

THE INFLUENCE OF CONCENTRATION AND ANION NATURE ON THE SUPPORT EFFECT

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Abstract

The kinetic of decomposition of copper formate, acetate, propionate and butyrate under non-isothermal conditions was studied. The support materials were carborundum and silica and the concentrations of the supported compounds were 15, 20, 25 and 30 mass%. In order to avoid the effects of thermal gradients and dilution, a series of parallel samples of carboxylate/support mixtures with the same concentration were studied. The support effect was estimated by the difference between the isokinetic temperature of the supported, respectively mixed carboxylate series, and is discussed in connection with the precursor concentration and the nature of the carboxylate anion. The suggestion of considering the thermodynamic activation function instead of the Arrhenius parameters for discussion on compensation effect was argued.

Keywords: compensation effect and support effect, isokinetic temperature, non-isothermal kinetics, supported precursors

Introduction

In order to obtain supported catalysts, the thermal decomposition of the precursors on the support is a compulsory step [1]. But very seldom the kinetic analysis of the data obtained under non-isothermal conditions lead to the intimate reaction mechanism. And also there is a lack of information on thermal behavior of precursors supported on different materials.

In non-isothermal kinetics, the compensation effect, i.e. the linear dependence of E (activation energy) and $\ln A$ (pre-exponential factor natural logarithm) is rather a rule [2] and unfortunately a source of debate [3].

In our previous work [4], the thermal behavior by decomposition in non-isothermal conditions of copper formate and acetate, both supported on carborundum and silica, were studied. The observed compensation effect was regarded as a support effect [5, 6].

In this paper we continue with the study of non-isothermal decomposition of copper propionate and butyrate and, based on the kinetic data obtained in the present and in the previous paper [4], we carry out an analysis about the influence of concentration and anion nature of the precursor on the support effect.

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Experimental

The used support-materials were: Carborundum SiC (Carlo Erba) and silica SiO₂ (Johnson Matthey). The precursors were copper propionate and butyrate self-prepared from CuO with the corresponding amount of propionic respectively butyric acid.

The supported samples were prepared from aqueous solution of the corresponding carboxylate, into a rotating vacuum evaporator. Four concentration steps were used: 15, 20, 25 and 30 mass%. Also a series of comparative samples of a mechanical mixture of support and precursor, with the same concentration steps were prepared and studied in order to avoid the effects of thermal gradients and of dilution.

The thermogravimetric (TG) curves were recorded in static air atmosphere, with a Q-1000 Derivatograph (MOM, Hungary), using Pt crucible and the corresponding support as reference compound.

The sample mass was calculated for a content of 60 mg of active substance, independent from the nature or concentration of carboxylate. The heating rate was 10 K min⁻¹ in the range 298–773 K.

Results and discussion

The experimental protocol avoids the necessity of using different heating rates. According to Zsakó [7], many curves methods are based on hypotheses in disagreement with the experimental data and the kinetic parameters derived by means of these methods depend very much on the used calculation procedure.

By the mentioned two-parallel series of samples (supported and mixed, respectively), the influence of the experimental conditions on the variation of the kinetic parameter are the same, with the exception of the effect due to supporting the precursor.

Kinetic parameters. Thermodynamic functions of the transition state

The TG data were used to evaluate the non-isothermal kinetic parameters of decomposition and were processed by the integral method of Flynn and Wall [8]:

$$\lg F(\alpha) = \lg \frac{AE_a}{R} - \lg a - 2.315 - 0.457 \frac{E_a}{RT} \quad (1)$$

with the same conversion integral:

$$F(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1-n} \quad \text{for } n \neq 1 \quad (2)$$

and

$$F(\alpha) = -\ln(1 - \alpha) \quad \text{for } n = 1 \quad (3)$$

In Eqs (1)–(3) α is the conversion, a is the heating rate, n is the reaction order, T is the temperature and A , E_a are the Arrhenius kinetic parameters.

In the purpose of establishing the reaction order, diagrams of $\lg F(\alpha)$ vs. $1/RT$ were attempted. The n value for which the best linear correlation was obtained is considered the true reaction order. From the slope and the intercept of this linear diagram, the activation energy and the preexponential factor were determined. The values of n , A and E_a were used to simulate the TG curves in coordinate (x, T) , where $x=(1-\alpha)$, and experimental points are then recorded in the same coordinates. If the points lie on the simulated curve, this confirms the correctness of the used integral method.

Since the physical meaning of the apparent kinetic parameters n , E and A derived by means of the single curve method is not clear enough [9, 10], we suggest the enthalpy ΔH^* and the entropy ΔS^* of the transition state as descriptive parameters for the compensation effect and the related support effect.

