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KINETICS OF SOLID STATE REACTIONS Co^{2+}, Cu^{2+} AND Zn^{2+} BASIC CARBONATES WITH SOME ALIPHATIC ACIDS

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Abstract

The kinetic description and mechanism of the solid-state reactions between metal basic carbonate (M=Co^{2+}, Cu^{2+} and Zn^{2+}) and aliphatic carboxylic acids (oxalic, tartaric, succinic and citric acids) were studied using non-isothermal analysis (TG, DTA) and capillary techniques. The reactions were found to proceed in all cases (except citric acid) by one mole of metal carbonate and two moles of metal carbonate and two moles of organic acid. The kinetic analyses of non-isothermal data were best described by each of the dimensional phase boundary R_2 and two-dimensional diffusion controlled reactions D_2. While the capillary technique showed that the initial reaction occurs at the phase boundary of the reactants and kinetically of the reacting controlled by diffusion mechanism in which the diffusion species through the product layers are the organic acids.

Keywords: composition effect, kinetic of solid, organic acid diffusion

Introduction

The theories of the rate processes of heterogeneous reaction have been the subject of various studies. There is a considerable diversity of mechanisms by which solids react and there are several factors, which may control, determine, influence or modify the rate limiting process [1]. The chemical transformations of solid organic compounds play an important role in explaining the rate of solid-state reactions and the change occurring in physical properties of organic compounds in terms of chemical process and crystal structure.

In the present study, we used the isothermal data obtained from TG, DTA (thermal analysis) and capillary techniques for investigating the kinetics of solid-state reactions between basic metal carbonates (Co^{2+}, Cu^{2+} and Zn^{2+}) and organic acids (oxalic, tartaric, succinic, and citric acids) using TG, DTA, thermal analysis and capil-

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lary techniques. It allows us to study the effect of varying each of chemical composition and crystal structure on the kinetics of the reaction.

Experimental

Materials and methods

Basic cobalt, copper and zinc carbonates supplied by BDH Chemical Ltd. Company, as well as oxalic, tartaric, succinic and citric acids of analytical grade were used in this work.

The products of the investigated reactions were first synthesized in a solution state. This is done by the drop-wise addition of alcoholic solution of organic acid to a suspended solution of the metal carbonate with well stirring till the end of the reaction (no more effervescence was observed). The resultant solution was concentrated and allowed to stand in ice bath for one hour. The precipitated salt was filtered off, dried in air and analysed.

To investigate the stoichiometric ratio of the reactions, the products were also synthesized in the solid state by mixing metal carbonates with the organic acids in a molar ratio similar to that obtained in solution state. The mixtures were finely divided in agate mortar, and then kept in a thermostat (below the eutectic and melting points of organic acid) for 24 h.

Kinetic studies

Capillary technique

Kinetics of solid-state reactions in capillary tubes were studied by the technique developed by Rastogi *et al*. [2]. Pyrex glass capillaries were used for this purpose. One end of the capillary was sealed and half of it was filled with organic acid (particle size 100 mesh cm^{-2}) with the help of a glass rod. The remaining half of the tube was filled with basic carbonate of the same particle size. After that, the other end of the capillary was sealed. The capillary tube was then kept in a thermostat at temperatures of 353, 363 and 373 K. The fluctuation in the temperature was not more than ±1.0 K. The reaction between the solid materials was indicated by observing the change in the colour at the interface of the reactants. The rate of the reaction was followed by measuring the thickness of the coloured product layer as a function of time with the help of a travelling microscope. The coloured products were separated manually by breaking the reaction tube and the amounts of metal content were analyzed volumetrically by titration using EDTA solution [3].

Elemental analysis (C and H) for the samples prepared in both solution and solid-state phases was carried out using Carlo Erba (Model 11.06) instrument.

Thermal analysis technique

The kinetics of the thermal reaction for the mixed solids were investigated using DTA and non-isothermal TG techniques by using thermal analyser (Shimadzu, model DT-30). Experiments were carried out in air atmosphere at a constant heating rate of 10 K min^{-1} and using α-Al_2O_3 as a reference material. DTA and TG curves were recorded in the temperature range between room temperature and the decomposition temperature of the investigated acids. Thermal changes of the solid reaction based on the mass loss obtained during the course of the reaction are used for calculating the kinetic parameters.

Infrared spectra

IR spectra for the samples obtained in each of solution and solid phases were scanned using Beckman Infrared 4220 double beam spectrophotometer and KBr disc technique.

