Journal of Thermal Analysis, Vol. 36 (1990) 629-637

DEHYDRATION KINETICS OF AN INDIAN CLAY

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(Received February 20; in revised form August 6, 1989)

Decomposition of clay from Garo Hills of Meghalaya (India) was studied by dynamic thermogravimetry. A fourteen kinetic equation procedure was applied for analysis of non-isothermal weight change upto a temperature of 1223 K. Two stages of decomposition were clearly distinguised i.e. the initial dehydration period at temperature 373 K to 673 K and the dehydroxylation period in the temperature range 723 K to 1073 K. First order decomposition mechanism was found to be applicable to both dehydration and dehydroxylation steps. Activation energies of 67 kJ/mol and 278 kJ/mol are estimated for the first and second steps with frequency factors of 16.3 s^{-1} and 5.16 $x10^6 s^{-1}$ respectively. The weight loss relating to the steps in TG curves allows determination of the contents of the basic mineral in the clay. Percentages of $Al_2O_3.SiO_2$ and total volatiles as calculated from weight loss data are in accordance with the results of classical chemical analysis.

This paper reports non-isothermal thermogravimetric analysis of the clay in the Garo Hill of Meghalaya (India) leading to the approximate estimate of the chemical constituents and important kinetic parameters.

A number of models have been developed for solid decomposition mechanism and methods have been worked out for solving the differential equation which could represent the decomposition of solids determined under isothermal and non-isothermal conditions. The retrieval of the kinetic parameters from the weight loss versus temperature data can be done by using one of several techniques such as those developed by Freeman and Carrol [1], Horowitz and Metzger [2], Gorbachev [3], MacCallum and Tanner [4], Coats and Redfern [5], and Reich and Stivala [6]. Other techniques are available for specific decomposition mechanisms such as those developed by Satava and Škvara [7] and Blazejowski [8]. Modified version of Coats and Redfern Technique [9] has been developed and found to be the easiest of all methods. This has further been modified to cover wide range of

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mechanistic model [10]. Terez [11] has proposed a procedure for a modified Freeman and Carroll method.

Theoretical

The process of clay dehydroxylation may be described by a fundamental equation of non-isothermal kinetics. The ultimate aim of analysing dynamic TG curve is a to linearize the data in the form of the decomposition fraction as a function of temperature, (T). Certain well established kinetic solid-state equations are employed to describe the TG curve and are associated with one or more rate determining mechanism. In the present paper we adopt three methods using nine of the basic kinetic equations (D_1, D_2, D_3, D_4, F_1, A_2, A_3, R_2, R_3). For all procedure of analysis, a least square fit for a straight line has been employed and the corresponding correlation co-efficient, r and standard error or deviation S_e were estimated.

The following methods are used in this paper

1) The method of Coats and Redfern (CR): In the original method [5], the authors assumed a first order reaction mechanism as well as fractional order down to zero.

In recent year, the method has been modified and extended to cover all of the nine currently accepted solid-state reaction mechanism [10]. The general equation is of the form:

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\left[\frac{AR}{\Phi E_a}\right] - \frac{E_a}{2.3RT} \qquad (1)$$

or

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\left[\frac{AR}{\Phi E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{2.3RT} \qquad (2)$$

where, T is the absolute temperature at the specified fraction, R is the gas constant, E_a is activation energy, A is the Arrhenius frequency factor and φ is heating rate. If the correct $g(\alpha)$ is used, a plot of the left hand side of the equation *vs.* $1/T$ should give a straight line from which the values of E_a and A could be estimated.

2) The method of Blazejowski (Blz): This method was applicable to certain solid-state reaction kinetics [8]. The basic equation involved is

$$\log \frac{g(\alpha)}{T} = \log \frac{A}{\Phi} - \frac{E_a}{2.3RT} \tag{3}$$

which is found to be suitable in the linearized procedure. Values of E_a and A then can be evaluated easily.

3) The method of Satava and Škvara (SS): According to this method, log $g(\alpha)$ is plotted against $1/T$ for each of the nine solid-state decomposition mechanism. From the slope of the best straight line, extending over the whole range of decomposition, E_a can be calculated from the approximate formulae:

$$E_a = -\tan\beta + \sqrt{\tan^2\beta + 8\tan\beta . T} \tag{4}$$

where tan β is the slope of the straight line and T is the temperature corresponding to 50% decomposition.

Experimental

Representative clay sample was ground to –325 mesh, washed in distilled water, decanted and dried before subjecting to DTA. TG, DTA and DTG were recorded with MOM (OD 103) derivatograph, taking 200 mg of clay sample. Reference samples was α-Al_2O_3 and heating rate was 4.66 K per second in static N_2 atmosphere.

