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Role of metal vanadate additives on the decomposition reaction kinetics of nickel tetrahydroxy carbonate as a precursor during the thermal genesis of nickel(II) oxide catalyst

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Abstract

The catalytic effect of copper and magnesium metavanadate additives on the thermal decomposition of nickel tetrahydroxy carbonate (NTHC) was studied using the TG and DTA methods. Mathematical analysis of the TG data showed that first order kinetics are applicable in all cases using the Coats–Redfern equation. Thermodynamic kinetic parameters (i.e. energy and entropy of activation and preexponential factor) are reported. Additionally, the kinetic parameters of the decomposition reaction were calculated adopting a computer oriented kinetic analysis of the $\alpha - t$ data, obtained in isothermal conditions in the temperature range 200–450°C. Comparative studies of the kinetics of the thermal decomposition of NTHC salt in isothermal and non-isothermal conditions were performed. These indicate that the overall rate of salt decomposition is controlled by the rate at which the gaseous products can diffuse away from the reaction centres. It was also concluded that the participation of oxygen in interface reactions yielded highly oxidized Ni^{3+} phases, which are necessary participants in the sequence of the anion (CO_3^{2-}) breakdown. Accordingly, advance of the interface proceeded by a "chain type" mechanism involving regeneration of the active intermediate Ni^{3+}. The effect of CuV_2O_6 additive was discussed on the basis of the redox couple $Cu^{2+} + e \rightleftharpoons Cu^{+}$, which accelerates the decomposition reaction via a charge-transfer mechanism. Mixing the salt with MgV_2O_6 resulted in a retardation effect, for which a tentative explanation has been made in terms of the ability of such an additive to occupy a grain boundary, which hinders the decomposition process. A decomposition reaction mechanism involving the participation of Ni^{3+} ions was proposed.

INTRODUCTION

Nickel tetrahydroxy carbonate, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (NTHC), is a parent of the oxidant nickel(II), which is frequently used as a catalyst for important catalytic reactions [1,2]. The structure of NTHC (the Zaratite mineral) has been established by Feitknecht [3] and Fenoglio [4]. They found that the space lattice corresponds to alternate layers of normal salt and hydroxide, and the cubic lattice has $a = 6.15$ Å. In general, the decomposition reactions of carbonates are endothermic and at least partially reversible [5]. The obtained values of activation energy for decomposition are comparable with the enthalpy of salt dissociation. Several careful studies indicate that the decomposition reactions of some carbonates commence at specific sites, identified at points of emergence of dislocations [6]. Moreover, it was concluded that not all such sites are equivalent; there is preferred nucleation at dislocations which glide in the [100] and [211] planes [6]. In addition, a preferred reaction has been ascribed [6] in the immediate vicinity of dislocation to a stereochemical disposition of reactant species, which is conducive to breakdown of the precursor to form the product, and not to elastic strain at the dislocation core.

The kinetic behaviour of the decomposition reaction may be controlled by many factors, such as particle size of the reactant, pressure of gases present and reaction rate. The unambiguous identification of the rate controlling step in a particular carbonate decomposition as either a bond rupture process at a certain interface or the diffusion of gas or heat is not always straightforward [7–9]. Kinetic and mechanistic studies have been largely concerned with several carbonates, including nickel carbonate, which has considerable technological importance [10,11]. Furthermore, it is well known that mixing the salt with different foreign additives results in some changes in the thermochemical behaviour of the salt [12–14]. These changes are due mainly to the catalytic action of these additives in accelerating or decelerating the decomposition reaction [15,16].

The aim of the present work is to study the role of metal vanadate additives in the thermal decomposition of NTHC. To accomplish this objective, the kinetics of decomposition were followed up isothermally and non-isothermally, with the intention of determining (i) the rate equation which best fits the experimental data, and (ii) whether the reaction is phase boundary or transport controlled.

EXPERIMENTAL

All the reagents used in the present study were of analytical grade (BDH Chemicals). The mixing of nickel tetrahydroxy carbonate (NTHC) with 10 wt.% copper metavanadate (CuV_2O_6) or magnesium metavanadate (MgV_2O_6), as thermally stable solid catalysts, was carried out in an agate mortar. Thirty minutes were needed to obtain a homogeneous mixture. In the case without additives the pure NTHC sample was also ground for 30 minutes.

