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The effect of the support by the thermal decomposition of some catalyst precursors

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Abstract

The thermal behavior by decomposition in non-isothermal conditions of copper formate and acetate, both supported on carborundum and silica, were studied. Appropriate kinetic treatment of the thermogravimetric curves led to a good estimation of the support effect. The suggestion of considering the thermodynamic activation function instead of the Arrhenius parameters for discussion on compensation effect was argued. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Non-isothermal decomposition; Compensation effect and support effect; Supported catalyst precursors

1. Introduction

The non-isothermal kinetics has been often used to discuss reaction mechanisms [1]. By the supported catalysts, the understanding of the chemical change occurring at the reaction interfaces, with progressive advance into the unchanged reactant, has been emphasized [2,3]. But very seldom lead the kinetic analysis of the decomposition of supported precursors to the intimate reaction mechanism. This is mainly due to limited knowledge of the catalyst surface and of the interactions at the interfaces.

Metal carboxylates are adequate precursors for obtaining supported catalysts, especially due to their low decomposition temperatures. Several studies have been performed on the thermal decomposition behavior of metal acetates [4,5] and a recent study on the kinetics of thermal decomposition of copper acetate is available [6]. But there is a lack of information on the thermal behavior of precursors supported on different materials.

In the present paper, a kinetic analysis of the thermal decomposition of copper formate and acetate supported on carborundum and silica is presented. The existence of a compensation effect was examined. Considering this effect as a real phenomenon, it can be regarded as a support effect [7].

2. Experimental

2.1. Materials

Two supports were used: carborundum, SiC (Carlo Erba) and silica, SiO_2 (Johnson Mattey). The precursors were reagent grade copper formate, $Cu(HCOO)_2\cdot H_2O$ and copper acetate $Cu(CH_3COO)_2\cdot H_2O$.

The supported samples were prepared from aqueous solution of the corresponding carboxylate, into a rotating vacuum evaporator. The concentration steps were 15, 20, 25 and 30 wt.%.

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In order to avoid the effects of thermal gradients and of dilution, comparative samples of mechanical mixtures of support/precursor, with the same concentration, were prepared and studied.

2.2. Non-isothermal experiments

The thermal curves were recorded with a Q Derivatograph (MOM Budapest) in static air atmosphere with the corresponding support as reference compound and Pt crucible.

The sample weight was 300 mg and the heating rate 10 K/min in the range 298–773 K. The Derivatograph was coupled to a PC and a dedicated program processed the TG data, used as input.

3. Results and discussions

3.1. TG diagrams and the decomposition step

In Fig. 1, an example of a TG diagram is given for 30 wt.% $Cu(CH_3COO)_2{\cdot}H_2O$ on SiO_2. For both mixed and supported samples two steps were observed, between 353–381 and 355–378 K, respectively. The first step corresponds to the loss of water. Indeed, for a 300 mg sample with 30% active substance it corresponds to 0.45 mmol of $Cu(CH_3COO)_2{\cdot}H_2O$ and the loss of one molecule of water leads to a theoretical mass variation of 9%.

The data in Fig. 1 indicate a mass loss of 8.7% for AcOS30 and 8.5% for AcOA30. This first decomposition step should be the subject of the kinetic analysis.

The second observed step corresponds to two successive reactions [1]

$$Cu(CH_3COO)_2 \rightarrow CuCO_3 + (CH_3)_2CO$$

$$CuCO_3 \rightarrow CuO + CO_2$$

but at the selected heating rate these processes are not well separated on the TG diagram.

3.2. Kinetic parameters: the thermodynamic functions of the transition state

The TG data (more than 20 points) were used to evaluate the decomposition non-isothermal kinetic parameters by the integral method of Flynn and Wall [8] and Ozawa [9]

$$\ln F(\alpha) = -\frac{1}{RT} + \ln\frac{A}{a} + \ln\frac{E}{R} - 5.33 \qquad (1)$$

with the conversion integral

$$\left.\begin{aligned} F(\alpha) &= \frac{1-(1-\alpha)^{1-n}}{1-n}, \quad && n \neq 1 \\ F(\alpha) &= -\ln(1-\alpha), && n = 1 \end{aligned}\right\} \qquad (2)$$

