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NONISOTHERMAL KINETICS OF ZINC OXIDE NONSTOICHIOMETRIZATION

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The results obtained by studying zinc oxide non-stoichiometrization are presented. The kinetic parameters values under nonisothermal conditions were calculated too. Both the nonstoichiometric zinc oxide composition and the kinetic parameter values are depending on the generating substances.

Zinc oxide, a compound with remarkable chemisorptive and catalytic properties, mediates a large number of processes, such as dehydrogenation [1], oxidation [2] and dehydration [3].

Both the catalytic and chemisorptive activities, as well as the electric and optical properties, are determined by the actual defect crystal structure this material exhibits.

Zinc oxide is a typical nonstoichiometric compound, the excess cations being located in the interstices.

Starting with a material structure free of defects, the nonstoichiometrization could be considered a result of its heating, according to the scheme:

$$(Zn^{2+} \mid \square^{+})(O^{2-} \mid \square^{-})(s) \rightarrow (e_2\,\delta \mid Zn^{2+}\,\delta \mid \Delta)(Zn_I^{2+}\delta \mid \square^{+})(O_I^{2-}\delta \mid \square^{-})\,(s) + \\ + \delta/2\,O_2\,(g) \qquad (1)$$

and

$$(Zn^{2+} \mid \square^{+})\,(O^{2-} \mid \square^{-})\,(s) \rightarrow (e\delta \mid Zn^{+}\delta \mid \Delta)\,(Zn_I^{2+}\delta \mid \square^{+})(O_I^{2-}\delta \mid \square^{-})\,(s) + \\ + \delta/2\,O_2\,(g), \qquad (2)$$

where, taking into account Rees' notations [4], $\square^{+}$, $\square^{-}$ and Δ represent the cationic, anionic and interstitial positions, e is the usual symbol for the electron, and the vertical lines indicate the disposal of the elements to their left on those to their right.

The semiconducting, optical and catalytic properties of zinc oxide are due to the electrons located on the interstitial zinc ions.

Indeed, they can easily be promoted into the conduction band, this phenomenon being accompanied by the appearance of both electric conductivity and a characteristic absorption band.

Gas reactants can be chemisorbed by zinc oxide through the same electrons, the phenomenon being followed by the corresponding catalytic reaction. The remarkable activity of nonstoichiometric zinc oxide can be assigned to its lattice energy, smaller than for the stoichiometric one.

It is known that any crystal lattice perturbation leading to the decreasing of its energy produces an increase of the reactivity with respect to the unperturbed lattice [5].

The above-mentioned considerations justify the kinetic study of the zinc oxide nonstoichiometrization phenomenon, the results of which are to be presented.

Experimental

Powdered zinc oxides obtained by the decomposition of zinc carbonate, zinc acetate dihydrate and the complex $[Zn(pald)_2](OH)_2$, prepared according to Ray and Sur [6], were used.

The generating substances were heated in a MOM Derivatograph, with a heating rate of 5.4°/min.

The nonstoichiometrization phenomenon was recorded starting from the temperature corresponding to the end of the decomposition to zinc oxide.

Considering the small amount of oxygen evolved during the nonstoichiometrization and the sensitivity of the apparatus, we used an appropriate amount of generating substance.

The kinetic parameters were obtained by processing the thermogravimetric curves by the Coats–Redfern method [7], extremely useful for processes which take place at rates such that the DTG curves can not be used. The conversion degrees α were calculated in the usual way for each nonstoichiometrization process.

Results and discussion

Zinc oxide nonstoichiometrization resulting from zinc carbonate

The heating of zinc oxide from 840° to 1500° leads to an intermediate $ZnO_{0.42}$ ($\delta = 0.58$), which settles around this composition.

Before the proper nonstoichiometrization, zinc oxide undergoes an endothermic transformation having a maximum rate at 920°, as results from the DTA curve (Fig. 1).

The nonstoichiometrization takes place with maximum rate at 1300°.

Kinetic analysis of the thermogravimetric curve led to the results shown in Table 1.

The reaction order value agrees with the almost symmetrical shape of the DTG curve.

The results obtained indicate the occurrence of the nonstoichiometrization according to a contracting sphere mechanism.

Table 1

The kinetic parameters of zinc oxide nonstoichiometrization

No.	The generating substance	n*	E. kcal/mole	Z. s^{-1}
1	$ZnCO_3$	2/3	42	$7.1\ 10^3$
2	$Zn(CH_3COO)_2.2H_2O$	1	13	$2.6\ 10^{-2}$
3	$[Zn(pald)_2](OH)_2$	1	21	$2.5\ 10^{-1}$

* n, E and Z stand for the reaction order, the activation energy and the pre-exponential factor