The non-isothermal decomposition of pure nickel tetrahydroxy carbonate (NTHC) or of NTHC mixed with metal vanadate were studied using thermogravimetric analysis (TGA) to monitor the percentage decomposed versus temperature. A Shimadzu TGA-4OH automatically recording thermobalance was used. Differential thermal analysis (DTA) experiments were performed on an automatically recording Shimadzu apparatus, type

DTA 3OH, in air. α-Al_2O_3 was used as the reference solid and the rate of heating was standardized at 10°C min^{-1}. The α–t results, where α is the fraction decomposed at time t, of pure NTHC and its mixtures with the catalysts were obtained as described elsewhere [17] in the temperature range 200–450°C. A Philips X-ray diffractometer (model PW1710) was used to record d values for the residual decomposition product of the catalysts.

RESULTS AND DISCUSSION

Figure 1 curve (a) is the DTA curve of nickel tetrahydroxy carbonate (NTHC) without additives. As reported previously [17], the endothermic peak at 95°C corresponds to the elimination of physically bound and some of the chemically bound water. The second broad endothermic peak located in the temperature range 225–350°C is due to the final decomposition step to form NiO as a solid product according to eqn. (1)

$$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O \rightarrow 3NiO + CO_2 + 6H_2O \qquad (1)$$

The thermal decomposition process of pure NTHC was also followed by recording the percentage weight loss accompanying the temperature increase (TG); this is also shown in Fig. 1 curve (b). It can be observed that pure NTHC decomposes in two steps. The first step is accompanied by a 19.70% weight loss. This weight loss corresponds to a dehydration process giving an intermediate having the composition $NiCO_3 \cdot 3Ni(OH)_2$ with a theoretically calculated value of 19.14%.

Indeed, the total weight loss occurring at the end of the second stage amounts to a value of 39.75%, which agrees very well with that (40.01%) anticipated theoretically for the decomposition of NTHC to form NiO as a final product. The TG curve of the pure sample was extensively analysed. The relevant portions of the TG curve were redrawn on an expanded scale, using standard curve sets. Four different mathematical kinetic methods

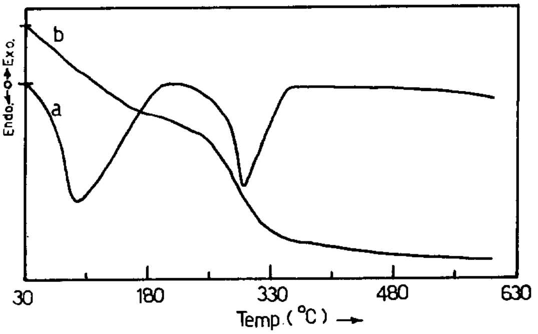


Fig. 1. DTA (curve a) and TG (curve b) curves for pure NTHC.

[18–21] were used to evaluate the kinetic data from the TG curve tracing. Our goal in this type of non-isothermal analysis is to estimate the reaction order. This can be easily achieved by observing the best straight line fitting the data with the exact solution for each method. For our analysis of the data on the thermal decomposition of pure NTHC, it was found that the appropriate equation which fits the data is in general a typical integral method which firstly can be formulated as

$$\int_0^{\infty} \mathrm{d}\alpha(1-\alpha)^n = A/\phi \int_0^T \exp(-E_a/RT)\, \mathrm{d}t \tag{2}$$

where α = reaction fraction decomposed; ϕ = heating rate; T = absolute temperature at time t; n = order of reaction; R = gas constant in cal and E_a = activation energy in J mol^{-1}.