With the determined kinetic parameters the rate constant k has been calculated by the Arrhenius equation

$$k = A e^{E_a/RT} \quad (4)$$

and from transition state theory [11], the enthalpy ΔH^* and entropy ΔS^* of the transition state have been determined by:

$$k = \frac{k_B T}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (5)$$

where k_B and h are the Boltzmann and Planck constants, respectively.

All the determined parameters according to Eqs (1) and (5), are systematized in Table 1.

The values for the increment on enthalpy ΔH^* , when going from precursor to the activated complex, are in fair concordance with their homologues for activation energies. With one exception all ΔS^* values are positive and large indicating that when going from the precursor to the activated complex, there is a considerable increase in the degree of freedom. The existence of an activated complex with a low degree of ordering is consistent with a reaction mechanism in which the controlling step is the activation of some bonds of the initial compound. By the one exception, i.e. copper butyrate on the rather inert carborundum, the ordering tendency due to C_4 -chain is in discussion.

Isokinetic temperature

By inspecting Table 1 the parallel variation of both $\ln A$ vs. E , respectively ΔS^* vs. ΔH^* for each precursor/support pair is a clear observed trend (Fig. 1).

This compensation effect [12] is described by:

$$\ln A = bE + c \quad (6)$$

or the equivalent

$$\Delta S^* = b' \Delta H^* + c' \quad (7)$$

from which the isokinetic temperature

$$T_i = 1/bR \quad (8)$$

respectively

$$T_i' = 1/b' \quad (9)$$

are obtained [13, 14].

Table 1 Kinetic and activation parameters

Symbol*	<i>n</i>	$E_a \cdot 10^{-5}/\text{J mol}^{-1}$	$\ln A$	$\Delta H^* \cdot 10^{-5}/\text{J mol}^{-1}$	$\Delta S^*/\text{J mol}^{-1} \text{K}^{-1}$
PCM15	1.7	2.245	55.34	2.208	203.27
PCM20	1.7	2.020	49.27	1.980	152.54
PCM25	1.7	2.170	54.19	2.135	193.68
PCM30	1.7	3.230	79.93	3.189	407.61
PCS15	1.0	1.480	36.42	1.446	46.14
PCS20	1.0	1.520	36.44	1.485	46.10
PCS25	1.0	1.484	35.06	1.446	34.62
PCS30	1.0	2.330	54.83	2.290	198.65
POM15	1.7	1.866	46.90	1.829	133.173
POM20	1.7	2.197	54.15	2.159	193.33
POM25	1.7	1.681	40.60	1.643	80.40
POM30	1.7	2.429	60.19	2.392	243.60
POS15	1.0	2.148	51.06	2.110	167.45
POS20	1.7	1.926	47.09	1.890	134.46
POS25	1.7	2.211	53.16	2.172	184.83
POS30	1.0	2.101	51.01	2.064	167.35
BCM15	1.3	2.170	53.64	2.132	189.20
BCM20	1.3	2.420	56.73	2.380	214.42
BCM25	1.3	2.210	52.81	2.170	181.97
BCM30	1.3	2.980	69.85	2.940	323.45
BCS15	0.1	0.971	21.22	0.931	-80.74
BCS20	0.1	0.952	21.87	0.951	-74.85
BCS25	0.1	1.140	27.01	1.110	-32.16
BCS30	0.1	1.425	33.75	1.388	23.68
BOM15	1.3	1.660	38.70	1.620	64.40
BOM20	1.3	1.380	32.79	1.340	15.78
BOM25	1.3	1.660	38.68	1.620	64.39
BOM30	1.3	1.993	47.19	1.960	135.23
BOS15	1.3	1.520	35.03	1.480	33.99
BOS20	1.3	1.606	38.91	1.570	66.50
BOS25	1.1	1.476	35.82	1.440	40.97
BOS30	0.9	1.153	27.24	1.120	-30.54

*Significance of the symbols: *P* – copper propionate; *B* – copper butyrate; *C* – carborundum support; *O* – silica support; *M* – mixed sample; *S* – supported sample; number – the concentration of precursor, in mass%

The corresponding values are systematized in Table 2. It is noticeable that by both Eqs (8) and (9) rather the same values of the isokinetic temperatures were obtained.

The differences of T_i for supported precursor and the corresponding mixed samples are related with the support effect [2, 15].

