

## The Kinetics of Thermal Decomposition of Nickel Formate Dihydrate in Air

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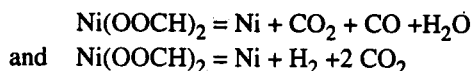
**ABSTRACT.** Differential thermal analysis-thermogravimetry (DTA-TG), and electron scanning microscopy (ESM) were used to study the decomposition of nickel formate dihydrate in air. The results showed that the decomposition proceeds in two successive TG steps, the first is due to dehydration and the second is due to decomposition of the anhydrous salt and oxidation to form NiO. Kinetic analysis of the isothermal TG data of the two steps in view of various heterogeneous solid-state reaction models showed that the dehydration step is best described by phase boundary models whereas the second step reactions are best described by the branching nucleation model. The changes in morphology that accompany the thermal decomposition of samples as revealed by ESM micrographs, were described and the kinetics and mechanism of the thermal decomposition reaction were discussed.

### Introduction

The chemical transformations of solids play an increasingly important role in modern technology, as sophisticated and costly solids can be produced by reaction of other, precursing solids<sup>[1]</sup>. The kinetics and mechanism of thermal dehydration and decomposition reactions of simple salts have attracted the interest of several investigators<sup>[2]</sup>. In calculating the kinetic parameters from the experimental data for a particular reaction, a comparison of the fractional reaction ( $\alpha$ ) -time curves with theoretical expressions derived for appropriate nucleation and growth models, has been widely used as evidence for the identification of the geometry of interface advance. There are a variety of factors which may control, determine, influence or modify the rate limiting processes<sup>[1,2]</sup>. In general, isothermal kinetic measurements are more reliable than non-isothermal data<sup>[3]</sup>, since the latter are subject to possible inaccuracies due to the influence of sample size and shape on heat flow.

The decomposition of nickel formate has been the subject of numerous kinetic

studies<sup>[4]</sup>. In N<sub>2</sub>-atmosphere, the decomposition is to the metal and this occurs by two concurrent routes<sup>[5]</sup>:



The Ni metal is produced with a high surface area and is immediately oxidized in air with violent exothermic reaction to form NiO. However, the decomposition to Ni powder in hardened oil flakes provides an unusual inert environment for the preparation of Ni catalyst<sup>[5]</sup>.

In the present study, the thermal dehydration and decomposition of Ni(OOCH)<sub>2</sub> · 2 H<sub>2</sub>O crystals were investigated using DTA-TG and ESM techniques. The changes in morphology of samples and the kinetics of the isothermal decomposition reactions analyzed in view of various heterogeneous solid state reaction models, were discussed.

### Experimental

Nickel formate dihydrate BDH grade, was used in this study without further purification. DTA-TG curves were determined using a Shimadzu DT 30 thermal analyzer. Samples weighing about 9 mg were placed in aluminum crucibles 0.1 cm<sup>3</sup> in volume, which was loosely covered. The samples were heated at a temperature rate of 20°C min<sup>-1</sup> under a pressure of 1.0 atm in air at a flow rate of 3.0 L h<sup>-1</sup>.

TG kinetic experiments were performed under isothermal conditions in air in an oven thermostated at different temperatures. Samples (weighing accurately about 100 mg) in small test tubes, were placed in the oven, then removed from the oven at different time intervals, cooled to room temperature in a dessicator, weighed and the weight loss was calculated. From the weight loss, the fractional reaction ( $\alpha$ ) was calculated.

Scanning electron microscopy micrographs were obtained for samples formed during the thermal decomposition using a JEOL T-300 scanning electron microscope.

### Results and Discussion

Fig. 1 shows the DTA-TG curves for the thermal decomposition of nickel formate dihydrate in air. The DTA curve shows one endo form peak at about 180°C due to dehydration and an exo peak at about 240°C due to decomposition and oxidation of the anhydrous salt to form NiO. The TG curve shows two steps which correspond closely to the endo and exo effects observed in the DTA curve. The first step shows a weight loss of about 20% (theoretical value = 19.2%) corresponding to the dehydration step. The second step shows a weight loss of about 47% (theoretical value = 49.5%), corresponding to the decomposition of the anhydrous salt to Ni powder and oxidation of Ni to NiO.