Magnetic measurements

The molar magnetic susceptibility χ_m of the products formed in both solution and solid phase was determined at room temperature using Gouy's method [4].

Results and discussion

The elemental analysis results for the samples obtained in liquid and solid phases, Table 1, show that the reaction proceeds by one mole of basic metal carbonates and two moles of organic acids (except in case of citric acid). The ratio between the different carbonates and the citric acid was found to be 1:1, 1.5:1 and 1.5:1 for Cu^{2+}-, Co^{2+}- and Zn^{2+}-carbonate, respectively, Table 1. This may be attributed to that the citric acid contains one carboxylic group more than that of other acids. The χ_m-values obtained in each of liquid and solid phases are almost equal, Table 1. This supports our results that the products formed in both phases are identical. The IR spectra of the products obtained from the reactions in both liquid and solid phases were found to be identical where strong absorption bands at 1630–1550 and 1410–1380 cm^{-1} due to asymmetric and symmetric carboxylate stretching vibrations, respectively were observed indicating the formation of metal–carboxylate bonds [5]. New bands appearing in the spectra of the products in range 600–300 cm^{-1} are taken as a good assignment for the metal–oxygen bond vibrations.

The reaction between the basic metal carbonate and the organic acid in solid phase occurs in manner in which the organic acid surface is tending to react with the carbonate anion to form carbonic acid followed by the immersion of metal cation into the carboxylate anion to form complex or salt of acid. So by thermal analysis techniques it is possible to follow the degree of conversion (α) in the reaction by means of TG and DTA measurements [6]. Hence by using several established mathematical reaction models [7], the mechanism and the kinetic parameters of the reaction can be

Table 1 Analytical data for the products of the reactions in solid and liquid phases

Reactants	C/%	H/%	Metal/%	*$\chi_M \cdot 10^{-3}$	Products
$CoCO_3 \cdot Co(OH)_2$+oxalic acid	13.21 (13.11)	2.16 (2.18)	32.43 (32.24)	4.0 (4.1)	$CoC_2O_4 \cdot 2H_2O$
$CuCO_3 \cdot Cu(OH)_2$+oxalic acid	14.99 (14.95)	–	39.82 (39.56)	8.3 (8.0)	$CuC_2O_4 \cdot 1/2H_2O$
$ZnCO_3 \cdot Zn(OH)_2$+oxalic acid	13.43 (13.31)	1.96 (1.66)	36.21 (36.24)	2.1 (1.9)	$ZnC_2O_4 \cdot 2H_2O$
$CoCO_3 \cdot Co(OH)_2$+tartaric acid	23.18 (23.19)	1.82 (1.93)	28.05 (28.50)	2.0 (1.9)	$CoC_4H_4O_6$
$CuCO_3 \cdot Cu(OH)_2$+tartaric acid	18.34 (18.08)	3.81 (3.77)	23.32 (23.92)	0.9 (0.8)	$CuC_4H_4O_6 \cdot 3H_2O$
$ZnCO_3 \cdot Zn(OH)_2$+tartaric acid	21.37 (20.57)	2.46 (2.59)	28.54 (28.25)	0.9 (0.9)	$ZnC_4H_4O_6 \cdot H_2O$
$CoCO_3 \cdot Co(OH)_2$+succinic acid	27.36 (27.43)	2.34 (2.29)	33.92 (33.71)	2.0 (1.7)	$CoC_4H_4O_4$
$CuCO_3 \cdot Cu(OH)_2$+succinic acid	26.33 (26.74)	2.17 (2.23)	35.06 (35.38)	1.4 (1.1)	$CuC_4H_4O_4$
$ZnCO_3 \cdot Zn(OH)_2$+succinic acid	26.12 (26.47)	2.16 (2.21)	35.74 (36.04)	2.8 (3.0)	$ZnC_4H_4O_4$
$CoCO_3 \cdot Co(OH)_2$+citric acid	24.45 (25.96)	1.76 (1.80)	29.94 (31.87)	4.0 (4.4)	$Co_3(C_6H_7O_8)_2$
$CuCO_3 \cdot Cu(OH)_2$+citric acid	20.42 (20.51)	2.20 (2.28)	32.81 (36.18)	3.4 (3.0)	$Cu_2C_6H_8O_9$
$ZnCO_3 \cdot Zn(OH)_2$+citric acid	26.11 (25.08)	2.87 (2.74)	33.99 (34.16)	5.9 (6.1)	$Zn_3(C_6H_8O_8)_2$

* – χM is the molar magnetic susceptibility; Results of liquid phases are in pharentheses

deduced (α, T, and t) from the data obtained from DTA and TG curves. This was done using different kinetic models, Table 2, and by applying the regression analysis method to get the best fit for the experimental results.

