$ *vs.* $1/T$, and was found to be 59.4 $kJ \cdot mol^{-1}$ ($r = 0.9899$, Table 2).

From the slopes of these same plots, the value of n appears to increase with increase of temperature. A mean value of $n = 1.025$ was estimated. The application of such an equation by correlating $\ln (1/1-\alpha)$ *vs.* t yields satisfactory straight lines over the whole range of kinetic curves (mean correlation coefficient $r = 0.9844$). The estimated rate constants are shown in Table 3, and an excellent Arrhenius straight line plot ($r = 0.99437$) is obtained. From its slope, the activation energy of dehydroxylation is estimated to be 93.5 kJ/mol^{-1}.

Table 2 Kinetic parameters estimated by applying the method of Austin and Rickett to the isothermal dehydroxylation of Manito nontronite

	673 K	693 K	713 K	733 K	753 K
n	0.8410	0.8810	1.0790	1.1220	1.2091
$\ln k$	−2.7163	−2.3653	−2.0164	−1.9189	−1.5388
$-r$	1.0000	1.0000	0.9998	1.0000	0.9973
			$E_a = 59.4$ kJ·mol^{-1} $-r = 0.9899$		

Table 3 First order kinetic parameters estimated from $F_1(\alpha)$ equation, applied to isothermal dehydroxylation of Manito nontronite

	673 K	693 K	713 K	733 K	753 K
$\ln k$	−3.6902	−3.0623	−2.6462	−2.2294	−1.9106
$-r$	0.9859	0.9874	0.9856	0.9861	0.9772
			$E_a = 93.5$ kJ·mol^{-1}, $-r = 0.98473$		

c) The 9-function method

A more elaborate analysis of the isothermal weight-loss rate curves was made by plotting $g(\alpha)$ *vs.* t, according to the tabulated values of the principal nine equations given by Sharp et al. [12] and Satava and Skvara [13], i.e. D_1, D_2, D_3, D_4, F_1, A_2, A_3, R_2 and R_3. The data evaluated via the least squares linear fit are listed in Table 4. It should be mentioned that, in order to cover the whole of the decomposition curves, the $\Delta\alpha$ steps were smaller at 673 K (0.03 α) and increased to reach 0.05 at 733 and 753 K.

Table 4 reveals some interesting results:

i) Although the $F_1(\alpha)$ function proved in the Hancock and Sharp method to be the most probable dehydroxylation mechanism, the F_1 function ($\alpha = 0.10$–0.95) here does not provide the best fit to the kinetic data (cf. the correlation coefficients in Table 4).

ii) The best mechanisms to fit the present data are those governed by a diffusional effect (D_2, D_3 and D_4). The poorest fits relate to the equations derived by Avrami and Erofeev (A_2 and A_3, mean $r = 0.9251$).

iii) The highest activation energies are those calculated from the diffusion-controlled processes, and the lowest are those from the Avrami–Erofeev equations.

iv) On the basis of the best straight line fit to the isothermal dehydroxylation of nontronite, the mechanisms D_2, D_3 and D_4 ($r = 0.9900$–0.9946) yield a mean

Table 4 Kinetic parameters estimated from the 9-functions (isothermal dehydroxylation)

Temp., K	Parameter	D_1	D_2	D_3	D_4	F_1	R_2	R_3	A_2	A_3
673	ln *k*	−4.6492	−5.1490	−6.5188	−6.6063	−3.8211	−4.2784	−4.6437	−3.3637	−3.4889
	$-r$	0.9423	0.9992	0.9963	0.9984	0.9865	0.9775	0.9796	0.9428	0.8949
693	ln *k*	−4.0532	−4.5598	−5.9218	−5.9964	−3.1195	−3.9882	−4.3357	−3.1956	−3.3869
	$-r$	1.0000	0.9995	0.9750	0.9934	0.9831	0.9744	0.9775	0.9167	0.9184
713	ln *k*	−3.5510	−4.0063	−5.2121	−5.4011	−2.7186	−3.6718	−3.9779	−2.9561	−3.1898
	$-r$	0.9904	0.9907	0.9959	0.9940	0.9797	0.9519	0.9716	0.9376	0.9155
733	ln *k*	−3.0929	−3.4734	−4.6226	−4.8478	−2.2846	−3.2819	−3.5720	−2.6287	−2.8945
	$-r$	0.9852	0.9901	0.9912	0.9981	0.9841	0.9697	0.9749	0.9477	0.9268
753	ln *k*	−2.778	−3.0791	−4.1271	−4.4322	−1.9432	−3.0268	−3.3059	−2.4128	−2.7183
	$-r$	0.9761	0.9866	0.9911	0.9886	0.9811	0.9597	0.9672	0.9374	0.9132
	$-\bar{r}$ (mean)	0.9789	0.9932	0.9900	0.9946	0.9829	0.9666	0.9742	0.9364	0.9138
	E_a^*	100.2	111.0	129.0	116.7	97.7	68.0	72.6	52.2	42.8
	$-r$	0.99723	0.99985	0.99891	0.99918	0.99404	0.99767	0.99839	0.99209	0.98359
	Se × 10^2	6.43	1.64	5.21	4.39	9.35	3.56	3.54	5.69	6.76