Samples of the salt hydrate, the dehydrated salt and the nickel oxide formed at the end of the thermal decomposition reactions were examined by scanning electron microscopy. ESM micrographs of these samples are shown in Fig. 2. The original sample consists of small crystallites (Fig. 2a), most of them have particle size diameter less than

10mm. Dehydration leads to rounding of crystal edges and faces due to release of water of hydration (Fig. 2b). The SEM photograph of nickel oxide formed by heating Ni  $(\text{OOCH})_2 \cdot 2 \text{H}_2\text{O}$  in air for 1hr at about  $280^\circ\text{C}$  (Fig. 2c), shows aggregates of small cubes of blackish NiO and the particle size is reduced to less than one-half in comparison to the original crystals. The decrease in particle size increases significantly the surface area of the final product.

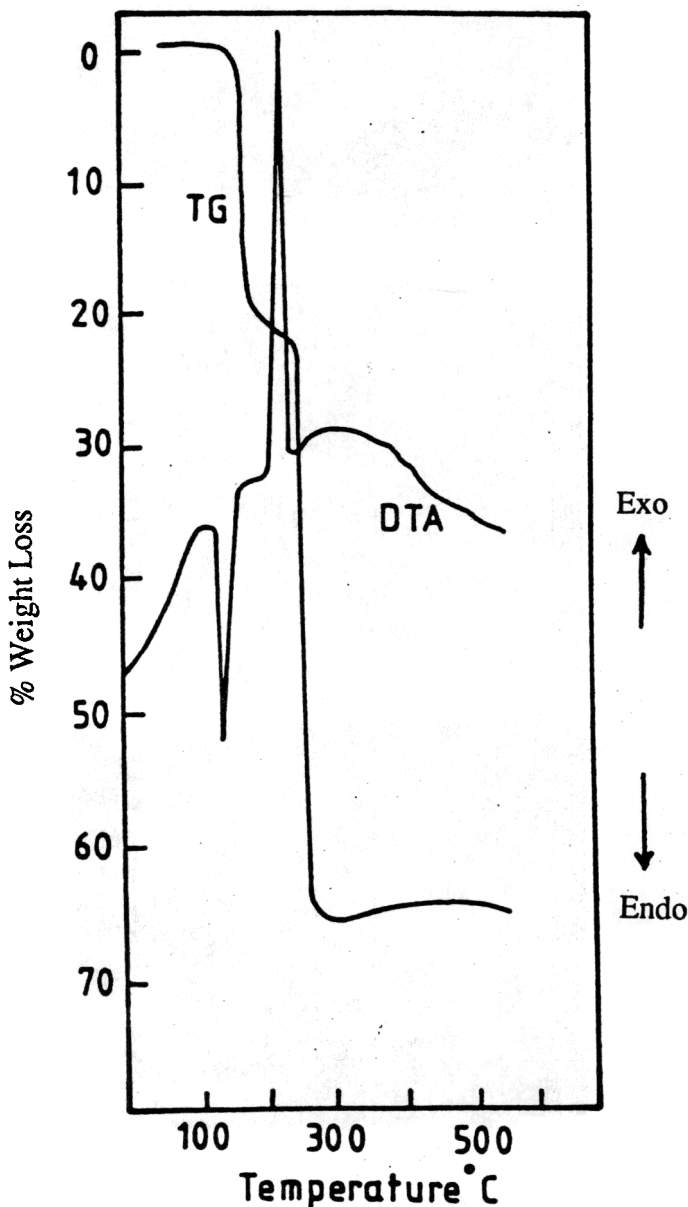


FIG. DTA-TG curves of nickel formate dihydrate in air.

