

## The thermogravimetric analysis of nanoporous carbon materials used as effective catalyst carrier

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The main purpose of thermogravimetric study of the synthesized and the initial samples of nanoporous carbon materials was to establish their thermal stability and to obtain when possible mathematical relationships that describe them.

The studies were conducted on derivatograph of Hungarian company Paulik under the following conditions: weight ranged between 50–100 mg, channel sensitivity: 1 mV, heating rate: 10 °C/min, maximum temperature: 900 °C.

Kinetic calculations were performed according to the method described in the literature [1–3, 7] with the software implementation [4, 8]. Methods of non-isothermal kinetics that were employed for the calculations enabled to use data from one study of non-isothermal thermogravimetric (derivatographic) analysis to calculate kinetic constants of chemical processes, which were accompanied by a change in the mass [1].

In the isothermal studies, environmental temperature and temperature of the sample is always different, thus there is a sample quasistationary temperature field, particularly in case of low temperature rise rate. Quasistationary temperature field makes it possible to take (to a first approximation) that the temperature of the sample increases linearly. Deviation of the actual sample temperature from the expected value is due to self-heating and auto refrigeration of the sample.

For non-isothermal process, the conversion can be calculated by the following formula [2]:

$$x = \frac{G_0 - g}{G_0 - G_\infty}, \quad (1)$$

where  $g$  – factor to measure the properties of time, mg;  $G_0$ ,  $G_\infty$  – initial and final value.

In most cases weight loss is used as a  $G$  (weight loss is calculated from the TG curve), since this parameter can be determined with sufficient accuracy from the derivatograms.

In isothermal conditions, the rate of decomposition of the process is:

$$W = \frac{dx}{d\tau} = k_0 \exp(-E/RT) \cdot f(x) \quad (2)$$

$t$  – time, s;

$k_0$  – pre-exponential factor, 1/s;

$E$  – activation energy, J/mol;

$R$  – universal gas constant,  $R = 8,31$  J/mol K;

$T$  – temperature, K;

$f(x)$  – concentration of the kinetic equations, dimensionless.

In non-isothermal conditions at a temperature linear increase  $T = T_0 + q \cdot t$  and  $dT = q \cdot dt$ , where  $q$  – heating rate, K/sec. We get  $dt = dT / q$ , and the equation (1.2) takes the form as follows:

$$W = \frac{dx}{dT} = \frac{k_0}{g} \exp(-E/RT) \cdot f(x) \quad (3)$$

In this paper we used the differential method to determine the function  $f(x)$ .

Hereinafter, the algorithm [5] of experimental data processing, calculating of  $E$ ,  $k_0$  and kinetic constants is to approximate the dependence  $x = f(T)$  by a cubic spline function with subsequent differentiation. As a result we receive the experimental values of the process rate  $W = dx / dT$ . After this, we arrange arrays to search for the kinetic constants with provision for the form of the function  $f(x)$ , which was deployed as the most used expressions [7]. We calculate the kinetic constants and perform statistical analysis of the results.

Calculated data for activation energy and reaction order for the non-isothermal process in the first approximation can be used as process characteristics.

This algorithm was implemented in BASIC language, and calculations were performed on IBM PC / XT computer.

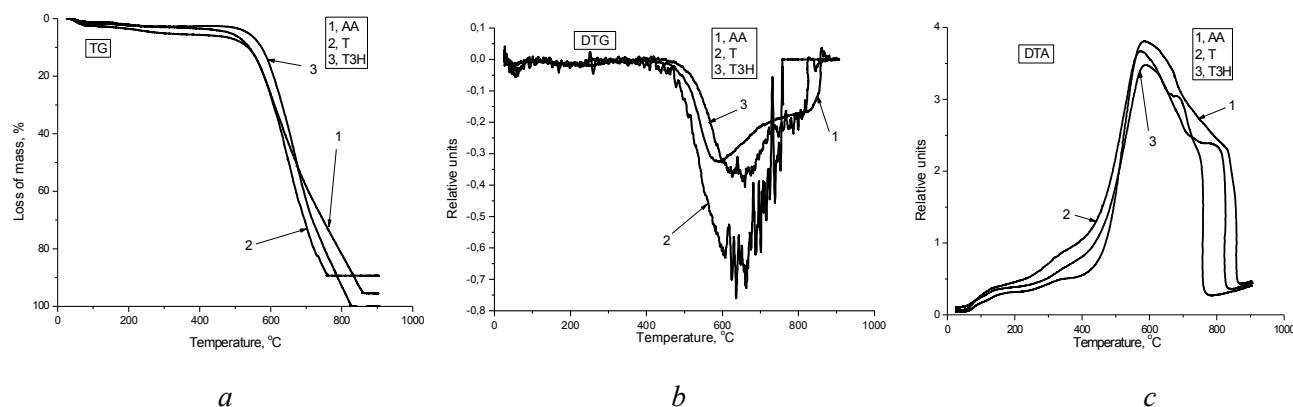
The ECM allowed to achieve high accuracy in calculation of rate  $W$ , which is a remarkable aspect when employing a differential method. Thus, the employed version of the differential method compares favorably with the integral method [9].

