

INFLUENCE OF IRON ION ADDITIONS ON THE THERMAL DECOMPOSITION OF BASIC ZINC CARBONATE

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Thermal decomposition of pure basic zinc carbonate (BZC) and doped or mixed with iron ions were studied using TG, DTA and kinetics of isothermal decomposition. The TG and DTA investigations revealed that, the presence of iron ions retards the decomposition processes of (BZC). Also, the retardation effect increases on increasing of iron concentration up to 50 at.%. The curves of isothermal decomposition show the usual sigmoidal character. The decomposition velocity constant (K) values are plotted vs. $1/T$ according to Arrhenius equation gave a plot of good straight lines with activation energies of 43.7, 48.2, 53.2 and 57.1 kJ mol^{-1} for pure (BZC) and incorporated with 1, 10, 30 and 50 at.% Fe^{2+} respectively. The products of the thermal decomposition of pure BZC and mixed with iron ions are characterized using X-ray diffraction, IR spectroscopy, surface area determination and the surface porosity. These investigations showed that iron ions are effectively incorporated into zinc oxide lattice in the range of 30-50 at.%, which gave a ZnFe_2O_4 spinel.

Mixed oxides, especially binary system, have been employed successfully in many industrial catalytic processes [1, 2]. The combination of two transition metal oxides may affect their stoichiometry and their surface, electrical, catalytic and thermal properties [3-5]. It was observed that the presence of foreign ion in the host lattice of solids markedly influences the reaction rate of solid-phase reaction [6]. This fact has been attributed to the change in the defect structure of reacting substances [7, 8]. On addition it was found that [9, 10], the active sites as well as the electronic structure of the semiconductor surface are changed in the presence of foreign cations.

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However, in view of the oxide-oxide interaction in the mixture at appropriate temperature, knowledge of the thermolysis becomes an essential prerequisite to the understanding the catalytic properties of new compound formed. Therefore, the present investigation is devoted to study, the rule of iron ions in the decomposition processes of basic zinc carbonate (BZC). On the other hand the solid substances occurred in the thermal decomposition are characterized using different techniques. The techniques employed in this work are TG, DTA, kinetics of isothermal decomposition, surface area (*S_{BET}*), X-ray diffraction and IR absorption spectroscopy.

Experimental

Materials

AnalaR grade of basic zinc carbonate (BZC) and iron(II) carbonate were used. Doping or mixing of (BZC) with iron(II) carbonate were prepared as the following method. A calculated amounts of iron(II) carbonate together with BZC with ratios ranging from 1 to 50 at.% were admixed carefully using doubly distilled water till formation of homogeneous pastes, dried over a water bath to dryness. The products were dried in an oven at 100° to constant weight. The samples were calcined up to 500° for 4 h in a muffle furnace in presence of air atmosphere.

Techniques

Thermogravimetry (TG) and differential thermal analysis (DTA) of pure BZC and doped or mixed with iron ions were carried out using an automatically recording thermobalance, type 160 KS (West Germany), the rate of heating was kept at 10 deg/min⁻¹ and 170 mg sample of each solid specimen was employed in each experiment. Kinetics of isothermal decomposition of BZC and treated with iron ions was studied in atmospheric pressure using Sartorius thermobalance (type 7085-02). The nitrogen adsorption measurements were made at 77 K by means of a conventional volumetric apparatus. The surface area was calculated from the adsorption data using the linear form of BET equation [11]. Porosity of samples were investigated using *V_a-t* plots [12] and adopting the pore volume distribution method [13]. An X-ray diffraction (XRD) of the thermal products of pure BZC and treated with iron ions were performed with a Philips diffractometer (type PW 2103/00) using a Cu target and Ni filter. IR absorption spectra of calcined samples of

pure BZC and mixed with iron ions were obtained by KBr disc technique in the range of $1600\text{--}200\text{ cm}^{-1}$, using Perkin Elemer model 599 B infrared spectrophotometer.

