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SOME CRITERIA FOR DECIDING UPON THE SUPPORT EFFECT

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Abstract

Criteris for deciding upon the support effect by the thermal decomposition of precursor/support systems are discussed. Instead of the linear relationship between lg$A$ and E, two new criteria determined by the calculated rate maximum were suggested. Dimensionless criteria based on the rate, conversion and temperature values at the inflexion point of the TG diagram lead to a parameter able to describe the support effect in a synthetic and quantitative manner. The experimental data were the TG-curves for the decomposition of ammonium metavanadate, molybdic acid and ammonium phosphomolybdate, supported on carborundum and silica.

Keywords: dimensionless parameters, discrimination possibilities, non-isothermal kinetics, supported precursors, support effect

Introduction

In non-isothermal kinetics, the compensation effect, i.e. the variation in paralell of E (activation energy) and ln$A$ (pre-exponential factor) is a rather 'normal' phenomenon [1]. By the thermal decomposition of a certain substance deposited on a certain support, the pair values of E and ln$A$ for different concentrations of deposited substance presents the above-mentioned parallelism. In such cases the compensation effect is assigned to a 'support effect' [2, 3].

The present paper deals with argumentations and critical analysis of some criteria for deciding upon a support effect. The suggested criteria were obtained by an adequate processing of the TG-curves, the first and essential step being the determination of the non-isothermal kinetic parameters, i.e. the activation energy, pre-exponential factor and reaction order, respectively. The next step is investigating the compensation effect and the corresponding discussion upon the magnitude of the support effect. In a previous work [4] on the thermal decomposition of some catalyst precursors, the support effect was estimated by the difference of the isokinetic temperature between a supported and a mechanical mixture of a precursor/support pair having the

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same concentration of precursor. Unfortunately, the variation of this parameter was rather insignificant.

Experimental

Ammonium metavanadate (V), molybdic acid (M) and ammonium phosphomolybdate (P) were supported on carborundum (C) and silica (S), respectively, at concentration from 10 to 40 mass%. Parallel samples of mechanical mixtures of the same concentration were studied in order to avoid the effects of thermal gradients. Experimental details and the non-isothermal kinetic parameters were presented in the mentioned previous work [4].

Results and discussion

The kinetic analysis begins with the calculation of the reaction rate (in mg min^{-1}) *vs.* current experimental temperature diagram. The expected maximum at the inflection point of the sigmoid-curve was observed (see some examples in Fig. 1).

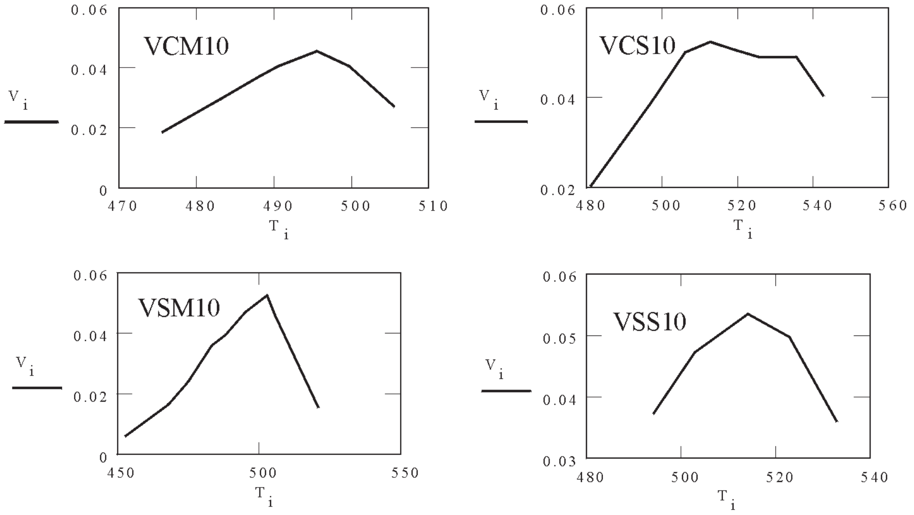

Fig. 1 Calculated diagrams of reaction rate (mg min^{-1}) *vs.* temperature (example)

The dependence of this maximum *vs.* concentration of precursor is presented in Fig. 2. A rather insignificant variation is observed, with the exception of an important rise in the range of 15–20 mass%. This suggests a potential descriptive ability of the r_{max} in respect of the support effect. The significance of the maximum of a rate *vs.* temperature diagram in respect of the kinetic parameters determined by non-isothermal methods is theoretical analyzed as follows.

