PREPARATION OF HIGHLY DISPERSED ZINC OXIDE BY THERMAL DECOMPOSITION
OF BASIC ZINC CARBONATE

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ABSTRACT

A study is carried out on the effect of the duration and tem-
perature of basic zinc carbonate decomposition on the specific sur-
face area of the resulting zinc oxide. The influence of the experi-
mental conditions on the decomposition kinetics and mechanism is
also investigated. The kinetic parameters and the prevailing mecha-
nism of decomposition are determined by the integral method on the
basis of the TG curves.

INTRODUCTION

Highly dispersed zinc oxide has a wide application in hetero-
geneous catalysis. It can be prepared by thermal decomposition of
basic zinc carbonate. The kinetics and mechanism of this process
can be studied by thermal analysis methods (TG, DTA, TGT). Accord-
ing to recent theoretical results [1-3], the kinetics and mecha-
nism of thermal decomposition determined by these methods are fun-
ctions of the experimental conditions rather than of the process
itself. One of the aims of our study was to check this conclusion
practically.

EXPERIMENTAL

Highly dispersed zinc oxide was prepared by thermal decomposi-
tion of basic zinc carbonate [4]. Depending on the preparation con-
ditions, the initial precipitate may contain different zinc-ammonia
and basic carbonate complexes [5]. The precipitate used was obtained
under conditions ensuring the prevalence of basic zinc carbonate
complexes of the type $m \ ZnCO_3 .n \ Zn(OH)_2 .k \ H_2O$, which was confirmed
by the results of the X-ray analysis. The data were compared with
ASTM [6]. The lines obtained corresponded to $ZnCO_3(OH)_6 .H_2O$ (ASTM
index 11-287). This composition was also indicated by the IR spec-
trum of the precipitate [7]. The zinc carbonate used had a specific
surface area of 2 m^2/g as determined by a modified BET method [8].

The thermogravimetric measurements were made by a MOM 1500
derivatograph at different heating rates and sample weights.

'n- The kinetics and mechanism of the decomposition were determined
by an integral method using TGA data[9-14].

RESULTS AND DISCUSSION

The effect of the decomposition temperature on specific surface
area of the dispersed zinc oxide was estimated for a preliminary
determined optimum decomposition time (τ =180 min). The depen-
dence passes through a clearly expressed maximum. The largest spe-
cific surface area (62 m^2/g) corresponds to temperatures of 250-
270^oC.

Pre-treatment of the TG curve by the integral method[9-14]
showed an activation energy of the process of ~ 59 kJ/mol.

The effect of the experimental conditions on the kinetics and
mechanism of thermal decomposition was studied at different heating
rates using a constant sample weight (200 mg). The TG curves obtain
ed are illustrated in Fig. 1. The kinetic analysis data for each
curve are given in Table I.

TG measurements were carried out at the same heating rate but
with different initial sample weights. The curves obtained can be
seen in Fig. 2. The results concerning the kinetics and mechanism
of decomposition are presented in Table II.

CONCLUSION

The optimum range of the preparation of highly dispersed zinc
oxide with the largest specific surface area is 250-270^oC. The pro-
cess of basic zinc carbonate decomposition to ZnO has an activation
energy of 59 kJ/mol.

With increasing heating rate and initial sample weight the
process occurs at higher temperatures. The change in these two pa-
rameters does not affect the kinetics and mechanism of decompositi-
on. In both cases the process is described well by equations con-
cerning the propagation of phase boundaries and the volume growth
of initial nuclei. The mean activation energy found in the first
case is 67 kJ/mol, and in the second - 56 kJ/mol.

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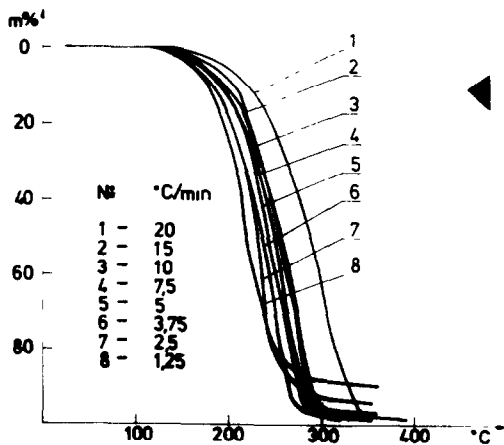11. J. Zsako, J. Phys. Chem. 72 (1968) 2406

Fig. 1. TG curves of basic zinc carbonate decomposition at different heating rates, a sample weight of 200 mg, a medium crucible size and air atmosphere

Fig. 2. TG curves of basic zinc carbonate decomposition for different sample weights, $q=10\,^{0}C/min$; atmosphere- air; open crucibles

Table I

Crucible	Weight mg	T °C	Decomp velocity mg/min	Ea, kJ/mg	$g(\alpha)$	Correlation coefficient r	Standart deviation S	Dispersion δ min
polypate	70	267 (endo)	2,27	50,2	$[1-(1-\alpha)^{1/3}]^{1/3}$	0,9994	0,012	0,003
little (open)	200	223 (endo) 262 (exo) 285 (endo)	5,88	56,5	$[-\ln(1-\alpha)]^{1/3}$	0,9949	0,041	0,041
middle (open)	370	278 (endo)	9,53	50,2	$[-\ln(1-\alpha)]^{1/3}$	0,9912	0,058	0,064
big (open)	1650	310 (endo)	13,9	58,6	$[1-(1-\alpha)^{1/3}]^{1/2}$	0,9987	0,025	0,009

Table II

q °C min	T °C	Decomp velocity mg/min	Ea, kJ/mol	$g(\alpha)$	Correlation coefficient r	Standart deviation S	Dispersion δ min
1,25	200(exo) 253(endo)	0,77	75,3	$[-\ln(1-\alpha)]^{1/2}$	0,9971	0,045	0,034
2,5	210(exo) 255(endo)	1,61	54,4	$[-\ln(1-\alpha)]^{1/3}$	0,9861	0,066	0,135
3,75	255(endo)	2,82	58,6	α	0,9963	0 039	0,043
5	248(endo) 268(endo)	2,94	66,9	$[1-(1-\alpha)^{1/3}]^{1/2}$	0,9964	0,046	0,042
7,5	275(endo)	4,67	66,9	$[1-(1-\alpha)^{1/3}]^{1/2}$	0,9993	0,02	0,056
10	223(endo) 262(exo) 285(endo)	5,88	56,5	$[-\ln(1-\alpha)]^{1/3}$	0,9949	0,041	0,041
15	285(endo)	7,32	58,6	$[1-(1-\alpha)^{1/3}]^{1/2}$	0,9978	0,036	0,032
20	320(endo)	11,98	58,6	$[1-(1-\alpha)^{1/3}]^{1/2}$	0,9976	0,034	0,015