* values of E_a are in kJ · mol^{-1}

activation energy of 118.9 ± 8.0 kJ/mol^{-1}, where the standard error of the estimate, *Se*, ranges between 1.64 and 5.21×10^{-2}.

Nonisothermal dehydroxylation of Manito nontronite

The dynamic TG curve is plotted in Fig. 3 in the form of the weight change (3a) and the fraction of dehydroxylation, α, (3b) against temperature. The low-temperature weight loss up to 573 K is considered to represent the dehydration, whereas beyond this temperature it is associated with the dehydroxylation of nontronite.

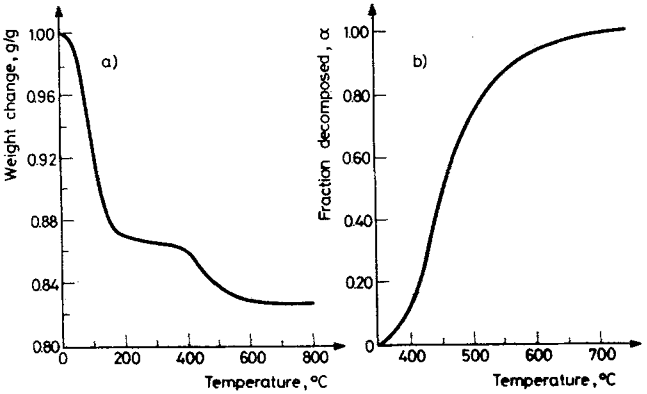

Fig. 3 (a) TG of Manito nontronite. (b) Fraction decomposed as function of temperature in the dehydroxylation region of Manito nontronite

The analysis of dynamic thermogravimetry aims ultimately at linearizing the data by plotting the function log $g(\alpha)$ as a function of $1/T_\alpha$. The nine basic kinetic equations tabulated by Satava and Skvara [13] were tested with the help of the least squares straight line fit. Table 5 shows the estimated values of the activation energies (E_a) and correlation coefficients (r). The nine tested functions are those of the well-established notations (previously mentioned). The activation energy is evaluated from the slope of the straight line, $\tan\beta$, and the temperature of 50% decomposition, $\bar{T}$, using the approximate relationship [11]:

$$E_a = -\tan\beta + \sqrt{\tan^2\beta + 8\tan\beta\cdot\bar{T}}$$

It is apparent that all nine functions give an unsatisfactory fit for the nonisothermal dehydration of Manito nontronite ($r = 0.91254$–0.96615). Consequently, five additional kinetic functions were tried (cf. Table 1 for the unsymbolized equations). From the additional results (Table 5), it is clear that both

Table 5 Kinetic parameters evaluated for the nonisothermal dehydroxylation of nontronite

Method No.	Notation	α = 0.1–0.9		α = 0.1–0.8	
		E_a^*	$-r$	E_a^*	$-r$
1		65.8	0.91219	82.1	0.94784
2	D_1	119.3	0.91254	152.6	0.95058
3		26.4	0.91179	32.9	0.95302
4	R_2	74.9	0.92991	80.9	0.95487
5	R_3	79.1	0.94649	95.6	0.96479
6	F_1	89.3	0.96165	92.9	0.97290
7		62.6	0.96088	64.9	0.97170
8	A_2	49.2	0.96615	56.7	0.97198
9	A_3	35.2	0.96038	36.5	0.97042
10	D_2	138.1	0.93587	150.8	0.95836
11	D_4	131.8	0.92211	164.3	0.95443
12	D_3	154.5	0.94663	160.4	0.96486
13		125.3	0.98797	136.7	0.99025
14		107.1	0.98062	120.5	0.98348

* values of E_a are in kJ · mol^{-1}

the second-order and the $1^1/_2$-order expressions hold best (r = 0.98797 and 0.98062, respectively).