Results and discussion

TG and DTA analysis

TG and DTA curves of pure BZC and doped or mixed with iron ions are represented in Fig.1. Curve(a) illustrates the TG and DTA analysis of pure BZC. It shows that the decomposition process takes place in three stages. The first endothermic peak located at about 100° corresponds to the physically adsorbed water. The second sharp and strong endothermic peak located at 258° corresponds to the formation of ZnO. The third exothermic peak located at 578° may be related to the dissociation of ZnO into interstitial Zn metal [14, 15]. The influences of iron ion additions on the decomposition processes of BZC are shown in Fig.1. Curves (b, c, d and e) for 1, 10, 30 and 50 at.% respectively. These curves reveal that the presence of iron ions with BZC increases the maximum of the decomposition temperatures to higher values such as 264, 275, 291 and 300° for 1, 10, 30 and 50 at.% respectively. These results indicate clearly that Fe^{2+} ions treatment generally retards the thermal decomposition of BZC. Indeed, the addition of 30 and 50 at.% Fe^{2+} added a new three endothermic peaks noticed at 425, 640 and 740° . As mentioned before [16-18], Zn^{2+} and Fe^{3+} oxides interact in a series of stages. The initial layers of the product being to form by surface diffusion at the most favourable sites at 250 to 400° , their formation is reflected by increase in the rate of emanation release. The small endothermic peak located at 420° may correspond to the phase transition from $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ lattice structure [19]. The third peak located at 740° is probably caused by the formation of zinc ferrite spinel [20,21]. A strong broad endothermic peak extended between $100\text{--}150^\circ$, followed by $\approx 7\%$ loss in weight, was observed in the DTA curves of the solid located with 30 to 50 at.% Fe^{2+} . Such a peak corresponds to departure of physisorbed water indicates an important increase in the hygroscopic nature of the treated solid. Interesting results are that the thermal decomposition of BZC and ZnO was around 255° while the addition of iron ions divates the decomposition temperature to higher values. These results are found in agreement with the results obtained by Morrijani *et al.* [22].

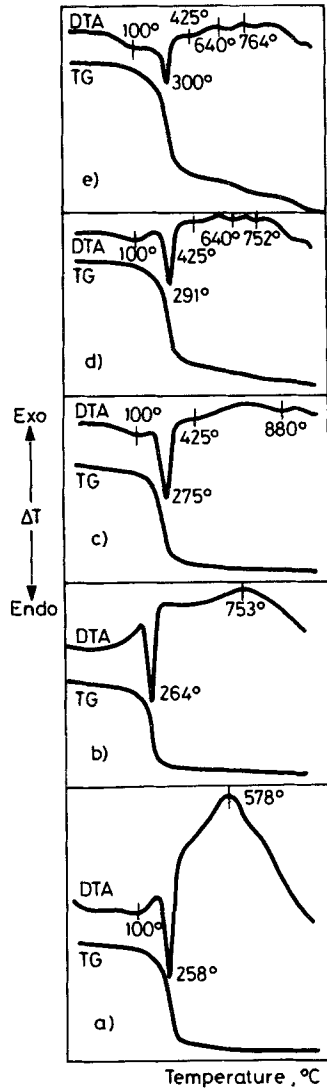


Fig. 1 TG and DTA curves of pure BZC (a) and incorporated with iron ions, 1 at.% (b), 10 at.% (c), 30 at.% (d) and 50 at.% (e)