Generally, the term $\mathrm{d}\alpha(1-\alpha)^n$ has two different solutions, namely

$$1-(1-\alpha)^{1-n}/1-n \text{ for } n \neq 1 \tag{3}$$

and

$$-\log(1-\alpha) \quad \text{for } n=1 \tag{4}$$

The right hand side in eqn. (2) has the solution

$$\frac{ART^2}{\phi E_a}\left(\frac{1-2RT}{E_a}\right)\exp(-E_a/RT) \tag{5}$$

and after taking logarithms we obtain

$$\log\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right) = \log\left(\frac{AR}{\phi E_a}\frac{(1-2RT)}{E_a}\right) - \frac{E_a}{2.303RT} \tag{6}$$

for $n \neq 1$ and

$$\log\left(\frac{-\log(1-\alpha)}{T^2}\right) = \log\left(\frac{AR}{\phi E_a}\frac{(1-2RT)}{E_a}\right) - \frac{E_a}{2.303RT} \tag{7}$$

for $n=1$. In ordinary thermal decomposition reactions, the term log $((AR/\phi E_a)(1-(2RT/E_a))$ is practically constant and plots of

$$\log\left(\frac{(1-(1-\alpha)^{1-n}}{T^2(1-n)}\right) \text{ vs. } 1/T \quad \text{for } n \neq 1$$

and

$$\log\left(\frac{-\log(1-\alpha)}{T^2}\right) \text{ vs. } 1/T \quad \text{for } n=1$$

result in a straight line with a slope of $E_a/2.303R$ for the correctly chosen

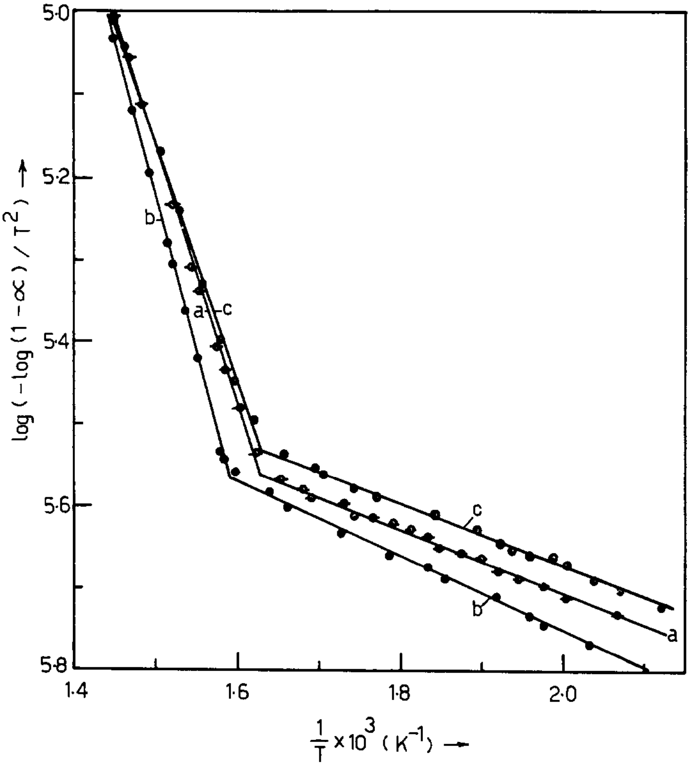


Fig. 2. Coats–Redfern plots for the non-isothermal decomposition of pure NTHC (curve a), NTHC + MgV_2O_6 (curve b) and NTHC + CuV_2O_6 (curve c).

value of n. For a first order process, Coats and Redfern [19] formulated the corresponding equation in the form

$$\log\left(\ln\frac{\frac{\omega_\alpha}{\omega_\alpha-\omega}}{T^2}\right)=\log\left(\frac{AR}{\phi E_a}\left(1-\frac{2RT}{E_a}\right)\right)-\frac{E_a}{2.303RT} \tag{8}$$

where $\omega_\alpha - \omega$ = mass loss at the completion of the reaction and ω = mass loss up to time t.

