Cairo University

THE USE OF DIFFERENT METHODS OF ANALYSIS IN STUDYING THE KINETICS OF DECOMPOSITION OF SOME SALTS OF USE IN THE CERAMIC INDUSTRY

By

Rahman Hussein Thabet Morsy

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
in
CHEMICAL ENGINEERING

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
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Under The Supervision of

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FACULTY OF ENGINEERING, CAIRO UNIVERSITY
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Title of Thesis:

The use of different methods of analysis in studying the kinetics of decomposition of some salts of use in the ceramic industry

Key Words:
Methods of Analysis; Decomposition; Kinetics; Ceramic industry.

Summary:
This thesis studies the different methods of analysis used in determining the kinetics and mechanisms of three different salts of use in the ceramic industry. Non-isothermal analysis was carried out for sodium borates (borax), basic zinc carbonate and basic cobalt carbonate. Four different methods of analysis has been performed to determine the reaction mechanism and calculating the values of activation energy. The results showed that Coats-Redfern method gives more reliability results and it was possible to determine the controlling mechanism as well. Otherwise Flynn-Wall-Ozawa method gives the values of activation energy higher than the figures obtained by other methods. The values obtained by Kissinger and linear regression methods are closed to that obtained by Coats-Redfern method. The reaction mechanisms have ranged from chemical reaction controlled mechanism, diffusion controlled mechanism and Erofeev model with formation of nuclei followed by grain growth.

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LIST OF SYMBOLS

Symbols	Variable	Unit
A	Frequency factor	min^{-1}
E	Apperant activation energy	$J.mol^{-1}$
h	Plank's constant	$6.626\times10^{-34}\ m^2.kg.s^{-1}$
K	Reaction rate constant	$(mol/m^3)^{1-n}.min^{-1}$
K_B	Boltzman constant	$1.38x10^{-23}\ m^2.kg.s^{-2}.K^{-1}$
n	Order of reaction	Dimensionless
P	Shap factor	Dimensionless
R	Universal gas constant	$8.314\ J.mol^{-1}.K^{-1}$
r_c	Radius of unreacted core	m
T	Absolute Temperature	K
T_0	Initial temperature	K
t	Time	min
W	Weight	mg
Z	Number of collision	$Collision.min^{-1}$
α	Conversion	Dimensionless
β	Heating rate	$^oC.min^{-1}$
τ	Time for complete conversion	min
ΔG^+	Gibbs free energy	$J.mol^{-1}$
ΔH^+	Enthalpy of activation	$J.mol^{-1}$
ΔS^+	Entropy of activation	$J.mol^{-1}.K^{-1}$

LIST OF ABBREVIATIONS

TG	**Thermogravimetry**
F.W.O	**Flynn-Wall-Osawa**
C-R	**Coates-Redfern**
TGA	**Thermogravimetric analysis**
DTG	**Derivative Thermogravimetry**
DTA	**Differential thermal analyzer**

Abstract

Study of decomposition of salts is an important point of research when dealing with salts that have high temperature applications. A study of decomposition of some salts used in the ceramic industry was undertaken to further understand and quantitatively model this process; the effect of key processing parameters (including heating rate, temperature and time) on the decomposition process were examined. This thesis deals with the kinetics of non-isothermal analysis of borax (sodium borate), basic zinc carbonate and basic cobalt carbonate. Non-isothermal analysis was carried out on these four salts using a thermal analysis unit. The heating rate was varied (2,5,10 and 15^{o}C/min). Every salt was heated in air from ambient temperature up to above its decomposition temperature. Kinetic calculations for non-isothermal runs were carried out and the values of activation energies calculated at different conversions using the Flynn-Wall-Ozawa and Kissinger methods. The average value of activation energy was calculated for borax, basic zinc carbonate and basic cobalt carbonate. Results were confirmed by applying the Coates-Redfern and Multi-linear regressions methods that helped disclosing the reaction mechanism.

Chapter 1 : Introduction

Salts firing and salt glazing have been common practice in ceramic industry for centuries. Borax or sodium borates is an important boron compound, it's a salt of boric acid. It has wide variety of uses; it is a component of many detergents, cosmetics, enamel and glazes. It is also a component of glass, pottery and ceramics; which is used as an additive in ceramic slips and glazes to improve fit on wet, greenware and bisque.

Basic zinc carbonate is a material with a variety of applications, one of the most important applications is its use as a precursor for the production of zinc oxide by thermal decomposition process. Zinc oxide has numerous uses in the industry such as in electronics, solar cells and as an industrial catalyst. For material science applications, zinc oxide has high refractive index, high thermal conductivity binding, and antibacterial properties. Consequently, it is added into materials and products including plastics, ceramics, glass, cement, rubber, lubricants, pigments, adhesive, foods, and concert manufacturing etc.

In general cobalt compounds like, cobalt oxide is used as pigment in glass and ceramics, it provide blue coloring in porcelain and glass, also used as drying agent for paints, vanishes and inks.

Basic cobalt carbonate also has coloring application as it decomposes to cobalt oxide at high temperature. It tends to disperse better in glaze but can produce blisters because of the CO_2 gas evolution at high temperature.

Metallurgical transformation and reactions are mostly heterogeneous in nature. They involve more than one phase and are often characterized by the presence of distinct phase boundaries. In any given system, the rate of reaction at a given time depends basically on three factors, namely, the nature of the system, the time of reaction and the temperature. The reaction rate is usually determined as the rate of change of conversion. Reproducible kinetic results require assessing the mechanism of the reaction besides taking into consideration the effect of several parameters, such as purity of the material, its particle size, ambient atmosphere, etc…

When the reaction is associated with weight changes it is customary to study its kinetics using TGA to obtain values of activation energy. This is simply a record of the change in weight against temperature at constant heating rate.

There are numerous methods that can be used to this aim using TGA. Some of them can disclose the reaction mechanism besides calculating the value of activation energy. The most commonly applied method in this respect is the Coats – Redfern method and the main advantage of this method is that it needs only one TG run to disclose the reaction mechanism as well as calculating the activation energy. Another commonly used method that doesn't depend on the reaction mechanism is the Flynn – Wall – Ozawa (FWO) method, this method relies on performing at least four TG runs at different heating rates and to determine the temperatures at constant values of conversion. It has the advantage that it gives a value of activation energy that does not depend on knowing the reaction mechanism. There is another method to determine activation energy by using DTG curves; the DTG curve represents a relation between