

## **SOME ASPECTS ABOUT KINETICS OF ISOTHERMAL DEGRADATION OF LAYERED HYDROUS TITANATE INTERCALATED WITH *n*-ALKYLDIAMINES**

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### **Abstract**

Thermogravimetric data were used to calculate the kinetics of isothermal degradation of layered tetratitanate intercalated with *n*-alkyldiamines  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$  ( $n=2, 3, 4, 6$  or  $8$ ). The hydrous matrix showed two mass loss steps from the thermogravimetric curve, corresponding to the release of physisorbed and lattice water molecules. For the intercalated matrices a third mass loss was observed due to the release of organic moiety. From these values, the amine intercalated matrices can be ordered in the following sequence of thermal stability;  $\text{C}_4 > \text{C}_2 > \text{C}_3 \cong \text{C}_6 > \text{C}_8$ . Kinetic studies were carried out to the release of lattice water molecules. The kinetic model that best adjusted the experimental isothermal TG data was the diffusion mechanism controlling process.

**Keywords:** intercalation, kinetics, thermogravimetry

### **Introduction**

The stability of the alkaline metal titanates in acidic solutions is restricted by transformation into protonic oxides [1, 2]. However, the resulted compound retains a layer structure, which is similar to that of the alkaline materials. A considerable attention was devoted for such compounds due to their prominent abilities in intercalation, ionic exchange process, photochemical and semiconductor properties as well as catalytic activities [3–5].

The acidic layered tetratitanate that is also called layered hydrous titanium dioxide, exhibits distinct intercalation behavior towards various cations and some organic compounds [5–7]. This property can be explored to use this material to remove and immobilize radioactive nuclides such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  from high-level liquid waters [8].

A significant amount of investigation is devoted to ion-exchange reactions, with the great majority focused on structural features of these exchangers, mainly exploring the excellent chemical and thermal stabilities and also the facility in developing favourable ion-exchange properties [5–7, 11].

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In recent years, thermogravimetric (TG) methods have been widely used to study the kinetics of various solid-state decomposition reactions [12–15]. Isothermal TG has been widely applied to the study of various solid-state processes. The shape of the thermogravimetric curves is a function of the reaction kinetics and hence, the information obtained from these curves is useful in evaluating the kinetic parameters and reaction mechanism.

Some studies on behavior kinetics of the thermal decomposition have been carried out with metallic complexes [12, 13, 16, 17]. On the other hand, kinetic data for the layered materials is found only for  $\alpha$ -titanium phosphate matrix in studies of ionic exchange and intercalation [18].

The purpose of this publication is to report the kinetic parameters for the isothermal degradation of intercalated matrix involving *n*-alkyldiamines,  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$  ( $n=2, 3, 4, 6$  or  $8$ ), with hydrous titanium dioxide ( $\text{H}_2\text{Ti}_4\text{O}_9 \cdot n\text{H}_2\text{O}$ ). Special attention is focused on the effects caused by the diamine chain length on the structure and release of lattice water molecules.

## Experimental

All chemicals employed were of analytical grade and were used without further purification. The layered starting material, potassium tetratitanate,  $\text{K}_2\text{Ti}_4\text{O}_9$ , hydrous titanium dioxide,  $\text{H}_2\text{Ti}_4\text{O}_9$  and the intercalated material was prepared, characterized and stored as previously described [19].

Thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance, under nitrogen atmosphere, by isothermal and non-isothermal heating techniques. The carrier gas flow was always  $50 \text{ mL min}^{-1}$ ; sample masses were  $5.0 \pm 0.5 \text{ mg}$ , with size of 300 mesh. For experiments carried out under non-isothermal conditions, the instrument was programmed to heat the sample from room temperature at a constant heating rate of  $10^\circ\text{C min}^{-1}$ . For isothermal experiments, the temperature program was varied, depending on the isothermal temperature.

The isothermal mass-loss data were treated kinetically with the aid of a computer program in terms of the most commonly proposed models found in the literature [14, 20]. The linearity of the kinetic plots was checked in terms of correlation coefficients (*r*) and standard deviations (*sd*) to determine the kinetic model and Arrhenius parameters.