Because $1 - 2RT/E_a \approx 1$, a plot of $\log(\ln(\omega_\alpha/(\omega_\alpha - \omega))/T^2)$ against $1/T$ for pure NTHC was drawn in Fig. 2 curve (a). It provides a line broken at 350°C, indicating that more than one step is involved in this decomposition reaction. The E_a values were calculated from the corresponding slopes; A was obtained from the intercept, and the entropy of activation ΔS^* was determined from the equation [19]

$$A=\frac{KT}{h}\exp(\Delta S^*/R)$$

where K is the Boltzmann constant, h is the Planck constant and T is the

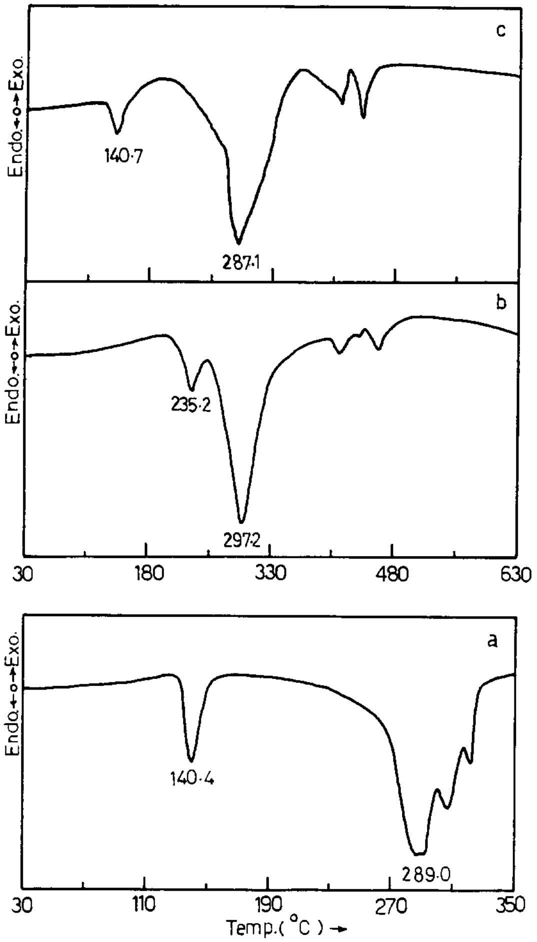
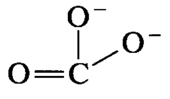


Fig. 3. DTG curves for the decomposition of pure NTHC and NTHC mixed with catalysts (symbols as in Fig. 2).

peak temperature from the DTG curve of Fig. 3(a). The obtained kinetic data for the non-isothermal kinetics are summarized in Table 1. The higher value of E_{a_2} relative to E_{a_1} reflects the tendency towards decomposition with the evolution of carbon dioxide

$$MCO_3 \rightarrow MO + CO_2 \qquad (9)$$

The ease with which this reaction proceeds increases with increasing affinity of the cation to polarize the carbonate anion, splitting it into O^{2-} and CO_2



$$O{=}C(O^-)(O^-) \longrightarrow CO_2 + O^{2-} \qquad (10)$$

TABLE 1

Kinetic parameters of activation for the non-isothermal decomposition of pure NTHC and its mixtures with MgV_2O_6 and CuV_2O_6

Sample	Activation parameter						E_a(total) (kJ mol^{-1})
	E_a (kJ mol^{-1})		A (s^{-1})		ΔS (J K^{-1} mol^{-1})		
	Stage		Stage		Stage		
	I	II	I	II	I	II	
NTHC	7.70	57.44	3.1×10^{-6}	9.5×10^{-4}	−0.97	−0.84	65.14
NTHC $+MgV_2O_6$	8.50	70.20	3.3×10^{-6}	1.2×10^{-3}	−0.97	−0.84	78.60
NTHC $+CuV_2O_6$	7.09	51.06	3.0×10^{-5}	7.9×10^{-4}	−0.92	−0.84	58.15

From the preceding, it might be supposed that covalent character [22] in predominantly ionic compounds always destabilizes the compound. This is not so; instability results from polarization [22] of the anion causing it to split into a more stable compound (oxide) with the release of gaseous acidic anhydrides. The kinetic data are unreliable where the influence on the reverse reaction of the CO_2 gas present has not been positively characterized. Since the rate of a solid phase decomposition reaction is usually assumed to be directly proportional to the area of the active interface, a comparison of the fractional reaction (α)–time curves, measured for a particular reaction, with adoption of the exact theoretical expression derived from the appropriate models [23–25], can be used as evidence for the identification of the geometry of interface advance. This technique [26] has been shown, however, to be most valuable in identifying the temperature range of stability and the decomposition intermediates.