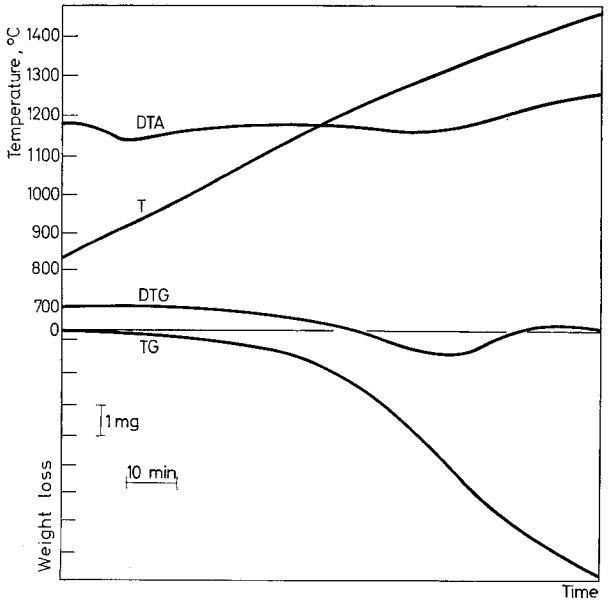

Fig. 1. DTA, DTG and TG curves of zinc oxide nonstoichiometrization resulting from zinc carbonate decomposition

Zinc oxide nonstoichiometrization resulting from zinc acetate dihydrate

The DTA curve corresponding to zinc oxide heated from 860° to 1500° exhibits two endothermic phenomena, occurring with maximum rates at 920° and 1300° (Fig. 2), at the same time the nonstoichiometrization leading to the compound $ZnO_{0.982}$ ($\delta = 0.018$).

At higher temperatures, $ZnO_{0.982}$ also undergoes a process of nonstoichiometrization, the phenomenon going on above 1500°, the maximum temperature that could be reached.

The kinetic parameters of nonstoichiometrization:

$$ZnO\,(s) \rightarrow ZnO_{0.982}\,(s) + 0.009\,O_2\,(g) \qquad (3)$$

determined by kinetic analysis of the TG and T curves, are also given in Table 1.

The two endothermic transformations observed prove the existence of at least three varieties of zinc oxide, that can be assigned to the formation of interstitial zinc species: $e \mid Zn^+ \mid \Delta$ and $e_2 \mid Zn^{2+} \mid \Delta$.

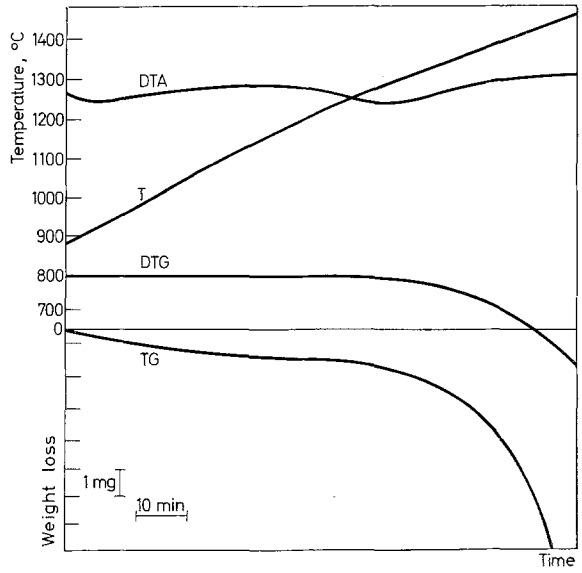

Fig. 2. DTA, DTG and TG curves of zinc oxide nonstoichiometrization resulting from zinc acetate dihydrate decomposition

The experimental results obtained show the different behaviour of zinc oxide according to the generating substance.

Zinc oxide nonstoichiometrization resulting from $[Zn(pald)_2](OH)_2$ decomposition.

The nonstoichiometrization phenomenon was followed from 950° to 1500°, leading to the compound $ZnO_{0.87}$ ($\delta = 0.13$).

Kinetic analysis of the heating curves led to the kinetic parameters values given in Table 1.

In this case too the given data reveal a different behaviour with respect to the previous cases.

Conclusions

1. Depending on the generating substance, the heating of zinc oxide leads to nonstoichiometric forms of different compositions.

2. The thermogravimetric data indicate that zinc oxide nonstoichiometrization resulting from zinc carbonate decomposition leads to a compound of formula $ZnO_{0.42}$.

3. The kinetic parameters of the nonstoichimetrization also vary according to the generating substance of the zinc oxide.

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RÉSUMÉ — On présente les résultats d'une étude sur la formation d'oxyde de zinc non-stœchiométrique. Les valeurs des paramètres cinétiques en conditions non-isothermes sont également calculées. La composition de l'oxyde de zinc non-stœchiométrique ainsi que les valeurs des paramètres cinétiques dépendent du composé de départ.

ZUSAMMENFASSUNG — Die Ergebnisse der Untersuchungen der Nichtstöchiometrisierung von Zinkoxid werden vorgeführt.

Die Werte der kinetischen Parameter unter nicht-isothermen Bedingungen wurden ebenfalls berechnet.

Sowohl die nichtstöchiometrische Zusammensetzung des Zinkoxids als auch die Werte der kinetischen Parameter hängen von der das Phänomen auslösenden Substanz ab.

Резюме — Представлены результаты, полученные при изучении окиси цинка нестехиометрического состава, а также вычислены значения кинетических параметров при неизотермических условиях. Нестехиометрический состав окиси цинка и кинетические параметры зависят от способа получения вещества.