Results and discussion

Thermogravimetric curves are shown in Fig. 1. The TG curve shows clearly two distinct zones of dehydration. The first zone is indication of loss of water which is physically adsorbed on clay surfaces while the second zone is due to loss of structural water i.e. loss due to dehydroxylation. One may easily infer that the clay is basically of the kaolinitic ($Al_2S_2O_5$ $(OH)_4$) structure from which removal of hydroxyl takes place above 723 K, the peak temperature being obtained between 773 K to 873 K. The peak temperature

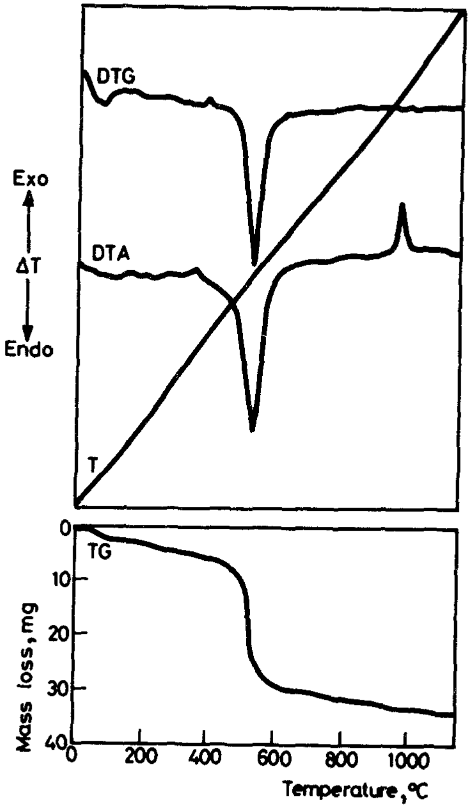

Fig. 1 TG, DTG, DTA curves of the clay

832 K obtained here with finely ground washed clay sample is thought to be representative of the clay, though in general peak temperature varies with impurities present, heating rate, water vapour pressure and other experimental conditions [12]. The first dehydration step is involved with a loss of about 4% water while the dehydroxylation step involved a loss of about 13% water which is almost equal to the percentage of structural water present in kaolin. From the initial mass of sample taken and the process of dehydration of single mineral and following a standard procedure [13], the kaolin content was found to be 92% which implies that Al_2O_3 and SiO_2 contents in the clay are 36.34% and 42.81% respectively. Chemical analysis of the clay shows an Al_2O_3 content of 36.9% and SiO_2 content of 44.56%. Thus

the thermoanalytical results show reasonable accuracy in supporting kaolin as the predominant nature of the clay.

The two dehydration steps are transfered into kinetic curves and shown as fractional decomposition (dehydration and or dehydroxylation) vs. temperature. Table 1 shows the kinetic parameters namely E_a and A for the nine mechanistic model using all fourteen functions and the three methods mentioned earlier. The results pertain to the entire range of decomposition and statistical test for the goodness of fit was performed following a standard procedure [14] in a computer (HCl India, System IV). Both dehydration and dehydroxylation of the clay follow first order kinetic mechanism though there is some proximity to second order mechanism. Earlier workers have established first order kinetic mechanism for pure kaolin [15]. But some workers report a diffusion controlled reaction in vacuo. It may be belived that most observation of first order kinetics can be reinterpreted in accordance with a diffusion controlled mechanism. Pseudo phase boundary controlled mechanism was also proposed by some workers [16] with E_a and A values of 172.62 kJ/mole and $14.85\text{x}10^{10}\text{s}^{-1}$ respectively.

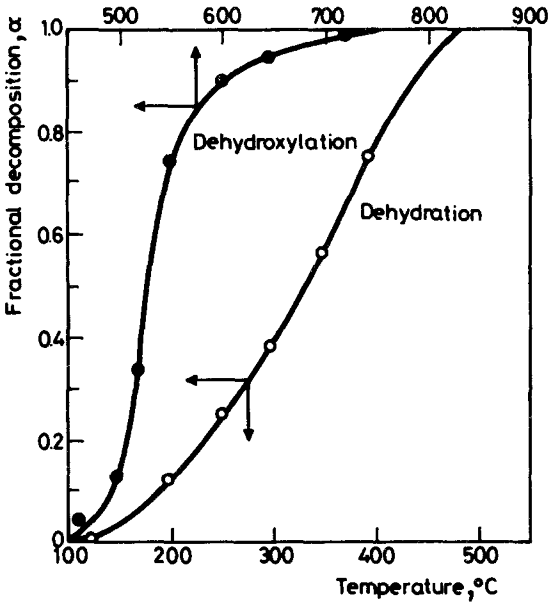

Fig. 2 Fraction decomposed as function of temperature

Table 1 Kinetic parameters for clay dehydration / dehydroxylation. A. Initial dehydration period