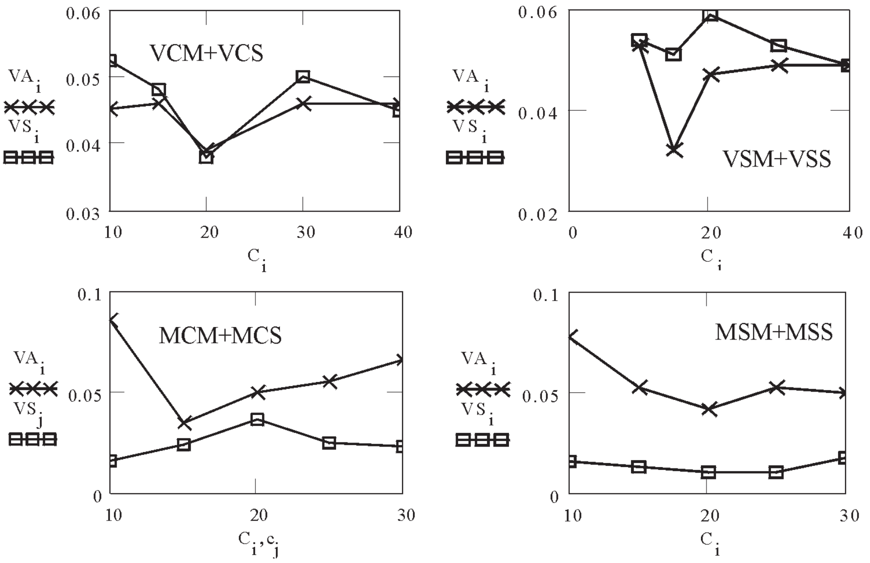

Fig. 2 Reaction rate maximum (mg min^{-1}) *vs*. precursor concentration (%)

For the reaction rate of thermal decomposition in non-isothermal conditions we consider:

$$r = k(1-\alpha)^n \tag{1}$$

where k – rate constant, α – conversion and n – reaction order.

With the reaction rate

$$r = \mathrm{d}\alpha/\mathrm{d}t \tag{2}$$

and a constant heating rate

$$\beta = \mathrm{d}T/\mathrm{d}t \tag{3}$$

Equation (1) became

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} e^{-E/RT} (1-\alpha)^n \tag{4}$$

where k follows the Arrhenius formalism.

For the maximum of the rate *vs*. temperature diagram, i.e. $(\mathrm{d}r/\mathrm{d}T)=0$ or $(\mathrm{d}^2\alpha/\mathrm{d}T^2)=0$ it results:

$$r_{\max} = \frac{\beta}{n}(1-\alpha_{\max})\frac{E}{RT_{\max}^2} \tag{5}$$

The connection between the three values of the inflection point, i.e. $r_{\max}$, $\alpha_{\max}$ and $T_{\max}$, suggests a dimensionless criterion