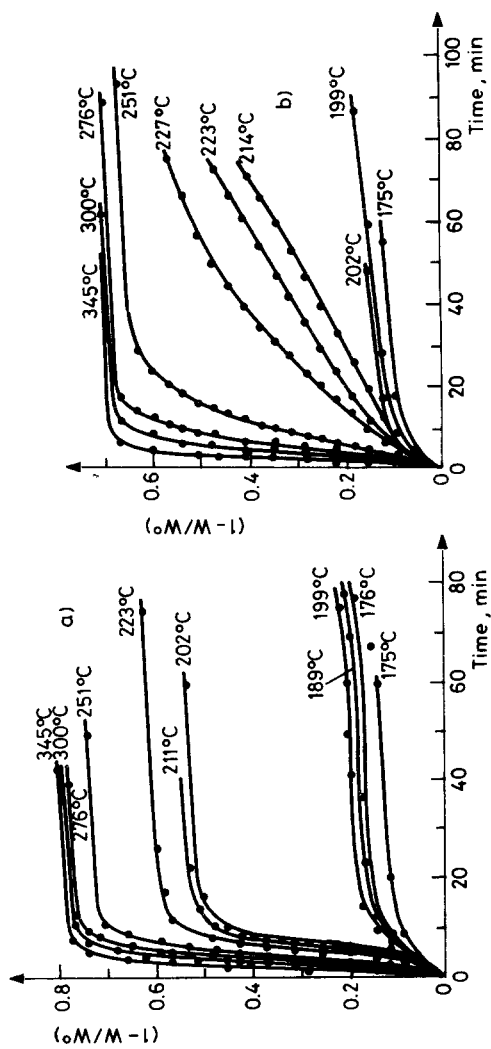


Fig. 2a, b Isothermal decomposition of pure BZC (a) and incorporated with 1 at.% Fe²⁺ (b)

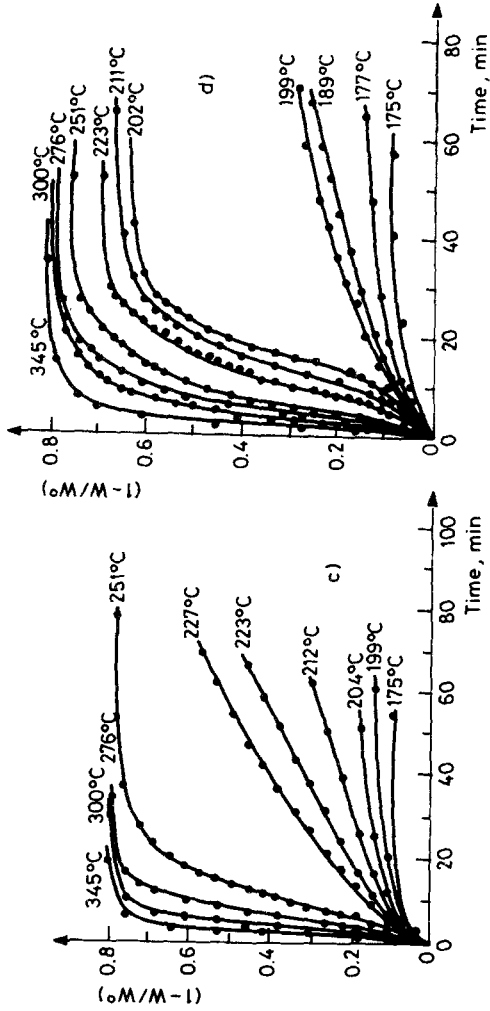


Fig. 2c, d Isothermal decomposition of BZC incorporated with 10 at.%Fe²⁺(c) and 50 at.% Fe²⁺(d)