Mechanism		Blz method				CR method				SS method		
Method	Notation	E_a, kJ/mol	A, s^{-1}	r	S_e	E_a, kJ/mol	A, s^{-1}	r	S_e	E_a, kJ/mol	r	S_e
1		56.13	0.51	-0.97	-0.04	46.01	1.95	-0.96	-0.026	187.60	-0.98	1.4
2	D_1	122.40	83.46	-0.98	-0.13	112.30	773.40	-0.97	-0.084	314.82	-0.98	2.79
3		11.96	0.017	-0.93	-0.01	1.825	0.003	-0.33	-0.005	72.17	-0.98	0.47
4	R_2	62.34	0.53	-0.986	-0.03	55.21	0.02	-0.97	-0.01	181.47	-0.99	1.21
5	R_3	64.59	0.46	-0.988	-0.02	54.46	2.07	-0.98	-0.01	160.70	-0.99	1.15
6	F_1	69.34	2.39	-0.942	-0.22	59.20	11.72	-0.98	-0.014	168.35	-0.99	1.02
7		42.85	0.26	-0.99	-0.01	32.71	0.71	-0.98	-0.007	112.41	-0.99	0.68
8	A_2	29.60	0.087	-0.986	-0.01	19.47	0.14	-0.96	-0.004	111.90	-0.99	0.51
9	A_3	16.36	-0.0289	-0.981	-0.004	6.22	0.015	-0.85	-0.002	57.21	-0.99	0.34
10	D_2	130.20	104.00	-0.986	-0.09	120.10	1.03×10^3	-0.98	-0.06	320.72	-0.98	2.54
11	D_4	133.20	32.90	-0.98	-0.08	123.10	3.34×10^2	-0.98	-0.56	302.57	-0.99	2.46
12	D_3	139.30	66.71	-0.99	-0.07	129.20	7.10×10^2	-0.99	-0.05	339.18	-0.99	2.30
13		85.70	15.86	-0.994	-0.03	75.57	98.92	-0.99	-0.62	133.99	-0.99	1.38
14		77.13	2.95	-0.994	-0.02	67.00	16.33	-0.99	-0.01	212.15	-0.99	1.08

Table 1 Kinetic parameters for clay dehydration / dehydroxylation. **B.** Dehydroxylation period

Mechanism		Blz method				CR method				SS method		
Method	Notation	E_a, kJ/mol	A, s^{-1}	r	S_e	E_a, kJ/mol	A, s^{-1}	r	S_e	E_a, kJ/mol	r	S_e
1		132.50	9.74	-0.812	-0.312	116.20	58.61	-0.772	-0.168	349.60	-0.844	4.24
2	D_1	281.30	4.75x10^{4}	-0.829	-1.122	265.00	65.00	-0.812	-0.624	490.60	-0.844	8.49
3		33.32	0.034	-0.72	-0.039	17.045	0.0298	-0.463	-0.021	154.49	-0.844	1.41
4	R_2	168.90	63.31	-0.862	-0.326	152.70	500.30	-0.836	-0.179	423.92	-0.882	4.51
5	R_3	184.60	125.40	-0.879	-0.32	168.30	1.09x10^{3}	-0.858	-0.178	455.64	-0.896	4.56
6	F_1	222.00	5.03x10^{3}	-0.912	-0.386	205.70	5.3x10^{4}	-0.898	-0.196	531.43	-0.923	4.59
7		142.65	36.98	-0.905	-0.173	126.30	241.71	-0.882	-0.088	370.22	-0.923	3.06
8	A_2	102.90	3.167	-0.898	-0.098	86.59	14.21	-0.862	-0.051	288.77	-0.923	2.29
9	A_3	63.15	0.2789	-0.882	-0.044	46.88	0.66	-0.807	-0.023	266.04	-0.923	1.53
10	D_2	322.10	4.3x10^{5}	-0.853	-1.174	305.90	6.8x10^{6}	-0.840	-0.660	733.29	-0.865	8.90
11	D_4	342.30	3.91x10^{5}	-0.865	-1.03	326.00	6.6x10^{6}	-0.854	-0.616	773.80	-0.876	8.99
12	D_3	385.40	7,88x10^{6}	-0.888	-1.09	369.10	1.5x10^{8}	-0.879	-0.640	860.50	-0.896	9.12
13		382.90	3.16x10^{3}	-0.954	-0.39	366.67	5.9x10^{9}	-0.972	-0.168	850.40	-0.977	4.09
14		294.20	3.6x10^{5}	-0.974	-0.35	277.90	5.16x10^{6}	-0.98	-0.170	720.55	-0.956	4.43