In order to follow the decomposition of pure NTHC isothermally, its α–t curves were constructed, and are given in Fig. 4(a) for the temperature range 200–450°C.

The use of computers permits the development of more sophisticated mathematical techniques for the kinetic analysis of each set of α and t using the different kinetic equations describing such reactions [23–25]. Analysis of the results indicates that the Ginstling–Brounshtein equation (three dimensional diffusion)

$$\left(1-\tfrac{2}{3}\alpha\right)-(1-\alpha)^{2/3}=kt \qquad (11)$$

represents the best fit of the data, with a correlation coefficient very close to unity.

One can therefore conclude that the over-all rate of the pure NTHC decomposition process is controlled by the rate at which the gaseous components can diffuse away from the reaction centres [27]. Moreover, we

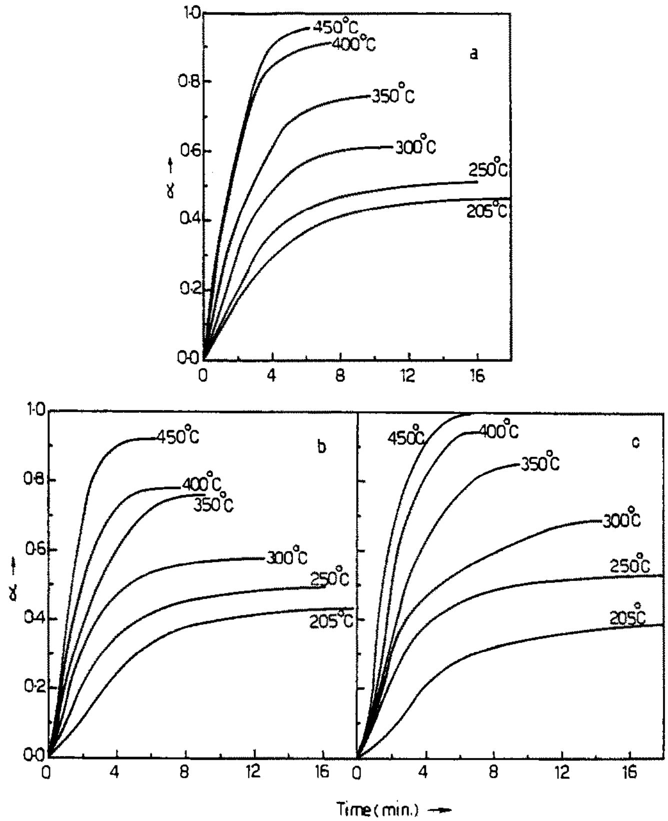


Fig. 4. α vs. t curves for the isothermal decomposition of pure NTHC and its mixtures with MgV_2O_6 and CuV_2O_6 ((a)–(c) respectively).

can decide that the structure and porosity of the solid product and its relationship with the reactant phase control the rate of escape of the volatile products by inter- and/or intragranular diffusion, so that the rapid and effectively complete withdrawal of CO_2 from the interface may be difficult to achieve experimentally. A similar feature has been described for the removal of water from crystalline hydrates, and attention has been drawn to comparable aspects of reactions of both types [28]. An application of the Arrhenius equation provides a continuous straight line, Fig. 5 curve (a), with a value of $E_a = 43.2$ kJ mol^{-1}, which is higher than the E_a value obtained from non-isothermal analysis: see Table 1.

This comparative study allows us to reconfirm the idea that the measured E_a value for such endothermic reactions may be sensitive to the presence of the reaction products [29,30] and, thus, depend on the reaction conditions. Moreover, the magnitude of E_a measured for the investigated decomposition reaction has often been ascribed to the energy barrier in the rate limiting step, which may be a bond rupture [31] or an electron transfer process.