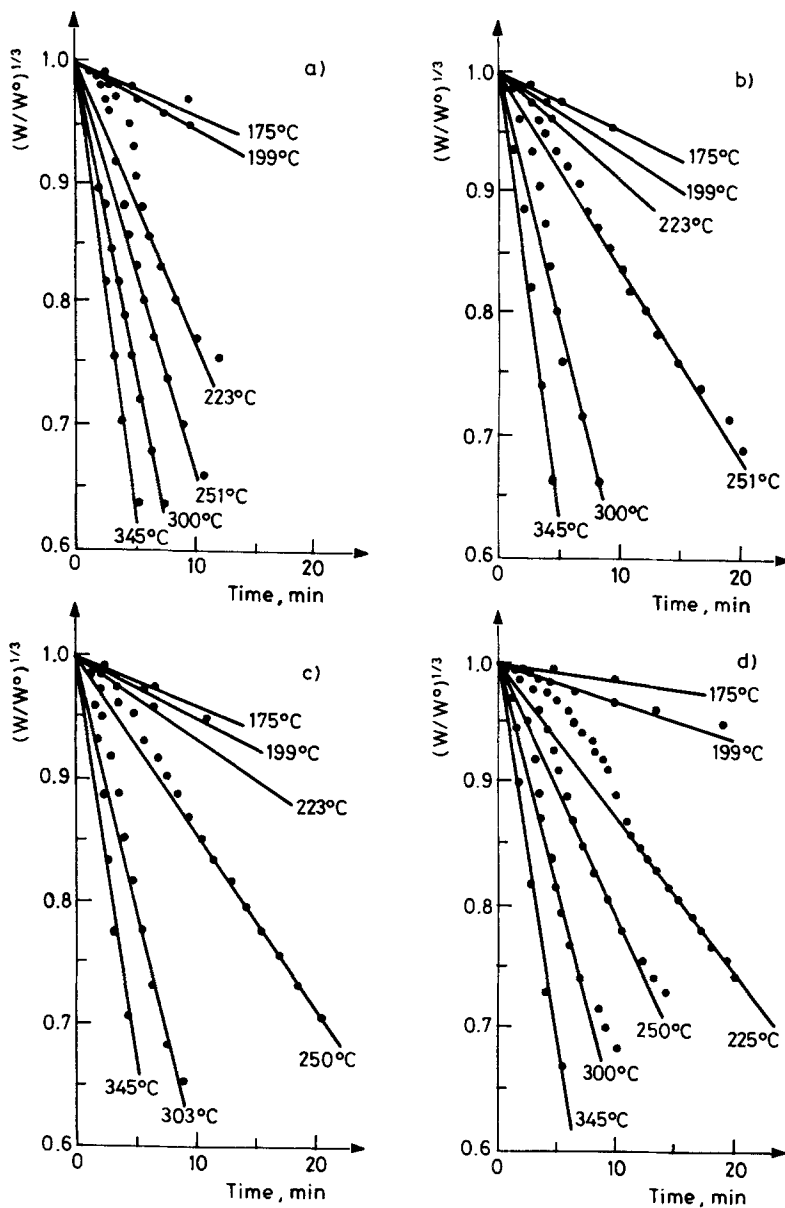


Fig. 3 $(m/m_0)^{0.33}$ vs. time at various temperatures of pure BZC (a) and incorporated with 1 at.% Fe²⁺ (b), 10 at.% Fe²⁺ (c) and 50 at.% Fe²⁺ (d)

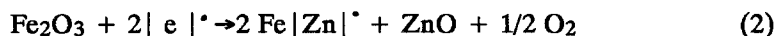
Kinetics of isothermal decomposition

TG and DTA results indicated a suitable range of 175-350° for kinetics of isothermal decomposition studies of pure and treated BZC. The results are shown in Fig. 2, curves (a, b, c and d) for pure BZC and treated with 1, 10 and 50 at.% Fe²⁺ respectively in which the increase in weight loss are plotted vs. time at each of the decomposition temperature. The curves show the usual sigmoidal character for all samples indicating that the autocatalytic processes of nucleation and growth commonly encountered in solids. It is to be noted that the sigmoidal character of the isothermal curves increases with increasing the temperature of thermolysis. The decomposition processes performed at the different temperatures may be satisfactorily represented by the equation proposed by Britton *et al.* [23] of the form,

$$\left(\frac{m}{m_0}\right)^{0.33} = Kt + b \quad (1)$$

where m_0 is the weight of volatile compounds, m is the weight of components remaining at time t , K is the velocity constant and b is a constant.

Thus plotting $\left(\frac{m}{m_0}\right)^{0.33}$ against t gave a good straight lines as indicated in Fig. 3. Curves (a, b, c and d) for pure BZC and doped or mixed with 1, 10 and 50 at.% Fe²⁺ respectively. The slopes of these lines determine the velocity constants at the various temperatures. Applying the Arrhenius equation and from the plot of $\log K$ against $1/T$, the activation energies of the decomposed samples were calculated and represented in Fig. 4. The values of activation energies were found to be 43.7, 48.2, 53.2 and 57.1 kJ mol⁻¹ for pure BZC and incorporated with 1, 10 and 50 at.% Fe²⁺ respectively. The magnitude of the activation energy measured for a solid phase decomposition has often ascribed to the energy barrier in the rate limiting step. Therefore, the presence of iron ions can be understood on the basis of the suggestion of Boldyrev [24]. He concluded that, the presence of foreign ions causes lattice deformation as well as either a change in the valence of ions or the appearance of additional cationic or anionic vacancies in the lattice which in turn will strongly affect the thermal decomposition rate as well as the energy barrier. Consequently, the introduction of iron ions into ZnO lattice positions during thermolysis will decrease the hole concentration either on the surface or in the bulk according to the following mechanism,



