

## STUDY OF ACTIVE CARBON NICKEL CATALYSTS IN PRESENCE OF AIR BY MODIFIED DTA CURVES

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DTA and TG curves from investigations on the oxidation of active carbon-nickel catalysts in a static air atmosphere with a derivatograph were used to construct modified DTA curves, the  $\Delta T/m_R$  plots (where  $m_R$  is the reactive mass of the sample). The  $\Delta T/m_R$  plots in the range from 200 to 850° led to the finding that the oxidation process is a two-stage reaction. In the diffusion region the reaction depends on the pore volume with pore radii from 75 to 7500 nm. The variations in the ignition temperature with the nickel content of the samples are presented.

It has been established that the presence of catalytic impurities in carbon accelerates the rate of the oxidation reaction. Consequently, this implies changes in the ignition temperature of the carbon. As pointed out by Dollimore and Jones [1], the ignition temperatures of carbons decrease with increase of the impurity content. This may be used to measure the reactivity of carbon. It is obvious that ignition results from the oxidation reactions occurring in the lower range of temperature. Generally, the mechanisms of these reactions depend on the carbon reactivity, the natures and reactivities of the catalytic impurities, the natures of the bonds between the carbon and the inorganic species, and the porous structures of the samples.

In the present paper, thermal studies of active carbons impregnated with various amounts of nickel have been carried out in terms of the oxidation reaction in the temperature range from 20 to 1000°. The usefulness of the  $\Delta T/m_R$  curves for the investigation of the active carbon – nickel catalysts in the presence of air has been considered.

### Experimental

Active carbon (after activation by steam) produced by the Polish firm ZEW Racibórz (the trade-name of the product is Depolaryt D) was sieved and the fraction ranging in particle size from 75 to 250  $\mu\text{m}$  in diameter was chosen. The active carbon was next divided into four groups: A-6/2, A-6/2–1, A-6/2–2 and A-6/2–3. Sample A-6/2 was subjected directly to the process of secondary activation, in contrast to the remaining samples, which were impregnated with aqueous solu-

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Table 1

Chemical compositions of the samples corresponding to the exothermic DTA maximum  $T_{\max}$  and the ignition temperature  $T_i$

Sample	Nickel content, wt %	Ash, wt %	Elemental analysis, wt. %					DTA exotherm, $T_{\max}$ °C	Ignition temp., $T_i$ , °C
			C	H	N	S	O diff.		
A-6/2	0.00	7.9	91.0	0.95	1.00	0.53	6.5	550	430
A-6/2-1	1.03	8.9	92.85	0.85	1.03	0.44	4.8	530	400
A-6/2-2	2.74	10.6	92.65	0.90	1.05	0.54	4.9	490	370
A-6/2-3	5.25	14.2	91.1	1.17	1.11	0.52	6.1	440	340

tions of  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  before the activation process. The aqueous solutions contained different amounts of the nickel salt (Table 1). All air-dried samples were activated in a stationary bed with carbon dioxide at  $600^\circ$  for 2 hours. The physicochemical properties of the samples after the process of activation are listed in Tables 1 and 2. The total porosity of each sample was determined by means of the helium adsorption method. The volume distribution of the pores and the mercury porosity in the radius range from 7.5 to 7500 nm were determined with a Carlo-Erba Ag-65 mercury porosimeter. For the reasons considered in the earlier papers [2, 3] the pore size ranges studied were divided into three groups, involving the following pore radii:

$$\begin{aligned} 7.5 \text{ nm} &\leq r_1 < 75 \text{ nm} \\ 75 \text{ nm} &\leq r_2 < 750 \text{ nm} \\ 750 \text{ nm} &\leq r_3 < 7500 \text{ nm} \end{aligned}$$

Before the measurements mentioned above, the samples were dried at  $105^\circ$ .