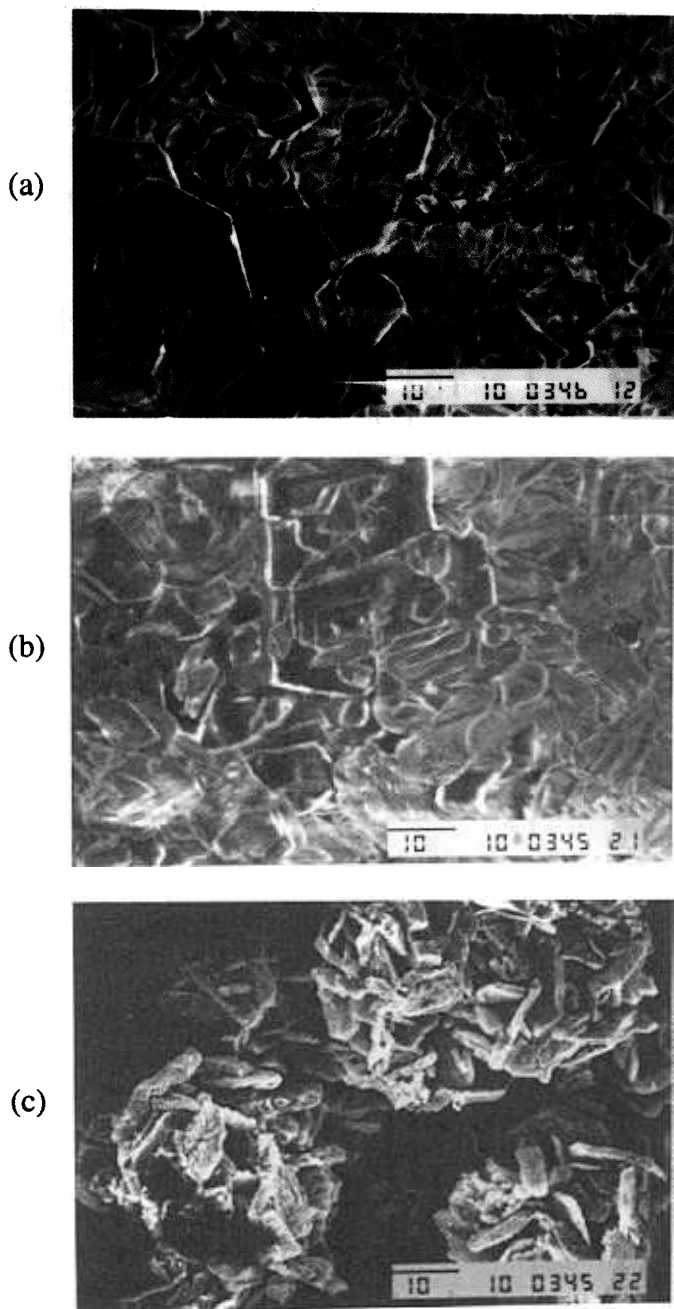


FIG. 2. ESM microscope of (a)  $\text{Ni}(\text{OOCH})_2 \cdot 2 \text{H}_2\text{O}$ ; (b) Anhydrous nickel formate,  $\text{Ni}(\text{OOCH})_2$ ; (c) Calcined nickel formate. at  $280^\circ\text{C}$  for 1 hr in air  $\times 1500$ .

Figure 3 and Fig. 4 show the isothermal fractional ( $\alpha$ )-time data obtained for the dehydration of the salt hydrate and for the decomposition and oxidation of the anhydrous salt, respectively. Kinetic analysis of the isothermal data were performed in view of various solid state kinetic equation models<sup>[6-8]</sup>, using a computer program. Under isothermal conditions the  $\alpha$ -t curves are expressed in the form  $g(\alpha) = kt$ , where  $k$  is the rate constant and the function  $g(\alpha)$  depends on the mechanism controlling the reaction and on the size and shape of the reacting particles. Table 1 list the  $g(\alpha)$  equation in this work. For the phase boundary controlled reactions, we have the contracting area or  $R_2$  model, and the contracting sphere or  $R_3$  model. For the diffusion-controlled reactions, analyses were performed with reference to a one-dimensional diffusion-controlled process in a cylinder,  $D_2$  function; Jander's equation for a diffusion-controlled reaction in a sphere,  $D_3$  function; the Ginstling-Brounshtein equation for a diffusion controlled reaction starting on the exterior of a spherical particle,  $D_4$  function; the Zhuravler-Losokhim-Tempelman diffusion equation,  $D_5$  function, and the Kroger-Ziegler diffusion equation,  $D_6$  function. If the solid-state reaction is controlled by nucleation followed by growth, then in this case, we may have the Mampel unimolecular law, where the rate-determining step is the nucleation process, described by the  $F_1$  function the Avrami equation for initial random nucleation followed by overlapping growth in two-dimensions,  $A_2$  function, the Erofeev equation for initial random nucleation followed by overlapping growth in three dimensions,  $A_3$  function, and the Prout-Tompkins equation for branching nuclei,  $A_1$  function.