where $\text{Fe} | \text{Zn} | \cdot$ represents Fe^{3+} ion substituted Zn^{2+} ion in their normal lattice site position and $| e | \cdot$ refers to a hole. From Eq.(2), it is clear that the presence of Fe^{3+} into BZC will lead to consumption of holes and consequently retards its decomposition rate. Also, it is observed, the retardation effect depend on the concentration of iron ions. Thus the mixed samples should require a higher activation energy to achieve thermal decomposition. Therefore, a higher activation energy must require a higher temperature to thermal treatment. The values of activation energies of mixed samples are in accordance with the disappearance of holes.

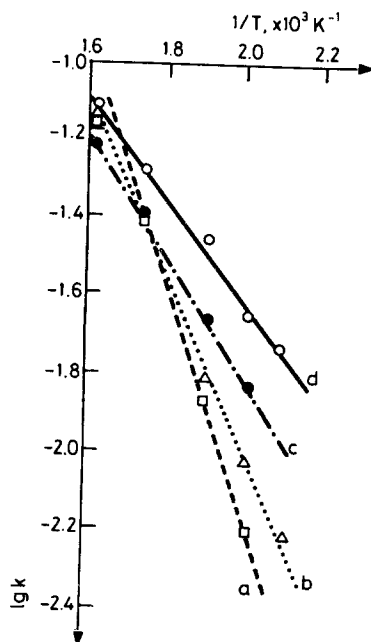


Fig. 4 Plot of $\log K$ vs. $1/T$ of pure BZC (a) and incorporated with 1 at.% Fe^{2+} (b), 10 at.% Fe^{2+} (c) and 50 at.% Fe^{2+} (d)

It is important to characterize the different catalysts produced during the thermal decomposition of original samples and to identify the formation of zinc ferrite spinel structure.

X-ray investigation of the thermal products of BZC and mixed with iron ions:

X-ray diffraction lines of pure BZC and mixed with 10, 30 and 50 at.% Fe^{2+} ions calcined at 500° are shown in Fig.5. Curve (a) shows the most intense lines located at $d(\text{\AA}) = 2.72, 2.51, 2.37$ and 1.83 are corresponded to ZnO lattice structure as compared with ASTM cards [20]. Curves (b, c and d) are corresponded to the XRD patterns of ZnO mixed with 10, 30 and 50 at.% Fe^{2+} ions respectively. Comparison of these lines with those of pure ZnO, indicate that new lines are appeared in case of 30 and 50 at.% Fe^{2+}

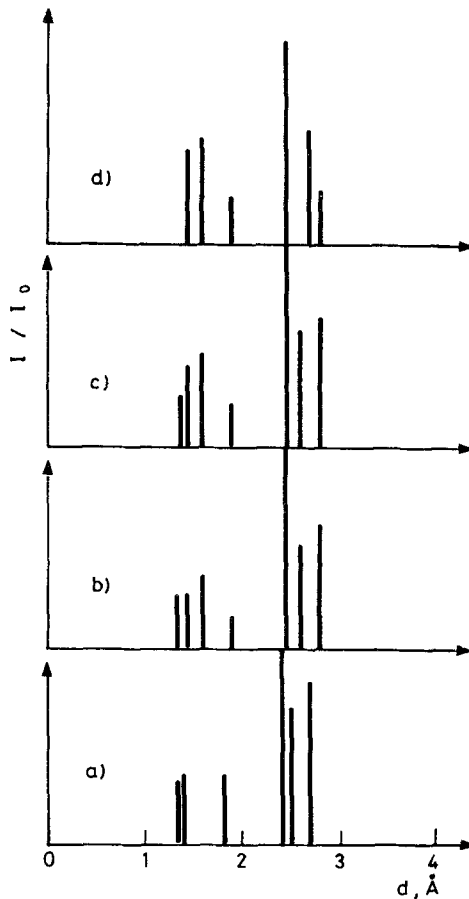


Fig. 5 X-ray diffraction patterns of the thermal products of pure BZC (a) and mixed with 10 at.% Fe^{2+} (b) 30 at.% Fe^{2+} (c) and 50 at.% Fe^{2+} (d) [samples calcined at 500°C for 4h in air]

ions. These new lines located at $d(\text{\AA}) = 2.76, 2.54, 1.59$ and 1.48 are characteristic the lattice of ZnFe_2O_4 [20, 21].