## Results and discussion

The general features associated with the interactive process involving guest molecules intercalated into a host matrix are characterized by the neutralization of the basic center of the organic polar molecule into the lamellar cavity in a typical Brønsted acid–base reaction [21]. Consequently, in this process a structural change of the intercalated phase takes place, and changes are directly followed via X-ray diffraction patterns. Usually, the final equilibrium in the solid/liquid interface points out an increase

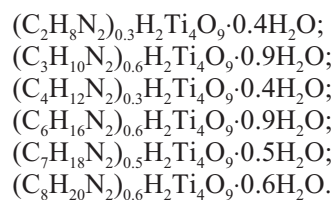
in the interlayer distance, to accommodate the guest molecule in the free space of the cavity [21].

**Table 1** Constant rates ( $k$ ), linear correlation coefficients ( $r$ ) and standard deviation ( $sd$ ) of the matrices in each range of temperature

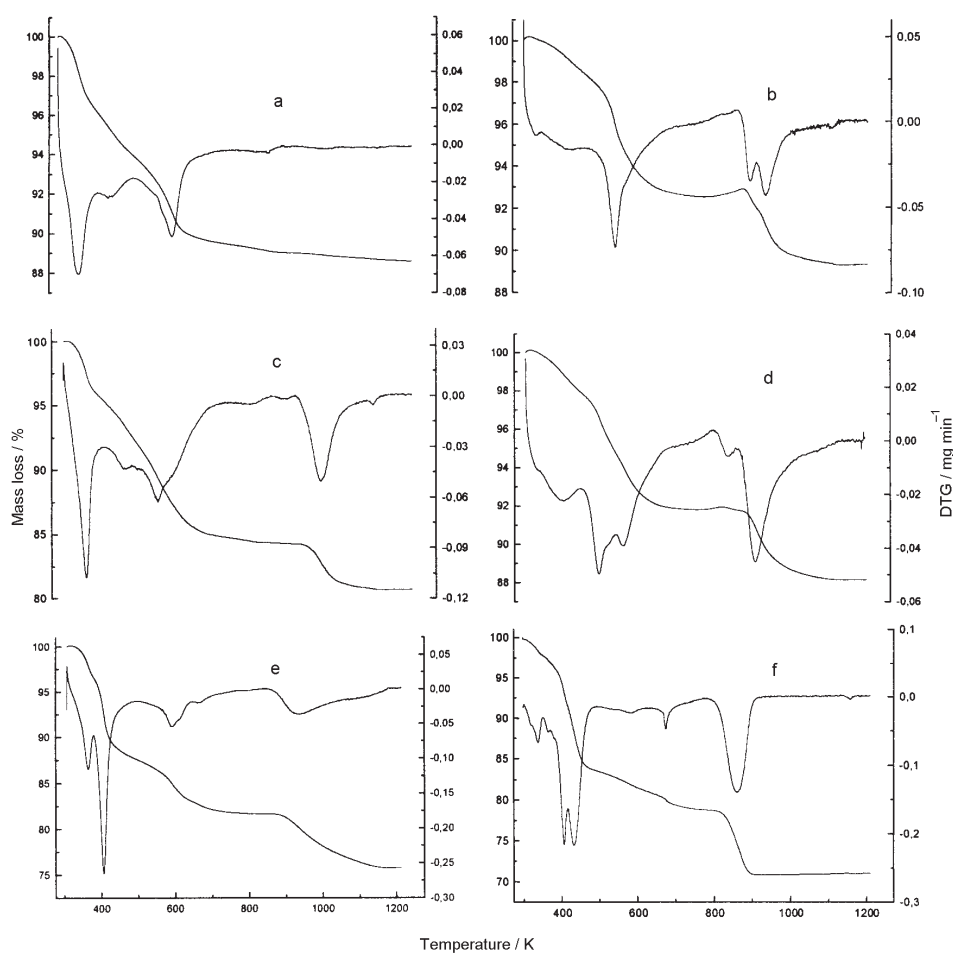
Matrix	Temperature/K	Mechanism	Parameter		
			$k \cdot 10^4 (\text{s}^{-1})$	$r$	$sd \cdot 10^2$
C <sub>2</sub>	906	D2	2.49	0.9920	2.18
	911		3.25	0.9865	2.64
	916		4.99	0.9873	2.35
	921		5.98	0.9912	2.23
	926		7.19	0.9901	2.45
C <sub>3</sub>	947	D2	5.25	0.9772	3.25
	953		6.17	0.9980	0.98
	958		7.68	0.9950	1.87
	962		8.42	0.9918	1.57
	967		9.29	0.9956	2.10
C <sub>4</sub>	908	D2	1.76	0.9936	2.95
	913		1.98	0.9926	2.27
	918		2.64	0.9891	3.21
	923		3.64	0.9981	1.15
	928		3.68	0.9989	0.82
	933		5.53	0.9987	1.32
C <sub>6</sub>	938	D4	5.72	0.9896	1.94
	873		4.31	0.9889	1.22
	883		7.46	0.9980	1.41
	888		7.68	0.9945	1.23
	893		9.21	0.9984	1.31
C <sub>7</sub>	898	D4	10.23	0.9950	0.58
	858		3.49	0.9992	0.87
	863		3.51	0.9947	1.78
	868		4.67	0.9975	1.32
	873		7.69	0.9846	1.02
	883		8.01	0.9953	1.64
C <sub>8</sub>	888	D1	9.11	0.9978	0.63
	853		15.16	0.9969	2.00
	858		15.63	0.9932	2.71
	863		22.17	0.9943	2.34
	868		27.31	0.9940	2.74
	873	33.00	0.9984	1.41	