Analysis of the mechanisms and kinetics of the reaction equations of solids was taken from the literature [7].

In this paper we study the thermal stability of the raw carbon materials. Research results of thermogravimetric analysis of activated anthracite AA, nanoporous carbon materials T and T3H are shown in Fig. 1.

Thus, up to 100 °C, loss of water adsorbed on the surface of the carrier occurs as evidenced by a small area of the peak. This fact is most clearly reflected in the differential thermogravimetric curves (DTG) (fig. 1, b).

In this temperature range the maximum weight loss is



**Fig. 1.** Thermogravimetric analysis curves samples AA, T, T3H: *a* – thermogravimetric analysis (TG), *b* – derivative thermogravimetric analysis (DTG), *c* – differential thermal analysis (DTA)

from 3% for T3H to 8% for activated anthracite (fig. 1, *a*). Kinetic reaction rate calculations in this temperature range were performed by equation 4 for the sample of activated anthracite, by equation 5 – for the T sample and by equation 6 – for the T3H sample.

$$W = 0,76 \cdot \exp(-11492/8,31T) \cdot (1-x)^{0,1} \quad (4)$$

$$W = 1,73 \cdot \exp(-21375/8,31T) \cdot (1-x)^{0,25} \quad (5)$$

$$W = 0,97 \cdot \exp(-17513/8,31T) \cdot (1-x)^{0,17} \quad (6)$$

After the kinetic study of the temperature range 500–850 °C (500–750 °C for T), we obtained kinetic equation 7 for the activated anthracite sample, equation 8 – for the T sample and equation 9 – for the T3H sample.

$$W = 3,7 \cdot 10^{-2} \exp(-52734/8,31T) \cdot \frac{(1-x)^{1,2}}{1-(1-x)^{2/3}}; \quad (7)$$

$$W = 4,8 \cdot 10^{-1} \exp(-127541/8,31T) \cdot \frac{(1-x)^{1,7}}{x^{0,7}}; \quad (8)$$

$$W = 5,37 \cdot 10^{-1} \exp(-158371/8,31T) \cdot \frac{(1-x)^{1,25}}{x^{0,25}}. \quad (9)$$

The coefficient of multiple correlation is 0.9777 for all the resulting equations, which makes these equations valid.

Based on type (4–6) equations and the received activation energies, it can be affirmed that within the temperature range up to 500 °C a simple diffusion process takes place, as indicated by the values of the reactions order (0.1–0.25) and by the values of the activation energies. Based on type 7 equation, the activation energies and the reaction order, it can be affirmed that a topochemical process that forms degradation centers on the surface (the set of “points”, such as defects in the structure) takes place in the T sample within the temperature range 500–750 °C. The situation is similar for the T3H sample and the activated anthracite sample. Based on type (8–9) equations, values of the reactions order and the activation energies, it can be affirmed that a dimensional topochemical process takes place in the samples within the temperature range 500–850 °C. Such

topochemical processes are typical for the processes that occur over the entire surface, not only at the “points”.

According to the thermogram, maximum destruction of the surface functional groups occurs continuously with exothermic effect within the temperature range 500–750 °C for T and 500–850 °C for T3H and activated anthracite (fig. 1, *a*). Within these temperature ranges, the main weight loss of the samples occurs: 85% for the T sample, 97% for the T3H sample and 87.5% for the activated anthracite sample. With further increase in temperature to 900 °C, equalization of the residual mass values is observed for the T sample at the level of 10.3% and for the activated anthracite sample at the level of 4.5%. No residual mass equalization is observed for the T3H sample since at 850 °C it becomes completely destroyed.

The conducted thermogravimetric studies suggest that T, activated anthracite and T3H are thermally stable within the temperature range up to 500 °C. If temperature exceeds 500 °C, full thermal degradation of the main matrix of T, T3, activated anthracite, and degradation of surface functional groups take place. Besides, it was found that the activated anthracite sample and the T sample contain a mineral component, which is thermally stable.

Furthermore, we studied thermal resistance of the activated anthracite samples, the T and the T3H samples modified with Ni metal with different mass fractions of metal. We performed kinetic reaction rate calculations. The results of thermogravimetric studies of activated anthracite, T and T3H are shown in Fig. 2.