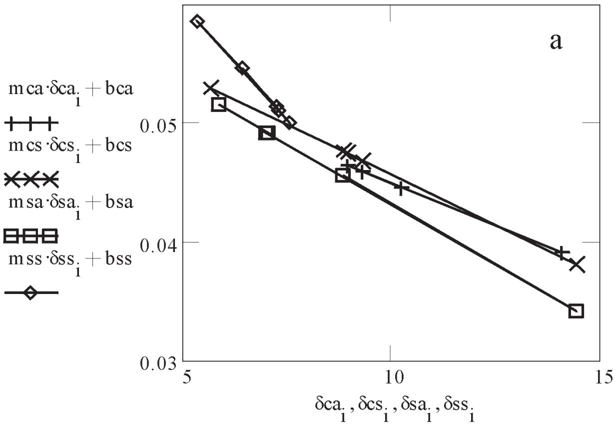

Fig. 3a Reaction rate maximum *vs*. δ parameter for ammonium metavanadate

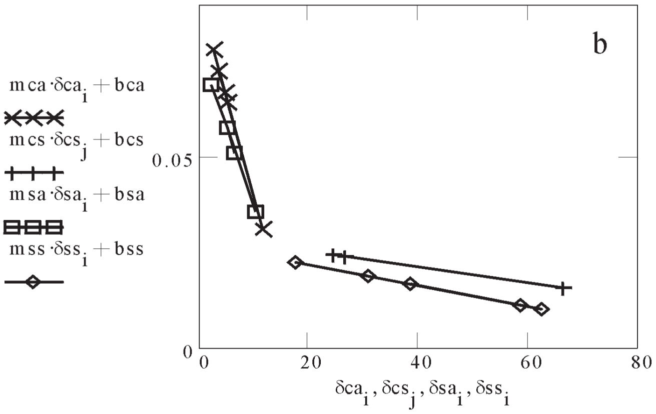

Fig. 3b Reaction rate maximum *vs*. δ parameter for molybdic acid

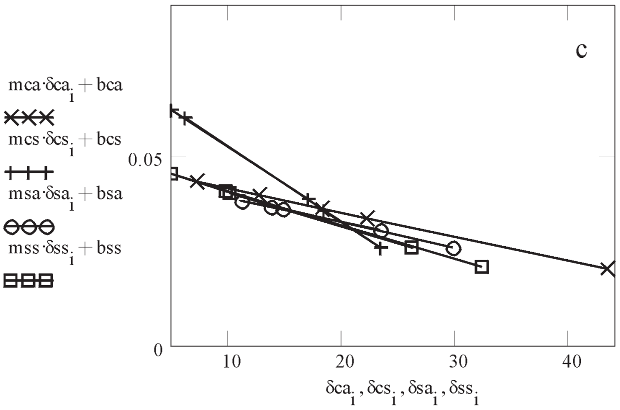

Fig. 3c Reaction rate maximum *vs*. δ parameter for ammonium phosphomolybdate

Table 1 Presentaion of synthetical γ parameter

Precursor	Symbol	Support	Type of sample	Conc./ mass%	$\lvert\gamma\cdot 10^3\rvert$	Symbol	Support	Type of sample	Conc./ mass%	$\lvert\gamma\cdot 10^3\rvert$
Ammonium metavanadate	VCM10	SiC	mixed	10	1.0	VCS10	SiC	supported	10	0.89
	VCM15			15	1.0	VCS15			15	1.0
	VCM20			20	1.0	VCS20			20	1.0
	VCM30			30	0.9	VCS30			30	0.9
	VCM40			40	0.9	VCS40			40	1.0
	VSM10	SiO_2	mixed	10	0.95	VSS10	SiO_2	supported	10	2.0
	VSM15			15	1.1	VSS15			15	2.0
	VSM20			20	1.0	VSS20			20	2.0
	VSM30			30	1.0	VSS30			30	2.0
	VSM40			40	1.0	VSS40			40	2.0
Molybdic acid	MCM10	SiC	mixed	10	2.5	MCS10	SiC	supported	10	0.38
	MCM15			15	3.0	MCS15			15	0.30
	MCM20			20	3.0	MCS20			20	0.35
	MCM25			25	3.0	MCS25			25	0.33
	MCM30			30	3.0	MCS30			30	0.35
	MSM10	SiO_2	mixed	10	2.5	MSS10	SiO_2	supported	10	0.42
	MSM15			15	2.5	MSS15			15	0.40
	MSM20			20	3.0	MSS20			20	0.45
	MSM25			25	2.5	MSS25			25	0.43
	MSM30			30	3.0	MSS30			30	0.40
Ammonium phosphomolybdate	PCM10	SiC	mixed	10	0.79	PCS10	SiC	supported	10	1.0
	PCM15			15	0.79	PCS15			15	2.0
	PCM20			20	0.14	PCS20			20	3.0
	PCM25			25	0.73	PCS25			25	2.0
	PCM30			30	0.39	PCS30			30	1.0
	PSM10	SiO_2	mixed	10	0.58	PSS10	SiO_2	supported	10	0.96
	PSM15			15	0.43	PSS15			15	0.56
	PSM20			20	0.49	PSS20			20	0.28
	PSM25			25	0.11	PSS25			25	1.0
	PSM30			30	0.61	PSS30			30	0.76

$$\delta = \frac{E}{RT_{\max}^2}\frac{\beta\alpha_{\max}}{r_{\max}} \tag{6}$$

Descriptive ability of two new criteria

The descriptive ability of the criterion δ is presented in Fig. 3 as a linear relation

$$r_{\max} = m\delta + b \tag{7}$$

The slope m is a good descriptor of the support effect: the three precursors present two different values for m, depending on the support type; that on corresponding to carborundum has approximately the same values.

By means of slope m, another criterion is suggested:

$$\gamma = \frac{mE\beta}{RT_{\max}^2} \tag{8}$$

Table 1 shows the values of γ for all the studied samples. The independence of γ *vs*. concentration is remarkable. At the same time it is a significant difference between γ values for mechanical mixtures, respectively for the supported samples. It suggests the possibility for describing the support effect in a synthetic and quantitative manner.

Conclusions

- The kinetic analysis of thermogravimetric data evidences a support effect by the thermal decomposition of ammonium metavanadate, molybdic acid and ammonium phosphomolybdate supported on carborundum and silica. Parallel studies on mixed and supported samples of the same concentration in active substances are necessary in order to avoid the major influences of dispersion and temperature gradients.
- The calculated maximum of the reaction rate leads to some criteria with better descriptive ability than the linear dependence between ln$A$ and E. These two parameters currently present a compensation effect, so that a calculated rate *vs*. temperature diagram is near to the kinetics of the decomposition reaction. By the kinetic analysis a vey good fitting between the simulated conversion *vs*. temperature curves and the experimental points are also necessary.
- The dimensionless parameter δ is a descriptor of rate maximum for the same precursor/support pair; the derived γ parameter is a quantitative descriptor of the support influence.

This criterion is based on the values of rate, conversion and temperature at the inflexion point of the simulated conversion *vs*. temperature diagram, i.e. at the point of maximum of the reaction rate. The derived γ parameter is a quantitative descriptor of the support influence.

The independence of γ values *vs*. concentration and the significant variation from mixed to supported series of samples are arguments for considering them a synthetic descriptor of the support effect.

- For a satisfactory acceptance of the suggested parameters, data on thermal behaviour of some other precursor/support system are necessary.

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