Table 2

Porosity data on the samples

Sample	Helium porosity, $V_{\text{He}}$ cm <sup>3</sup> /g	Mercury porosity, $V_{\text{Hg}}$ cm <sup>3</sup> /g	Pore radius range		
			7.5–75 nm	75–750 m	750–7500 nm
			Pore volume		
			$V_1$ cm <sup>3</sup> /g	$V_2$ cm <sup>3</sup> /g	$V_3$ cm <sup>3</sup> /g
A-6/2	0.223	0.105	0.020	0.031	0.054
A-6/2-1	0.200	0.069	0.025	0.022	0.022
A-6/2-2	0.201	0.087	0.017	0.030	0.040
A-6/2-3	0.292	0.170	0.019	0.044	0.107

The thermal studies were made with a MOM OD-102 derivatograph. Sample holders consisting of five platinum plates were used for both the samples and a reference substance. The two were uniformly distributed on each plate. In this way a uniform supply of air to the sample particles was ensured. The experimental conditions of the analysis were as follows: sample weight: 500 mg, heating rate  $5^\circ/\text{min}$ , final temperature  $1000^\circ$ , reference substance  $\alpha\text{-Al}_2\text{O}_3$ . The  $\Delta T = 0$  curve was produced when two sample holders (for both the sample and the inert material) contained  $\alpha\text{-Al}_2\text{O}_3$ . The ignition temperature was taken as the extrapolated onset of the exothermic DTA peak.

### Results and discussion

In an earlier paper [4] it was pointed out that important information on the oxidation mechanism of carbons might be acquired if the temperature difference  $\Delta T$  taken from the DTA curves was related to the mass  $m_R$  of the sample reacting with air at the given temperature (details in Fig. 1). This method takes into account the

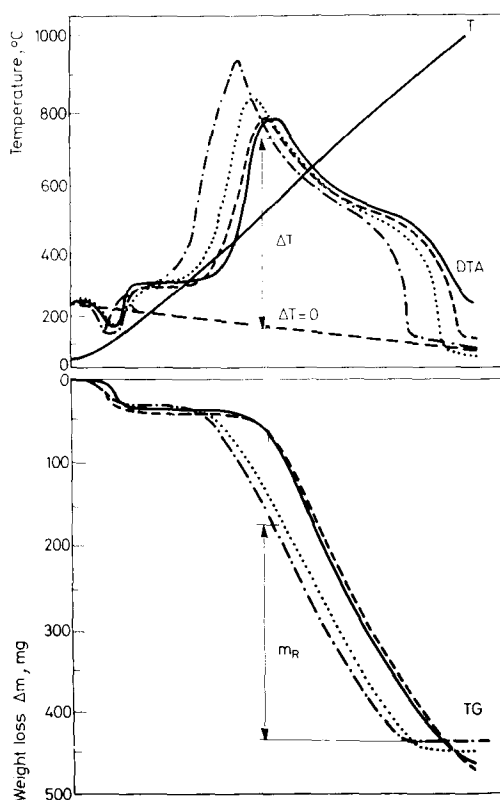


Fig. 1. TG and DTA curves of the samples. — A-6/2; - - - A-6/2-1; ..... A-6/2-2; - . - . - . A-6/2-3

diminution of the sample weight during the oxidation process. The  $\Delta T/m_R$  curves are shown in Fig. 2.

Heating of the samples in a static air atmosphere causes the water evaporation demonstrated by the endothermic DTA peak at  $100^\circ$  (Fig. 1). In the region of  $200^\circ$  the catalysts begin to sorb oxygen, mainly on the outer surfaces of the grains. This process is accompanied by solid-state diffusion [5] into the carbon mass, and also