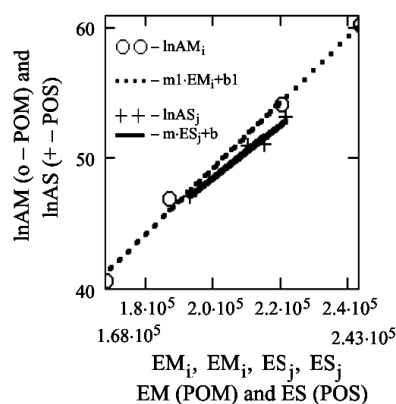


Fig. 1 Compensation effect by POM and POS

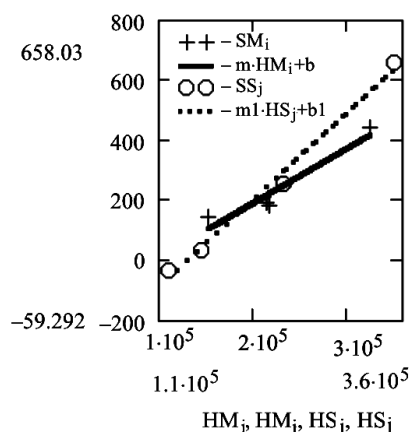


Fig. 2 Compensation effect 25%, + - CM, O - CS

In our case, the relevant observation is on the magnitude of the difference between the isokinetic temperature for the supported sample T_{iS} and that for corresponding mixture T_{iM} , also presented in Table 2. By the samples based on carborundum, these differences are in order of 10 K, while by silica based samples, these differences are in order of 10^2 K. Again, the exception is exhibited by the copper butyrate.

The compensation effect in these series, quantitatively expressed by the isokinetic temperature, suggests a support effect: a strong precursor/support binding (a high ΔH^* value) seems a serious disturbance of the original crystalline sites of the precursor, i.e. a higher positive value of ΔS^* ; the larger aliphatic chain of butyric anion partially screens this phenomenon.

Influence of concentration on the support effect

In order to elucidate the influence of the precursor concentration and of the nature of the carboxyl anion, the kinetic data from Table 1 and from [4] were suitable processed: by

each concentration step, we search after a compensation effect between the ΔH^* and ΔS^* values of the four anions. All copper carboxylate exhibits an obvious compensation effect in ΔS^* vs. ΔH^* diagrams drawn up at different concentrations (Fig. 2). The values of the corresponding isokinetic temperatures are systematized in Table 3.

Table 2 Isokinetic temperatures (T_i) for different sample type

Support	Anion	Sample type	T_i/K from E_a and $\ln A$	T_i/K from ΔH^* and ΔS^*	$\Delta T_i = T_{is} - T_{im}/K$
SiC	Formate [4]	Mixed	463.18	463.30	-10.70
		Supported	452.50	452.50	
	Acetate [4]	Mixed	376.86	377.30	-16.70
		Supported	360.54	360.60	
	Propionate	Mixed	481.30	479.00	50.85
		Supported	533.10	528.90	
	Butyrate	Mixed	571.50	573.00	-11.80
		Supported	462.90	458.90	
SiO ₂	Formate [4]	Mixed	404.00	404.60	102.15
		Supported	506.00	506.90	
	Acetate [4]	Mixed	394.30	393.70	313.90
		Supported	707.15	708.80	
	Propionate	Mixed	473.00	475.57	106.42
		Supported	580.30	581.15	
	Butyrate	Mixed	507.40	516.80	-31.50
		Supported	489.00	481.60	

Table 3 Isokinetic temperatures for different concentration

Concentration/ mass%	Sample type	T_i/K from ΔH^* and ΔS^*	$\Delta T_i = T_{is} - T_{im}/K$	T_i/K from ΔH^* and ΔS^*	$\Delta T_i = T_{is} - T_{im}/K$
		Support SiC		Support SiO ₂	
15	Mixed	542.0	-229.0	206	204
	Supported	313.0		410	
20	Mixed	492.0	-150.6	388	-9
	Supported	341.7		379	
25	Mixed	546.0	-200.0	467	4
	Supported	345.6		471	
30	Mixed	589.5	-269.5	618	-256
	Supported	320.0		359	

For carborundum, the supported samples exhibit rather the same isokinetic temperature (320–340 K) and this is not significantly influenced by the concentration of the precursors. It is also noticeable that the supported samples present a lower value

of the isokinetic decomposition temperature in comparison with the mixed ones. This suggests a significant disturbance of the crystalline situs due to supporting, with the consequence of a lower thermal stability.

By silica a completely different behavior is observed: the concentration of copper carboxylate strongly influences the value of the isokinetic temperatures and that of the differences ΔT_i . At low concentrations, the strong interaction between the support surface and the supported species lead to an increase of the thermal stability, but at too high concentrations, a disturbance lead again to a lower thermal stability.

Conclusions

A compensation effect was observed by non-isothermal decomposition of copper carboxylate precursors. For the explanation of the support effect ΔS^* vs. ΔH^* presents some advantages in comparison to $\ln A$ vs. E_a . Unfortunately ΔT_i is not a 'true' quantitatively measurement of the support effect, but it can act in a satisfactory way as a criterion for the evaluation of the magnitude of the support effect.

The concentration of the precursor is important by the rather active supports (like SiO_2), low concentration allows a very good interaction between the support surface and the precursor molecule. By higher concentration, the mutual interaction between the supported molecules leads to a disturbance and a lower thermal stability.

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