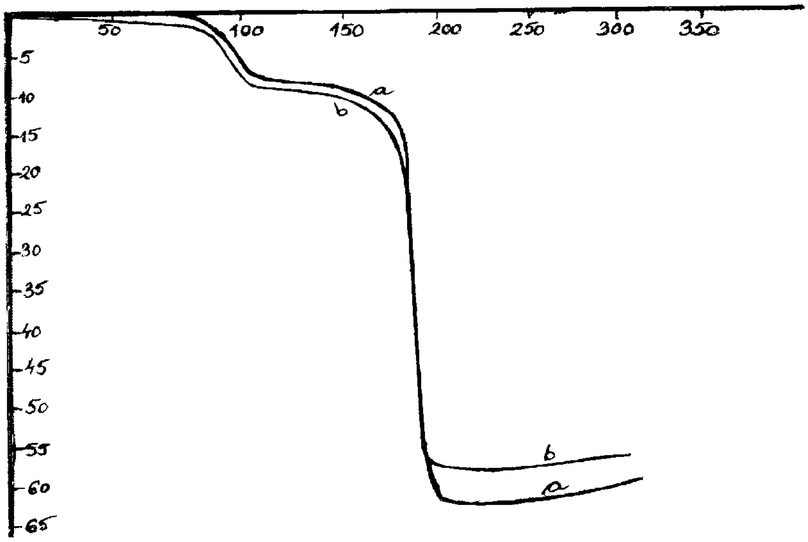

Fig. 1. TG diagram for 30 wt.% $Cu(CH_3COO)_2{\cdot}H_2O$ and SiO_2. (a) AcOA; (b) AcOS.

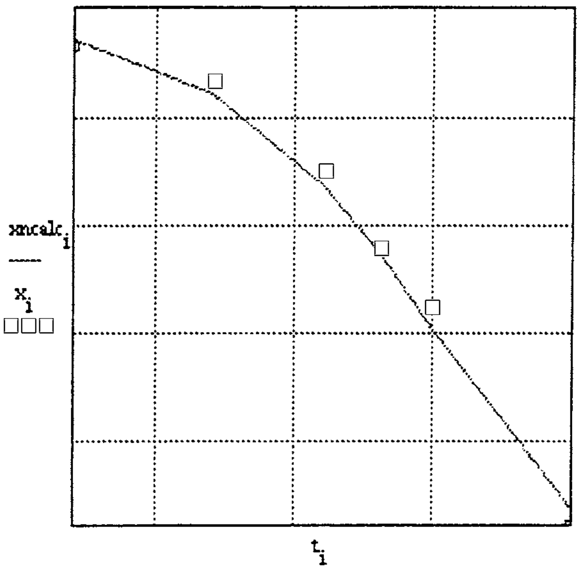

Fig. 2. The simulated □ vs. T curve for AcCA20.

In Eqs. (1) and (2) α is the conversion, a the heating rate, n the reaction order and A, E the Arrhenius kinetic parameters. The values of n, E and A were utilized to simulate the TG curves in coordinates (α, T) and the experimental points are then recorded in the same coordinates. If the points lie on the simulated curve, this confirms the accuracy of the measurement and verifies the correctness of the used integral method. An example of such a representation in given in Fig. 2.

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

$$k = A \exp\left(\frac{-E}{RT}\right) \tag{3}$$

and from the transition state theory [10], the enthalpy ΔH^* and entropy ΔS^* of the transition state have been determined by

$$k = \left(\frac{k_B}{h}T\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \tag{4}$$

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

All the determined parameters, according to Eqs. (1) and (4) 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. All ΔS^* values are positive and larger, indicating that when going from 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.

The values for the reaction order n are rather near to 1.0, corresponding to the loss of small molecules [11,12]. In any case, the majority of the n values are far from $n = 2/3$, the corresponding value for the contracting sphere model [13].

3.3. Compensation effect and isokinetic temperature

By inspecting Table 1, the parallel variation of both $\ln A$ versus E, respectively, ΔS^* versus ΔH^* for each precursor/support pair is a clear observed trend. This phenomenon called "the compensation effect" was first described by Constable [14] and is written as

$$\ln A = bE + c \tag{5}$$

or what it is equivalent to

$$\Delta S^* = b'\Delta H + c' \tag{6}$$

An example of this linear relationship is given in Fig. 3.

The constants b and b' are related [15,16] with the isokinetic temperature, i.e.

$$T_i = \frac{1}{b}R \tag{7}$$

or

$$T_i' = \frac{1}{b'} \tag{8}$$

The corresponding values are systematized in Table 2. It is noticeable that by both Eqs. (5) and (6) the same values of the isokinetic temperatures were obtained.

3.4. The support effect

By differences between the isokinetic temperatures of supported precursor and precursor/support