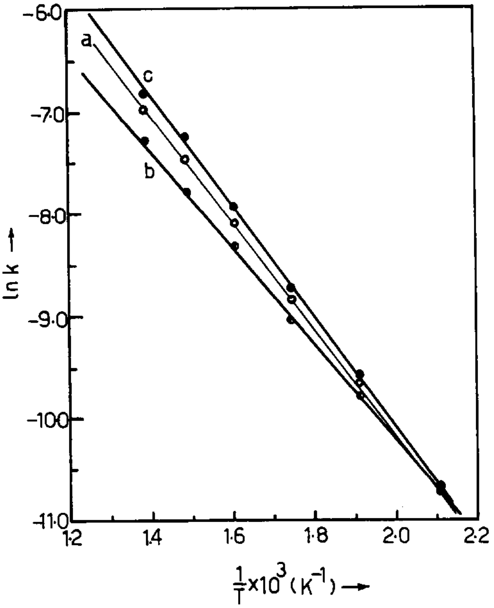


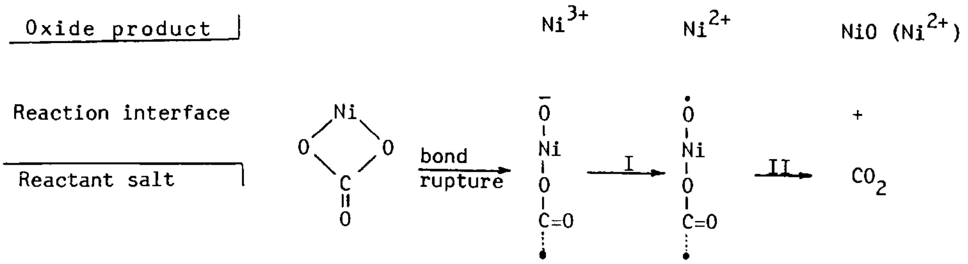
Fig. 5. Arrhenius plots for the isothermal decomposition of pure NTHC and its mixtures with the additives (symbols as in Fig. 4).

The rate of loss of mass vs. temperature (DTG) curves for pure NTHC and its mixture with either MgV_2O_6 or CuV_2O_6 are represented in Fig. 3(b) and 3(c).

Such a comparative study reveals that (i) the decomposition of NTHC is differently affected when it is mixed with the two additives, and (ii) the decomposition process proceeds via two stages, as previously concluded. Copper metavanadate (CuV_2O_6) catalyst does not alter the dehydration stage (at 140°C), but accelerates the final decomposition step. On the other hand, mixing NTHC with magnesium metavanadate (MgV_2O_6) results in a marked retardation in the dehydration stage (235°C) and a noticeable shift in the second decomposition temperature step to a higher value, i.e. from 289.8 to 297.2°C. The effects of these additives on the kinetic parameters of the two decomposition stages were calculated from analysis of the corresponding non-isothermal data of the TG curve, on the basis of the Coats–Redfern equation which best fits our data, and the results obtained are shown in Fig. 2 curves (b) and (c). The results depicted in Table 1 revealed that the mixing procedures brought significant changes in the kinetic parameters of the decomposition reaction. For example, in the decomposition process in presence of CuV_2O_6, a decrease in both the energy of activation and the frequency factor is observed, whereas in the case of magnesium metavanadate an increase in both parameters was observed. These findings give support for the accelerating effect of CuV_2O_6 and the retarding effect of MgV_2O_6 addition. Extending the thermal analysis to establish the α–t curves for NTHC mixed with the two vanadate catalysts, Fig. 4(b) and 4(c) were obtained under isothermal conditions. The application of the computer kinetic analysis in that direction for each set of α and t data in a way similar to that for pure NTHC reveals that the Ginstling–Brounshtein equation continues to be valid for describing the mechanism of the decomposition of the pure salt in the presence of vanadate additives. Using the Arrhenius equation to plot the curves of Fig. 5 curves (b) and (c), the apparent activation energies were obtained. The values are $E_a = 39.3$ and 44.6 kJ mol^{-1} for NTHC + CuV_2O_6 and NTHC + MgV_2O_6 respectively. The results are in good agreement with the observed acceleration and retardation effects of the two additives.