X-ray diffraction patterns for the intercalated matrices shown in an increase in interlayer distance of the free host from 920 pm to 1118, 1318, 1549, 1662, 1720 and 1834 pm for the sequence C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>6</sub>, C<sub>7</sub> and C<sub>8</sub> of *n*-alkyldiamines, respectively.

Based on thermogravimetry and CHN elemental analysis results. The composition results of the intercalated matrices can be represented in the following way:

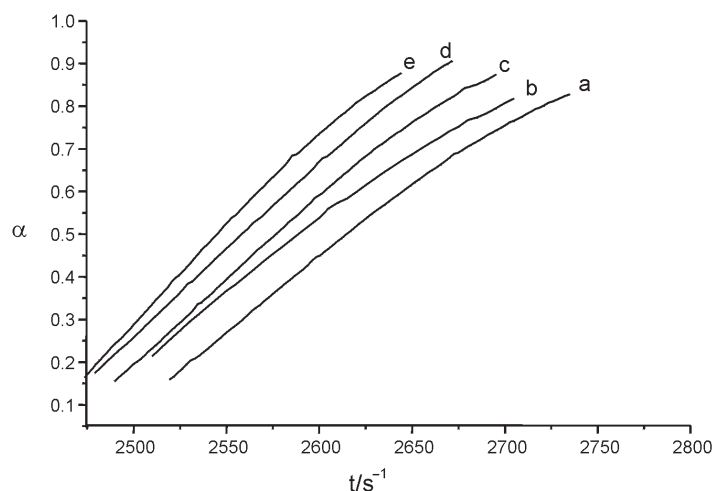


The thermogravimetric curve for the hydrated matrix exhibits two distinct mass loss steps. The first one is due to the release of physisorbed water molecules and the



**Fig. 1** Thermogravimetric and derivative curves for the matrix (a) and dialkylamines  $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$  intercalated matrices:  $n=2$  (b),  $n=3$  (c),  $n=4$  (d),  $n=6$  (e) and  $n=8$  (f)

second to the release of lattice water molecules. These last molecules are produced as a consequence of the condensation of the hydroxyl groups of the matrix. For the amine intercalated samples a third mass loss step was observed (Fig. 1) located between the two other previously described steps. It was attributed to the release of the organic moiety. The amine intercalated matrices can be ordered in the following sequence of thermal stability:  $C_4 > C_2 > C_3 \cong C_6 > C_8$ . This last sequence is in agreement with the fact that, the lower the amount of intercalated organic moieties, the higher the thermal stability of the synthesized hybrid is.