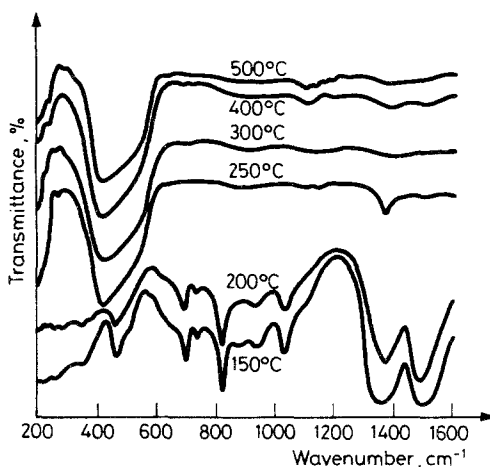


Fig. 6 IR absorption spectra of pure BZC and its calcination products for 4h in air

IR absorption spectra of the decomposition products of BZC and mixed with iron ions:

The infrared absorption spectra of the thermal products of pure BZC and mixed with iron ions are shown in Figs 6, 7. Figure 6 shows that the absorption bands of pure BZC calcined at different temperatures. It appears that, the samples calcined at 150 and 200° still have the spectrum of BZC. On increasing the calcination temperature up to 500°, the appearance of the band assigned at 410 cm^{-1} is corresponded to the formation of ZnO [25]. The IR absorption spectra of ZnO mixed with 10, 30 and 50 at.% Fe^{2+} ions are shown in Fig. 7 (curves *b*, *c* and *d*) respectively. These curves indicate that, new absorption bands are appeared at 540 and 380 cm^{-1} , these bands are corresponded to the formation of new phase i.e. ZnFe_2O_4 as predicted by XRD analysis. Curve (*a*) demonstrates that the absorption bands of pure ZnO calcined at 500° for comparison.

Surface area measurements using BET and V_a -t plots:

Specific surface area (S_{BET}) values are evaluated from the N_2 adsorption isotherms using BET equation on its normal range of applicability (0.05-0.3 P/P_0) and by adopting the value of 16.2 Å for the molecular area of nitrogen gas. The surface area (S_t) values are calculated by applying the V_a -t method. The variation of the texture data of BZC and its calcination products are cited in Table 1.

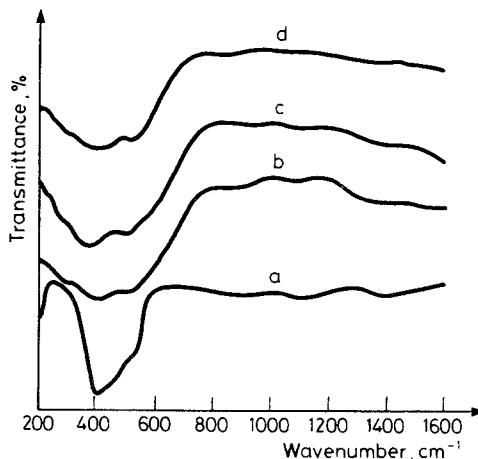


Fig. 7 IR absorption spectra of pure BZC (a) and mixed with 10 at.% Fe^{2+} (b) 30 at.% Fe^{2+} (c) and 50 at.% Fe^{2+} (d) [samples calcined at 500 °C for 4h in air]

The result indicate that, the S_{BET} value increases from 22.6 to 59.1 $m^2 g^{-1}$ when the original sample calcined from 150 to 250°. This is the result of the removal of the volatile compounds accompanying the thermal decomposition which leaving wide pores. The creation of these pores should increase the S_{BET} value reaching maximum at 250°. The maximum around 250° is mostly due to crystallization of the lattice to ZnO. This behaviour generally is expected in case of crystalline solid produces volatile gases during its thermal analysis. On the other hand, the maximum S_{BET} represents an overlap of two processes, i.e. activation and sintering. It is plausible to suggest that the activation process due to carbonate decomposition is slightly compensated by a low temperature sintering process. It is worth to mention that at this maximum, the degree of decomposition was about 85% (see Table 1). The gradual decrease in S_{BET} values after maximum may be due to the