Table 2 Kinetic model equations used in this work [7]

Reaction model	Symbol	$g(\alpha)$	$f(\alpha)$
Two-dimensional phase boundary	R_2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
Three-dimensional phase boundary	R_3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
One-dimensional diffusion	D_1	α^2	$1/2\alpha$
Two-dimensional diffusion	D_2	$(\alpha+(1-\alpha)\ln(1-\alpha)$	$-l/\ln(1-\alpha)$
Three-dimensional diffusion	D_3	$[1-(1-\alpha)^{1/3}]^2$	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}$
Four-dimensional diffusion	D_4	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	$3/2[(1-\alpha)^{-1/3}-1]$
Random nucleation	A_2	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
Random nucleation	A_3	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
Random nucleation	A_4	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
First order kinetics	F_1	$-\ln(1-\alpha)$	$(1-\alpha)$
Second order kinetics	F_2	$1/(1-\alpha)$	$(1-\alpha)^2$
Third order kinetics	F_3	$[1/(1-\alpha)]^2$	$(1-\alpha)^3$
Prout–Tompkins	B_1	$\ln[\alpha/(1-\alpha)]$	$\alpha(1-\alpha)$
Exponential law	E_1	$\ln\alpha$	α

The kinetics were studied from the non-isothermal data using a single heating rate. Three kinetic analysis methods were done here. Integral method is only applied on data obtained from TG curves [8] while the differential method is applied on those obtained from both TG and DTA curves [9]. The results obtained from the use of the three kinetic analysis methods can differentiate between reaction mechanisms more practically than those found by applying only one method.

The results of the different kinetic models showed that these reactions are best described by either two-dimensional phase boundary controlled reaction mechanism R_2 or by two-dimensional diffusion function D_2. The kinetic data for the R_2-mechanism are summarized in Table 3. It is noteworthy that the accuracy of kinetic results obtained is variable, depending on the composition of reactants and the calculation methods used. For the most reactions investigated it was noticed that the correlation coefficient values obtained using differential method are more closer to unity than those obtained by means of the integral method [10]. Generally, it was found that the reaction mechanism is not varied with changing the chemical composition of the investigated reactant.

The reaction investigated can be considered as an acid-base reaction type. The difference in reactivity and kinetic parameters may be due to the difference in the proton transfer capabilities of the organic acids to react with the carbonate anion when the reactants are present in contact with each other. Inspection of the whole kinetic

Table 3 Kinetic parameters for solid–solid reactions between organic acids and basic carbonates investigated using R_2-model by applying differential and integral methods on TG as well as DDTA method

Kinetic method	Organic acid	Cobalt carbonate			Copper carbonate			Zinc carbonate		
		E_a/ kJ mol^{-1}	A/s^{-1}	r	E_a/ kJ mol^{-1}	A/s^{-1}	r	E_a/ kJ mol^{-1}	A/s^{-1}	r
TG-differential method	oxalic	44.4	$10^{1.1}$	0.9990	36.1	$10^{1.4}$	0.9994	51.5	$10^{1.0}$	0.9997
	tartaric	50.3	$10^{1.2}$	0.9993	41.2	$10^{1.5}$	0.9989	59.2	$10^{1.0}$	0.9996
	succinic	19.0	$10^{3.5}$	0.9991	9.8	$10^{3.8}$	0.9994	28.1	$10^{3.3}$	0.9994
	citric	56.0	$10^{0.8}$	0.9989	49.2	$10^{0.9}$	0.9989	59.6	$10^{0.8}$	0.9993
TG-integral method	oxalic	48.8	$10^{1.7}$	0.9986	44.1	$10^{1.8}$	0.9990	51.9	$10^{1.6}$	0.9991
	tartaric	49.9	$10^{1.4}$	0.9990	45.5	$10^{1.5}$	0.9987	59.2	$10^{1.2}$	0.9990
	succinic	24.2	$10^{3.3}$	0.9990	18.5	$10^{3.4}$	0.9991	38.5	$10^{3.1}$	0.9990
	citric	67.3	$10^{0.6}$	0.9989	58.0	$10^{0.9}$	0.9982	68.2	$10^{0.6}$	0.9990
DDTA method	oxalic	46.0	$10^{1.9}$	–	38.8	$10^{1.6}$	–	53.5	$10^{1.9}$	–
	tartaric	48.0	$10^{1.5}$	–	46.2	$10^{1.8}$	–	50.5	$10^{1.5}$	–
	succinic	23.1	$10^{3.6}$	–	12.1	$10^{3.7}$	–	31.2	$10^{3.4}$	–
	citric	62.4	$10^{0.6}$	–	52.0	$10^{0.8}$	–	65.1	$10^{0.7}$	–