**Fig. 2** Decomposition according to D4 model for  $(C_6H_{16}N_2)_{0.6}H_2Ti_4O_9 \cdot 0.9H_2O$  at the temperature of a – 580, b – 585, c – 590, d – 595 and e – 600°C

**Table 2** Kinetic parameters activation energy ( $E_a$ ), pre-exponential factor ( $A$ ), coefficient of correlation ( $r$ ) and standard deviation ( $sd$ ) using Arrhenius equation

Matrix	Parameters			
	$E_a/kJ mol^{-1}$	$A/s^{-1}$	$r$	$sd$
Original	61	$3.96 \cdot 10^4$	0.9987	0.011
$C_2$	379	$1.89 \cdot 10^{18}$	0.9870	0.065
$C_3$	218	$6.28 \cdot 10^8$	0.9920	0.052
$C_4$	304	$5.76 \cdot 10^{13}$	0.9882	0.078
$C_6$	255	$8.38 \cdot 10^{11}$	0.9808	0.086
$C_7$	228	$2.65 \cdot 10^{10}$	0.9832	0.065
$C_8$	258	$8.75 \cdot 10^{12}$	0.9910	0.079

Some kinetic curves showing the extent of reaction for the experiment carried out under isothermal conditions are shown in Fig. 2, the fraction decomposition ( $\alpha$ ) the range  $0.15 \leq \alpha \leq 0.9$  vs. time ( $t$ ) curves at different temperature, which are related to

the decomposition of the amine. Kinetic obedience was determined by plotting various kinetic functions  $G(\alpha)$  vs.  $t$ , according to  $G(\alpha)=kt$ , where  $k$  is the apparent rate constant. The best fitting was found, as suggested by the shape of  $\alpha$  vs.  $t$  curves, with the diffusion mechanism controlling process, which can be observed in Table 1.

The kinetic parameters obtained through Arrhenius equation vs. velocity constants,  $k$ , relative to model of diffusion mechanism,  $D_n$  ( $n=1, 2, 3, 4$ ). Examples of this behavior are shown in Fig. 3, which refer to matrix  $C_4$ .

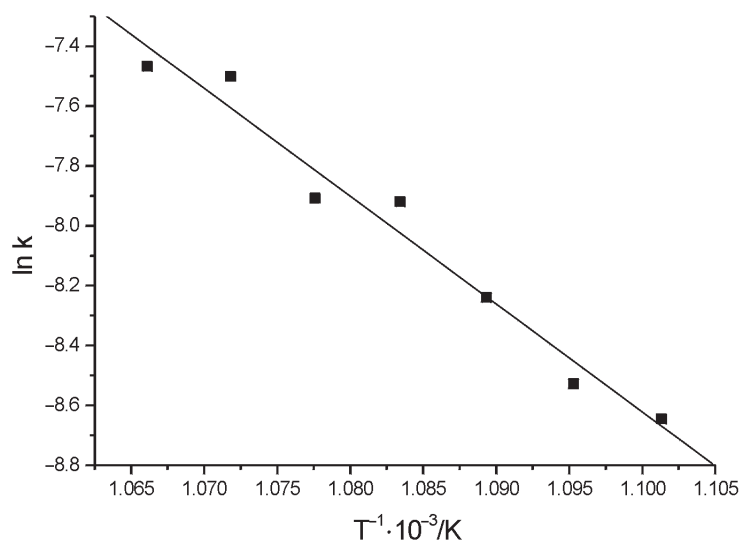


Fig. 3 Plot of Arrhenius equation for  $(C_4H_{12}N_2)_{0.3}H_2Ti_4O_9 \cdot 0.4H_2O$

As can be observed in Table 2, the activation energy related with lattice water molecules increases significantly with relation to the original matrix. However, these values are larger for matrices  $C_2$  and  $C_4$ , that is, the matrices with smaller amounts of amines. Thus, this behavior suggests a stronger interaction with OH groups. Consequently, the amine release occurs with a large disorganization in the layer, making the condensation of OH groups of the lamellar matrix difficult leading to the formation of titanium oxide.

## Conclusions

The obtained results showed that the thermoanalytical techniques are of great importance to understand the chemical behavior of lamellar solid matrices. The kinetics that better model was adjusted to the experimental data, using the method isothermal, was diffusion mechanism within the range  $0.15 \leq \alpha \leq 0.9$ . The values of the energy of activation are larger for matrices  $C_2$  and  $C_4$ , that is, the matrices with smaller amounts of amines.

The authors thank CNPq for fellowships and financial supports.

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