Having performed the kinetic studies, we received the following relationship:

for AA with 1% (wt.) Ni in the range of 20–500 °C

$$W = 3,76 \cdot 10^{-4} \exp(-21573/8,31T) \cdot (1-x)^{0,97}; \quad (10)$$

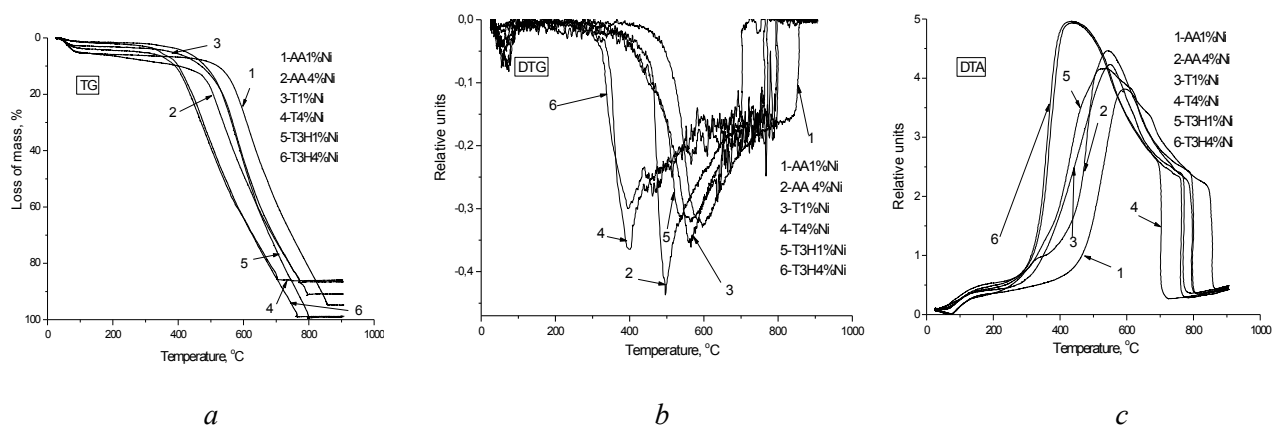
in the range 500–850 °C

$$W = 5,27 \cdot 10^{-2} \exp(-185270/8,31T) \cdot \frac{(1-x)^{2,8}}{1-(1-x)^{1/3}}; \quad (11)$$

for AA with 4% (wt.) Ni in the range of 20–450 °C

$$W = 3,27 \cdot 10^{-4} \exp(-20375/8,31T) \cdot (1-x)^{0,91}; \quad (12)$$

in the range of 450–850 °C



**Fig. 2.** Thermogravimetric analysis curves samples AA, T, T3H different metal Ni content: *a* – thermogravimetric analysis (TG), *b* – derivative thermogravimetric analysis (DTG), *c* – differential thermal analysis (DTA)

$$W = 5,28 \cdot 10^{-2} \exp(-201573/8,31T) \cdot \frac{(1-x)^{2,7}}{1-(1-x)^{1/3}}; (13)$$

for T and T3H from 1.25 and 1% (wt.) Ni in the range of 20–750 °C and 20–800 (equation 14–15), with a 4% (equation 16–17):

$$W = 1,36 \cdot 10^2 \exp(-576327/8,31T) \cdot \frac{(1-x)^{2,9}}{1-(1-x)^{1/3}}; (14)$$

$$W = 0,37 \cdot 10^1 \exp(-125310/8,31T) \cdot \frac{(1-x)^{1,3}}{1-(1-x)^{1/3}}; (15)$$

$$W = 2,32 \cdot 10^2 \exp(-637521/8,31T) \cdot \frac{(1-x)^{3,7}}{1-(1-x)^{1/3}}; (16)$$

$$W = 2,37 \cdot 10^1 \exp(-183542/8,31T) \cdot \frac{(1-x)^{1,9}}{1-(1-x)^{1/3}}. (17)$$

The coefficient of multiple correlation is 0.9793 for all the equations obtained, which allows us to consider them reliable.

The results of analysis of the thermogravimetric curves have scarcely changed both for the initial AA and for the Ni-coated AA sample (equation 4, 9 and 10–13). At the same time, according to type (14–17) equations, values of the reactions order and the activation energies, it can be affirmed for all the T samples and the T3H samples coated with Ni that within the entire temperature range a complicated topochemical process occurs. Such process is characteristic of the processes that occur over the entire surface, not only at the “points”. In other words, we can say that the