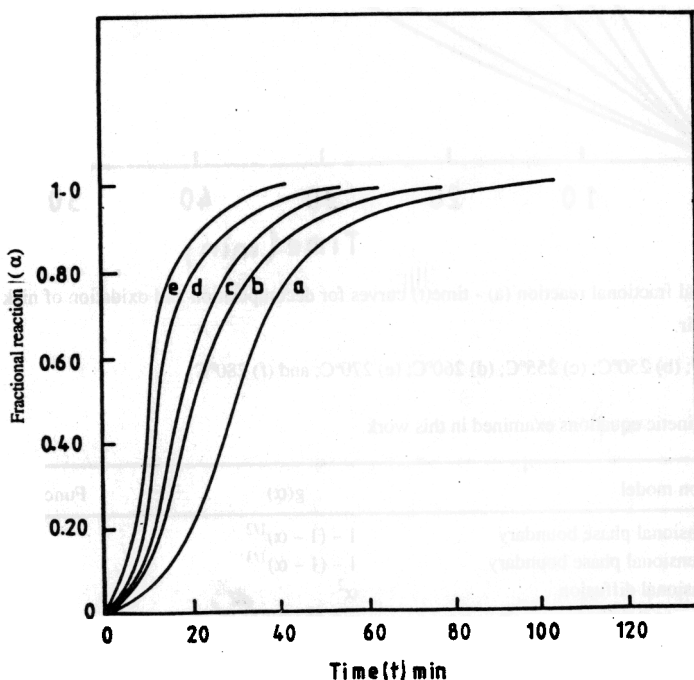


FIG. 3. Fractional reaction ( $\alpha$ ) - time( $t$ ) curve for the isothermal dehydration of Nickel Formate dihydrate in Air (a) 180; (b) 190; (c) 200; (d) 210; and (e) 220°C.

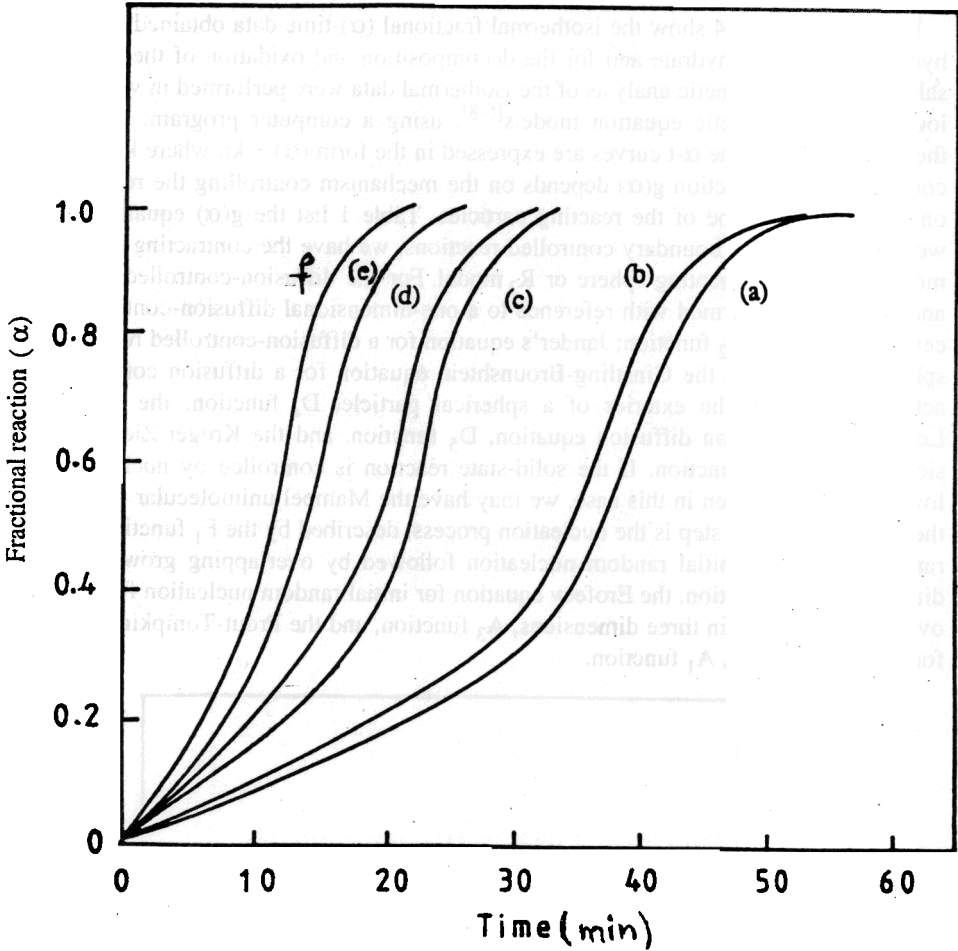


FIG. 4. Isothermal fractional reaction (a) - time(t) curves for decomposition and oxidation of nickel formate to NiO in air.