The catalysts used in this investigation, namely CuV_2O_6 and MgV_2O_6, have been well characterized structurally [32,33] and pre-investigated by means of a catalytic test reaction which involves an electron transfer [33]. Accordingly, it seems reasonable to assume that the effect of these additives on the thermal decomposition of NTHC is closely related to an electron transfer mechanism rather than to an abstraction of atomic oxygen during breakdown of the anion (CO_3^{2-}). Supporting evidence for this assumption emerged from scanning of the phase produced during the thermal treatment of NTHC by examining the X-ray diffraction data of the products at different reaction temperatures. Such scanning indicates that the major phase produced is NiO (2.09–2.41–1.48) [34] together with a minor phase which was characterized as being Ni_2O_3(2.80–2.02–1.77) [34]. Therefore the participation of oxygen in interface reactions yields highly oxidized residual phases (Ni^{3+}), which are necessary participants in the sequence of steps leading to CO_3^{2-} anion breakdown [35–37]. Accordingly, we conclude that interface advance proceeds by a "chain type" mechanism [36] involving regeneration of the active intermediate Ni^{3+}. This can be represented by Scheme 1.

From Scheme 1 it appears that the concentration of Ni^{3+}, which is influenced by an electron transfer mechanism analogous to chain initiation and termination, is expected to be sensitive to the availability of gases which may participate in surface and interface equilibria, and to oxygen in

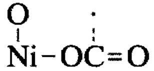


Scheme 1.

TABLE 2

Rate constants for the three dimensional diffusion decomposition reaction of pure NTHC and NTHC mixed with CuV_2O_6 and MgV_2O_6, in the range 200–450°C

Sample		Temperature (°C)					
		205	250	300	350	400	450
NTHC	$10^5\ k\ (s^{-1})$	2.10	6.38	14.20	30.05	57.57	93.97
	E_a (kJ mol^{-1})	43.20	43.20	43.20	43.20	43.20	43.20
NTHC	$10^5\ k\ (s^{-1})$	2.21	5.60	11.62	24.85	41.80	68.23
$+MgV_2O_6$	E_a (kJ mol^{-1})	44.60	44.60	44.60	44.60	44.60	44.60
NTHC	$10^5\ k\ (s^{-1})$	2.32	6.91	16.33	35.62	70.31	109.17
$+CuV_2O_6$	E_a (kJ mol^{-1})	39.30	39.30	39.30	39.30	39.30	39.30

particular. This is the picture in the case of pure NTHC. In the presence of CuV_2O_6 additive, the acceleration effect can be explained through the existence of the well known [38] redox couple $Cu^{2+} + e \rightleftharpoons Cu^+$. From the proposed scheme of anion breakdown, the high electron acceptability of Cu^{2+} enables the decomposition to be initiated through stage I. At this stage the radical  $\overset{\dot{\mathrm{O}}}{\overset{|}{\mathrm{Ni}}}-\mathrm{O}\overset{\cdot}{\overset{\vdots}{\mathrm{C}}}=\mathrm{O}$ is formed and Cu^{2+} becomes reduced to Cu^+. The next stage represents the formation of NiO as product and regeneration of Cu^{2+}. Therefore, the enhancement role of copper metavanadate may be attributed to the establishment of the potentially active Cu^{2+}/Cu^+ redox centre, and it seems likely that the two stages in the proposed scheme constitute the rate determining step. The observed decrease in the activation energy, $E_a = 39.3$ kJ mol^{-1} for the NTHC + CuV_2O_6 system, can thus be attributed to the expected pertinent enhancement of the electron transfer process across the product layer.

Finally, because of the absence of such a redox couple in the case of MgV_2O_6 catalyst, together with its ability to occupy a grain boundary between Ni^{2+}/Ni^{3+} couples, an isolating layer might be built up at this phase boundary. Therefore we can conclude that the diffusion throughout such a multiphase product layer might be expected to take place rather slowly, resulting in a retardation of breakdown of the salt.

All these considerations provide an explanation for the obtained variation in the kinetics of the decomposition of NTHC (see Table 2 and Fig. 5) on mixing the salt with metal vanadate catalysts.

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