**Table 1. Thermographic study samples AA, T and T3H**

Sample	Temperature range of mass loss, °C	E – activation energy, J/mol	Reaction order
AA	20–500	11.49	0.10
	500–850	52.73	1.20
T	20–500	21.38	0.25
	500–750	127.54	1.70
T3H	20–500	17.50	0.17
	500–850	158.37	1.25

destruction of these materials takes place uniformly according to the mechanism. The fact that favorably compares our artificially created monoporous carbon material T with the natural anthracite is that when used as a catalyst, the artificial carbon material T will most likely ensure a stable process flow. Besides, due to the presence of active metal on the surface, the degradation temperature ranges have changed. The destruction temperature range remained unchanged only for activated anthracite with mass fraction of 1% Ni. However, on the DTA curve, the second peak of the destruction became more distinct at 650–700 °C, which is caused by the influence of the active metal during destruction of the functional groups on the surface of the carrier and by changes in the mechanism of destruction of the main carrier matrix. This is confirmed by the data from Fig. 2 and kinetic equations 10 and 11. Increasing the nickel content up to 4% by weight, accelerates the oxidation reaction of the anthracite surface with its subsequent destruction. The destruction begins at 450 °C (Fig. 2 and Tab. 2)

**Table 2. Thermographic study samples AA, T, T3H coated with Ni**

Sample	Temperature range of mass loss, °C	E – activation energy, J/mol	Reaction order
AA 1 % (wt.) Ni	20–500	21.57	1.10
	500–850	185.27	2.80
AA 4 % (wt.) Ni	20–450	20.37	1.20
	450–850	201.57	2.70
T 1.25 % (wt.) Ni	20–750	576.33	2.90
T 4 % (wt.) Ni	20–750	637.52	3.70
(wt.) Ni	20–800	125.31	1.30
T3H 3 % (wt.) Ni	20–800	183.54	1.90

instead of 500 °C for the initial sample (Fig. 1 and Table 1) and completes at 800 °C instead of 850 °C for the initial sample (Fig. 2). Noteworthy, the increase in Ni mass fraction leads to increase in the residue after degradation. For the initial activated anthracite, the residue after degradation made up 4.5%, for 1% Ni – 5.2%, for 4% Ni – 9.1%. Deduction of the residue of the former reveals values that are close to Ni mass concentrations on the carrier, namely 0.1 for 7% Ni and 4.6 for 4% Ni. Thus, mass concentration of the metal in the sample can be accurately determined from the difference in residue of carbon material with metal and carbon material as it is.

The relationships similar to those that exist for activated anthracite with Ni are observed for T and T3H, however there are some differences. Unlike activated anthracite with mass fraction of 1% Ni, the shift of the destruction onset temperature from 500 °C to 450 °C occurs on the T sample with mass fraction of 1.25% Ni and on the T3H sample with mass fraction of 1% Ni (Figure 1, 2), while the destruction completion temperature remains unchanged for the T sample and decreases down to 800 °C for the T3H sample. Further increase in metal content on the T sample and on the T3H sample to 4% (wt.) contributes to the fact that destruction of the carbon surface takes place within the range of 350–700 °C (Fig. 2, a). This indicates that the carrier structure influences the metal activity in the reaction of the carrier surface oxidation.

1. Зедгинидзе И.Г., *Планирование эксперимента для исследования многокомпонентных систем*, Москва, Наука, 1976, 390.

2. Шестак Я., *Теория термического анализа: Физико-химические свойства неорганических веществ: Пер. с англ.*, Москва, Мир, 1987, 456.

3. Астрелин И.М., Концевой А.Л., Манчук Н.М., Костенко А.Б., *Синтез фторгидроксидкарбонатапатитов и расчет кинетических параметров их термолитиза*, *ЖНХ*, **34** (10), 1989, 2587–2592.

4. Костенко А.Б., Концевой А.Л., Астрелин И.М., *Журн. прикл. химии*, 1996, **69** (3), 382–385.

5. Кримець Г.В., Кримець Г.В., Астрелін І.М. та ін., *Наукові вісті НТУУ "КПІ"*, (2), 2009, Київ, Політехніка, 2009, 130–134.

6. Ахназарова С.Л., Кафаров В.В., *Оптимизация эксперимента в химии и химической технологии*, Москва, Высшая школа, 1978, 319.

7. Браун М., Доллимор Д., Галвей А., *Реакции твердых тел*, Москва, Мир, 1987, 360.

8. Эберт К., Эдерер Х., *Компьютеры. Применение в химии*, Москва, Мир, 1988, 416.

9. Zsaco J., *J. Phys. Chem.*, 1968, **72** (7), 2406–2411.

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## Термогравіметричні дослідження нанопоруватих вуглецевих матеріалів, що використовуються в якості ефективних носіїв каталізаторів

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Основною метою проведення термогравіметричних досліджень синтезованих та вихідних зразків нанопоруватих вуглецевих матеріалів було встановлення їх термічної стійкості і по можливості отримання математичних залежностей, які їх описують.

## Термогравиметрические исследования нанопористых углеродных материалов, используемых в качестве эффективных носителей катализаторов

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Основной целью проведения термогравиметрических исследований синтезированных и исходных образцов нанопористых углеродных материалов было установление их термической устойчивости и по возможности получения математических зависимостей, которые их описывают.