(a) 240°C; (b) 250°C; (c) 255°C; (d) 260°C; (e) 270°C; and (f) 280°C

TABLE I. Kinetic equations examined in this work.

Reaction model	$g(\alpha)$	Function symbol
Two-dimensional phase boundary	$1 - (1 - \alpha)^{1/2}$	$R_2$
Three-dimensional phase boundary	$1 - (1 - \alpha)^{1/3}$	$R_3$
One-dimensional diffusion	$\alpha^2$	$D_1$
Two-dimensional diffusion	$\alpha + (1 - \alpha) \ln(1 - \alpha)$	$D_2$
Jander's equation for		
Three-dimensional diffusion	$[1 - (1 - \alpha)^{1/3}]^2$	$D_3$
Ginstling-Brounshtein equation		
Three-dimensional diffusion	$[1 - (2\alpha/3) - (1 - \alpha)^{2/3}]$	$D_4$

TABLE I. Contd.

Reaction model	$g(\alpha)$	Function symbol
Zhuravler-Losokhim-Tempelman diffusion equation	$[(1/(1-\alpha)^{1/3}) - 1]^2$	D <sub>5</sub>
Kroger-Ziegler diffusion equation	$k \ln t = [1 - (1-\alpha)^{1/3}]^2$	D <sub>6</sub>
Mampel unimolecular law	$-\ln(1-\alpha)$	F <sub>1</sub>
Prout-Tompkins equation	$\ln[\alpha/(1-\alpha)]$	A <sub>1</sub>
Avrami	$[-(1-\alpha)]^{1/2}$	A <sub>2</sub>
Erofeev equation	$[-(1-\alpha)]^{1/3}$	A <sub>3</sub>

The computer output of the kinetic data analysis showed that the best models which describe the dehydration reaction are the phase boundary controlled reaction models. Calculation of the activation energy according to the R<sub>2</sub> - and R<sub>3</sub> - models gave a value of 34.5kJ mol<sup>-1</sup>. This value is relatively small and possibly indicates the influence of the catalytic action of trace amounts of Ni and NiO powders formed at a slow rate during the dehydration reaction. Since dehydration occurs at a measurable rate at temperatures about 200°C, the possibility that the lost water molecules are lattice water, rather than coordinated water, must be eliminated<sup>[7]</sup>. The regression analysis of kinetic data for the decomposition and oxidation of nickel formate in air to NiO showed that the reaction could be described by Mampel unimolecular equation where the rate-determining step is the nucleation process or by Prout-Tompkins equation where the reaction is controlled by the formation of branching nuclei. The average activation energy for this step is about 70 kJ mol<sup>-1</sup>. For decomposition of the anhydrous salt in vacuum, Brown *et al.*<sup>[3]</sup> found that the  $\alpha$ -t curves are sigmoid shaped, characteristics of solid phase nucleations and growth processes. The kinetic behaviour is significantly influenced by the disposition of crystallites of the reactant and depends on the rate of formation of Ni nuclei which is strongly inhibited by traces of water of crystallization. For decomposition in air, it is possible that since one is dealing with a sequence of chemical reactions involving exo- and endothermic steps, the resultant activation energy would be a composite value<sup>[9]</sup>, is probably controlled by a branching nucleation process since the experimental  $\alpha$ -t curves are sigmoid rather than deceleratory shaped.

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## كينيتيكية التحلل الحراري لفورمات النيكل المائية في الهواء

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المستخلص . تم في هذا البحث استخدام طرق التحليل الحراري التفاضلي والتحليل الحراري الوزني والمسح الإلكتروني المجهرى لدراسة تحلل فورمات النيكل المائية في الهواء . أظهرت النتائج بأن التحلل في التحليل الحراري الوزني يتم على خطوتين متتاليتين ، الخطوة الأولى تتضمن إزالة الماء والخطوة الثانية تتضمن تحلل الملح اللامائي والأكسدة لتكوين NiO . أظهر التحليل الكيتيكي لبيانات التحلل الحراري الوزني الأيزوثيرمي للخطوتين في ضوء النماذج المختلفة للحالة الصلبة غير المتجانسة بأن خطوة إزالة الماء يمكن وصفها بنموذج حدود الطور بينما الخطوة الثانية يمكن وصفها بنموذج التفرع النووي . تم وصف التغيرات في البنية التي تصاحب التحلل الحراري للعينات من صور المسح الإلكتروني المجهرى كما تم مناقشة كينيتيكية وآلية تفاعل التحلل الحراري .