Table 1
Kinetic and activation parameters

Symbol[a]	n	$E_a \times 10^{-5}$ (J/mol)	ln A	$\Delta H^* \times 10^{-5}$ (J/mol)	ΔS^* (J/mol K)
AcCA10	0.9	1.718	52.07	1.688	177.85
AcCA15	0.9	1.468	45.41	1.439	122.836
AcCA20	0.9	2.209	68.84	2.18	317.506
AcCA25	0.9	1.553	47.91	1.524	143.475
AcCA30	0.9	1.59	48.53	1.56	148.575
AcCS10	2.5	6.534	212.46	6.507	1512
AcCS15	2.5	2.812	90.36	2.783	496.43
AcCS20	2.5	3.566	111.38	3.536	670.96
AcCS25	2.5	3.528	109.82	3.499	658.03
AcCS30	2.5	3.14	98.35	3.108	562.65
AcOA10	0.9	0.452	–	0.4215	−144.13
AcOA15	0.9	1.954	58.67	1.923	232.74
AcOA20	0.9	2.267	68.47	2.236	314.15
AcOA25	0.9	1.783	53.45	1.752	189.295
AcOA30	0.9	1.68	51.61	1.651	174.271
AcOS10	1.3	1.958	60.34	1.928	246.734
AcOS15	1.3	2.437	66.49	2.403	296.811
AcOS20	1.3	1.807	56.59	1.778	215.689
AcOS25	1.3	1.894	58.06	1.865	227.723
AcOS30	1.3	2.147	66.68	2.118	299.516
FCA15	1.1	3.065	80.27	3.031	411.14
FCA20	1.1	3.17	82.22	3.135	427.167
FCA25	1.1	3.275	84.03	3.24	442.15
FCA30	1.1	3.4	91.47	3.365	484.99
FCS15	0.3	1.627	40.63	1.591	81.46
FCS20	0.3	1.525	39.71	1.491	74.08
FCS25	0.3	2.366	61.35	2.331	253.756
FCS30	0.3	2.196	56.70	2.161	215.225
FOA15	0.9	1.934	47.75	1.898	140.44
FOA20	0.9	2.475	63.96	2.44	275.411
FOA25	0.9	2.502	63.24	2.466	269.282
FOA30	0.9	2.621	68.83	2.587	316.052
FOS15	0.9	1.518	39.43	1.484	74.695
FOS20	0.9	1.415	36.25	1.381	45.213
FOS25	0.9	1.285	34.25	1.251	28.8
FOS30	0.9	1.677	43.33	1.643	104.136

[a] Significance of the symbols — Ac: copper acetate; F: copper formate; C: carborundum support; O: silica support; A: mixed sample; S: supported sample and the concentration of precursor, in wt.%.

mixtures, some authors [1,7] related these with a support effect.

In our case, the relevant observation is on the magnitude of the difference between the isokinetic temperature for the support sample T_{iS} and the corresponding mechanical mixture (T_{iA}), as is presented also in Table 2. By the samples based on carborundum these differences are in the order of 10 K, while by silica-based samples, these differences attain 10^2. Unfortunately, this ΔT_{i} parameter is not a ‘‘true’’ quantitatively measurement of support effect, but it can act in a satisfactory way as an evaluation criterion of the magnitude of the support effect.

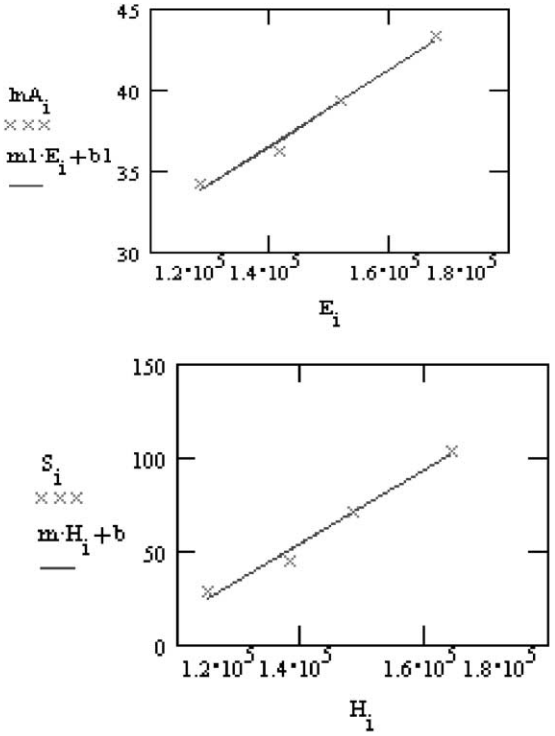

Fig. 3. Compensation effect corresponding to AcOS.

Table 2
Isokinetic temperatures (T_i)

Support	Sample	T_i (K) from E_a and $\ln A$	T_i (K) from ΔS^* and ΔH^*	$\Delta T_i = T_{iS} - T_{iA}$
SiC	FCA	463.18	463.3	−10.7
	FCS	452.5	452.5	
SiO_2	FOA	404	404.6	102.15
	FOS	506	506.9	
SiC	AcCA	376.86	377.3	−16.7
	AcCS	360.54	360.6	
SiO_2	AcOA	394.3	393.7	313.9
	AcOS	707.15	708.8	

4. Conclusions

Kinetic parameters calculated by means of a well-known equation for the non-isothermal decomposition of solids are in a very good agreement with the enthalpy and entropy of the activated complex. This activated complex is generated by an increase of the degrees-of-freedom, as a consequence of exciting appropriate bonds.

A compensation effect was observed for both $\ln A$ versus E and ΔS^* vs. ΔH^* relationships and appropriate values of the isokinetic temperatures were obtained. But for the explanation of this effect, the thermodynamic functions of the activated complex present some advantages. Indeed, the compensation effect can be suggested as support effect; a strong precursor/support bond (a high ΔH^* value) seems a serious disturbance of the original crystalline sites of the precursor, i.e. a higher positive value of ΔS^*.

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