data present knows that there is no correlation between the activation energy (E_a) and pK_a of the organic acid. This may be due to the differences in the nature and the crystal structure for each of the organic acids and the basic carbonates.

On the basis of E_a values, Table 3, the reactivity order for the organic acids towards the carbonates investigated was found to increase in the order:

Succinic>oxalic>tartaric>citric

The reactions investigated may be considered as anion exchange reaction in which the weakly acidic groups are anion exchange reactions where the weakly acidic groups (carbonate and hydroxyl) on M^{2+} are replaced by more favourable carboxylate anion. These reactions occur by proton transfer from the organic acid, which combines with carbonate and hydroxyl ions to liberate carbon dioxide and water as gaseous products. The reactivity of metal carbonates increases with decreasing

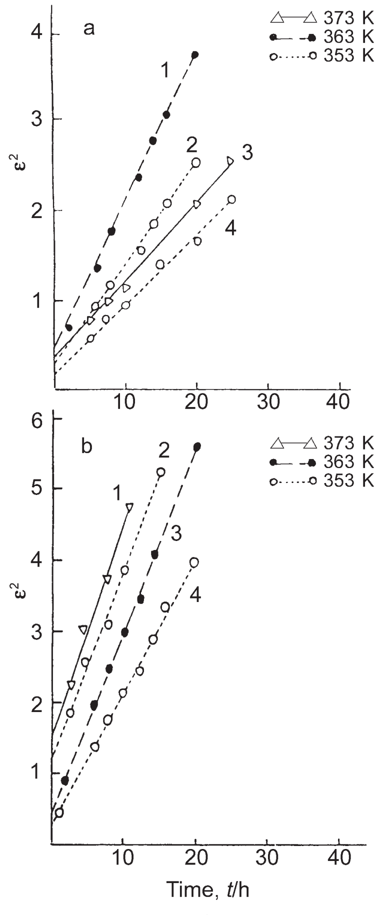

Fig. 1 Relation between square of thickness ε^2 *vs*. time (t) for the reactions between each of a – $CoCO_3 \cdot Co(OH)_2$ and (1, 2) – oxalic and (3, 4) – succinic acids; b – $CuCO_3 \cdot Cu(OH)_2$ and (1, 2) – succinic and (3, 4) – oxalic acids

the ionic radius of cations indicating that the diffusion of the cations may participate in increasing the order of the reactivity of the reaction. So the rate of the reaction may be controlled by the phase boundary and two-dimensional diffusion mechanism. The activation energy values (E_a) for the formation of the carboxylate are significantly lower than the heats of sublimation of the organic acids [11]. This can eliminate the significance contribution of vapour phase produced from the reactions (H_2O and CO_2).

The kinetics of the investigated solid reactions have been also determined by the capillary technique at 353, 363, 373 K under isothermal conditions. The thickness of the coloured product layer was measured as a function of time. The data obtained were compared with the various solid-state reaction models [12]. The kinetic data were found to be best described by the parabolic equation:

$$\varepsilon^2 = kt + c \qquad (1)$$

where c and k are constants.

Typical plots of ε^2 *vs*. t are given in Fig. 1. The parabolic nature of Eq. (1) indicates that the rate of the reactions investigated is controlled by diffusion mechanism reaction. The direction of the movement of coloured boundary formed at the surface of reactions indicates that the diffusing species through the product layer is the organic acid. The metal basic carbonates have a polymeric network in their crystals [13] and the binding forces are very strong covalent bonds through the crystals [1]. The diffusion of carbonates will thus require the breaking of many covalent bonds, whereas the organic acids investigated are held together by weak inter- or intramolecular hydrogen bonds and their diffusion requires very small amount of energy which is available at the temperatures at which these reactions have been studied.

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