Table 1 Textural parameters for BZC and its calcination products for 4h

Calc. Temp., °C	S_{BET} , $m^2 g^{-1}$	S_t , $m^2 g^{-1}$	S_{cum} , $m^3 g^{-1}$	$V_{P0.95}$, $cm^3 g^{-1}$	$V_{P_{cum}}$, $cm^3 g^{-1}$	$\frac{S_t}{S_{BET}}$	Degree of decomposition, %	Density $g\ cm^{-3}$
150	22.6	22.4	22.8	0.18	0.27	99.1	5.2	2.5
200	53.2	48.4	60.6	0.27	0.36	91.0	27.2	2.7
250	59.1	52.2	45.6	0.34	0.45	88.3	83.8	2.8
300	53.4	48.4	53.9	0.30	0.45	91.8	86.1	2.9
400	37.0	36.7	37.4	0.18	0.28	99.2	90.3	3.0
500	20.9	19.7	21.1	0.12	0.21	94.3	96.5	3.1

Table 2 Textural parameters for ZnO incorporated with iron ions calcined at 500°C for 4h

Catalyst	S_{BET} , $m^2 g^{-1}$	S_t , $m^2 g^{-1}$	S_{cum} , $m^3 g^{-1}$	$V_{P0.95}$, $cm^3 g^{-1}$	$V_{P_{cum}}$, $cm^3 g^{-1}$	$\frac{S_t}{S_{BET}}$
1 at. % Fe ²⁺	27.3	25.8	28.6	0.13	0.22	94.5
10 at. % Fe ²⁺	30.3	30.1	30.6	0.15	0.20	99.3
30 at. % Fe ²⁺	35.2	34.3	37.8	0.20	0.31	97.4
50 at. % Fe ²⁺	37.8	36.5	38.2	0.16	0.23	96.6

sintering process which is predominate at that range of temperature where solid densification takes place (see Table 1). The effect of iron ion additions on the surface parameters of ZnO has been studied and the results are cited in Table 2.

The results indicate that an increase in S_{BET} value on increasing of % mixing of iron ions up to 50 at.%. Generally the increase in S_{BET} value may be due to either zinc vacancies and holes in the low range of mixing or to the formation of $ZnFe_2O_4$ in the high range of mixing which has different surface properties compared to pure ZnO.

On examination the solid surface porosity of pure ZnO and treated with iron ions, the values of $S_{cum} > S_{BET}$ and the V_a-t plots are found to be upward divation which are indicating mesoporous nature.

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Zusammenfassung — Mittels TG, DTA und der Kinetik der isothermen Zersetzung wurde der thermische Abbau von reinem bzw. von mit Eisenionen versetztem basischen Zinkcarbonat (BZC) untersucht. TG- und DTA-Untersuchungen zeigen, daß der Zersetzungsprozeß

von BZC durch Eisenionen gehemmt wird. Dieser Hemmungseffekt wächst bis zu einer Eisenionenkonzentration von 50 mol%. Die Kurven der isothermen Zersetzung zeigen den üblichen sigmoiden Charakter. Aus dem Auftragen der Geschwindigkeitskonstante k des Zersetzungsprozesses (gemäß der Arrhenius-Gleichung) gegen $1/T$ ergeben sich in guter Näherung Geraden mit den Aktivierungsenergien 43.7, 48.2, 53.2 und 57.1 kJmol⁻¹ für BZC mit einem Fe²⁺-Gehalt von 0, 1, 10, 30 bzw. 50 mol%. Die thermischen Zersetzungsprodukte von reinem bzw. von mit Eisenionen versetztem BZC wurden unter Zuhilfenahme von Röntgendiffraktion, IR-Spektroskopie, Oberflächenbestimmung und Oberflächenporosität charakterisiert. Diese Untersuchungen ergaben, daß Eisenionen im Bereich 30-50 mol% in das Zinkoxidgitter eingebaut werden und dabei ein ZnFe₂O₄ Spinell entsteht.