The values of activation energy found out by SS method were considerably higher than those obtained by the other two methods for all the fourteen equations. This is reasonable since the sensitivity of SS method is relatively lower though it offers useful kinetic information in general [17]. The CR method gives smallest values of E_a for both the steps involved while Blz method gives values lying inbetween. However, Blz method reveals that the straight line fit is better for all fourteen mechanism in both the dehydration and dehydroxylation steps. Recent finding is that CR method extended to any $g(\alpha)$ is the most reliable method for non-isothermal analysis [18]. In the present case also, CR method shows better correlation (r =.98 and S_e $=17\text{x}10^{-2}$) for the first order mechanism resulting in E_a values of 67 kJ/mole and 278 kJ/mole for dehydration and dehydroxylation steps with corresponding A values of 16.3 s^{-1} and $5.16\text{x}106s^{-1}$ respectively while Blz method shows E_a values of 77 and 294 kJ/mole for the two steps with A values of $3s^{-1}$ and $4\text{x}10^5s^{-1}$ respectively (r =.994, S_e $=18\text{x}10^{-3}$ for dehydration and r =0.974, S_e = $3.49\text{x}10^{-1}$ for dehydroxylation).

Since kinetic law for kaolin dehydroxylation is reported to change at a conversion degree of greater than 60% [19], regression analysis was separately performed using data on conversion below 60%. Better correlation was obtained for the proposed mechanism using CR technique, the values of E_a and A being 262.1 kJ/mole and $4.01\text{x}10^6s^{-1}$ respectively (r =.992 and S_e $=7\text{x}10^{-3}$). The value of E_a calculated for the clay is higher than those for natural, synthetic as well as activated kaolin reported recently [20]. However, wide variation in E_a value (i.e. 200 to 840 kJ/mole) is possible depending on the sources of kaolin [21]. The value of A for the dehydroxylation step obtained in this work is significantly lower in comparison to figures in the range of 7.6 to $14.8\text{x}10^{10}s^{-1}$ reported in literature [16]. The observed variation may be attributed to differences in structural properties, particle size, particle packing in aggregate and the size and density of the aggregate of clay. However, the observed results would be quite reasonable for industrial design of calcination process.

Conclusion

1) Analysis of non isothermal thermogravimetric curves of an indian clay upto temperature of 1223 K revealed two stages of dehydration i.e. an initial dehydration period at temperature 373 K to 673 K and a dehydroxylation period in the temperature range 723 K to 1073 K.

2) First order decomposition mechanism was found to be predominant to both dehydration and dehydroxylation steps which are associated with activation energies of 67 kJ/mol and 278 kJ/mol respectively. The corresponding values of the frequency factor are $16.3 s^{-1}$ and $5.16 x 10^{6} s^{-1}$ respectively.

3) Analysis of the weight loss relating to steps in TG curves further reveals that the clay is basically kaolinitic in nature and that the Al_2O_3 and SiO_2 contents of the clay are 36.34% and 42.81% respectively which are comparable to the values of 36.9% and 44.56% as obtained by classical chemical analysis.

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Zusammenfassung — Mittels DTG wurde die thermische Zersetung von Ton aus der Garo-Hills-Gegend bei Meghalaya (Indien) untersucht. Zur Analyse der nicht-isothermen Gewichtsveränderungen bis zu einer Temperatur von 1223 K wurde ein Verfahren mit vierzehn kinetischen Gleichungen angewendet. Zwei Teilschritte der Zersetzung können eindeutig unterschieden werden, nämlich die anfängliche Dehydratationsperiode bei Temperaturen von 373 bis 673 K und die Dehydroxylierungsperiode bei Temperaturen zwischen 723 K un 1073 K. Für beide Vorgänge konnte als Reaktionsmechanismus eine Zersetzung erster Ordnung angewendet werden. Für den ersten un zweiten Teilschritt konnten Aktivierungsenergien von 67 kJ/mol bzw. 278 kJ/mol un Frequenzfaktoren von $16.3 s^{-1}$ bzw. $5.16 x 10^{6} s^{-1}$ ermittelt werden. Der aus den TG-Kurven hervorgehende Gewichtsverlust läßt auf den Gehalt des Tones an Basismineral schließen. Der prozentuelle Gehalt an Al_2O_3, SiO_2 und der gesamten flüchtigen Bestandteile, berechnet aus den Gewichtsverlusdaten, stimmt mit den Ergebnissen aus herkömmlichen chemischen Analysen überein.