A further step was tried with the object of attaining a better straight line fit to the present data. This was carried out by limiting the calculations to the range $0.1 \leqslant \alpha \leqslant 0.8$. Table 5 lists the results of this last trial too. It is invariably indicated that all 14 functions show a shift towards a relatively better fit to the tested curve data. Meanwhile, the second-order kinetic expression again seems to apply best (r = 0.99025).

Comparison of the data in Table 5 leads to the following findings:

i) The diffusion-controlled mechanisms (D_1, D_2, D_3 and D_4) offer relatively the poorest fit to the data (r = 0.91254–0.94663 and 0.95058–0.96486) in the two ranges of the tested fraction α. At the same time, they give the highest activation energies.

ii) The four expressions for the Avrami–Erofeev mechanisms (Eqs 6–9) apply indistinguishably to the data (the same correlation coefficients). Nevertheless, an increase in the power of the equation ($1/n$) brings about a linear increase in the estimated activation energy.

iii) The power law expressions (Eqs 1–3), similarly to the diffusion-controlled mechanisms, display a poor fit to the data. In contrast to the latter equations, the power law equations yield the smallest activation energies.

iv) The most probable mechanism describing the dehydroxylation of nontronite seems to be the second-order process, which is associated with an activation energy of 136.7 $\mathrm{kJ \cdot mol^{-1}}$.

General conclusions

1) Analysis of the isothermal dehydroxylation of Manito nontronite, in the temperature range 673–753 K, favours a diffusion-controlled mechanism (D_2, D_3 and D_4), which is associated with an activation energy of 118.9 $\mathrm{kJ \cdot mol^{-1}}$.

2) Analysis of the nonisothermal TG curves of Manito nontronite in the temperature range 623–1023 K indicates that a second-order dehydroxylation mechanism is the most predominant. A somewhat higher activation energy is calculated, i.e. 136.7 $\mathrm{kJ \cdot mol^{-1}}$.

3) The procedure suggested by Hancock and Sharp seems to be unjustified. On the basis of the value of m from their plots, or the value of n from Austin and Rickett plots, the evaluated activation energies are considerably lower than those estimated from the isothermal or nonisothermal TG curves.

4) Finally, it is concluded that the decomposition of the same material under isothermal or nonisothermal conditions is not necessarily governed or described by the same solid-state reaction mechanism.

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Zusammenfassung — Anhand isothermer und herkömmlicher Thermogravimetrie wurde die Dehydroxylierung eines amerikanischen Nontronites (Manito) verfolgt. Die isothermen TG-Kurven (673–753 K) wurden mittels der von Hancock und Sharp (1972). Ein kinetisches Vierzehngleichungsverfahren wurde zur Analyse der nichtisothermen TG-Kurven im Bereich 623–1023 K angestellt. Einer Dehydroxylierung unter diesen Bedingungen scheint eine Zersetzungsgleichung zweiter Ordnung besser zu entsprechen. Die Aktivierungsenergie für die isothermen bzw. nichtisothermen Prozesse beträgt 118,8 bzw. 136,8 kJ/mol.

Резюме — Методом обычной и изотермической термогравиметрии изучено дегидроксилирование американского нонтронита (Манито). Анализ изотермических кривых изменения веса (673–753 K) проводился по методу Хенкока и Шарпа. Для анализа неизотермических кривых, измеренных в области термператур 623–1023K, был использован метод четырнадцатого кинетического уравнения. При таких условиах реакция дегидроксилирования лучше всего описывается уравнением второго порядка. Энергии активации для изотермического и неизотермического раны, соответственно, 118,8 и 136,8 кдж/моль.