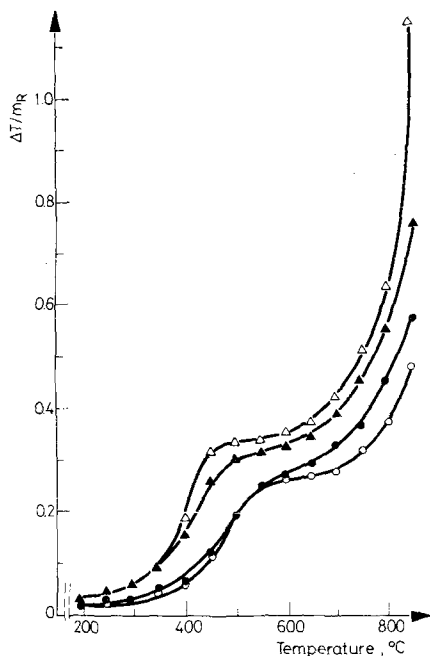


Fig. 2.  $\Delta T/m_R$  curves of the samples ● A-6/2; ○ A-6/2-1; ▼ A-6/2-2; ▽ A-6/2-3

by some degree of desorption of carbon-oxygen complexes from the surfaces. The reactions in this temperature region are controlled by the oxygen chemisorption. With increase in the temperature, the rate of liberation of carbon-oxygen complexes becomes more rapid. However, since heat is liberated least easily from the inside of the carbon grains, the temperature is raised and ignition takes place. The extrapolated onset of the DTA and the  $\Delta T/m_R$  curves is taken as the ignition temperature  $T_i$  (Table 1). With further increase in the temperature, the burning undergoes an acceleration, which is indicated by increases in the DTA and  $\Delta T/m_R$  curves. Simultaneously, the commencement of weight loss is observed in the TG curves. The DTA peak maximum ( $T_{max}$ ) corresponds to the curvature in the  $\Delta T/m_R$  plot, and may be attributed to the highest reaction rate [6].

As may be seen in Table 1 and Figs 1 and 2, the  $T_i$  and  $T_{max}$  values decrease as the nickel content in the samples increases.

Considerable difficulties in interpretation of the DTA curves are encountered when the  $T_{\max}$  value is overstepped. The  $\Delta T$  values decrease, although a rapid weight loss is visible in the TG curves. This contradiction may be resolved when the  $\Delta T/m_R$  curves are plotted. During the rapid oxidation, diminution of the reactive mass occurs, with ash formation on the carbon grains. Moreover, after the DTA maximum the exothermic process is accompanied by the endothermic reactions of carbon decomposition [4]. These phenomena cause the diminution of the exothermic effects recorded in the DTA curves. On the other hand, the  $\Delta T/m_R$  curves, as specific exothermic effects related to unit reactive mass of the sample,

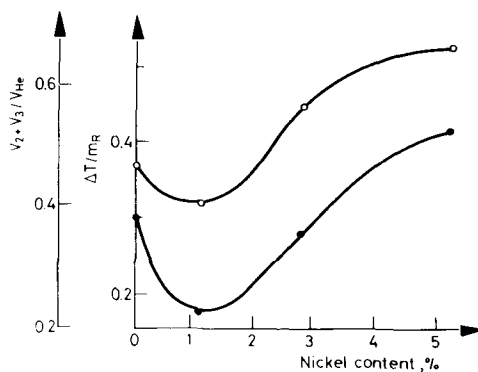


Fig. 3.  $\Delta T/m_R$  and  $V_2 + V_3/V_{He}$  as functions of the nickel content of the samples. ○  $\Delta T/m_R$ ;  
●  $V_2 + V_3/V_{He}$

pass into plateaux over the  $T_{\max}$  value (the DTA peak). This area may be attributed to the retardation of oxygen diffusion down the catalyst pores, caused by rapid release of the carbon oxides. Due to the static atmosphere of air used in these experiments, it is more difficult for the oxides to be released from the inside of the catalysts. Moreover, the access of oxygen down the pores is increasingly restricted. However, after some time, with the rise in temperature the diffusion of oxygen down the pores increases again; this corresponds to the exponential development of the  $\Delta T/m_R$  curves. It may be seen that, over the  $T_{\max}$  value, the  $\Delta T/m_R$  curves develop in the opposite direction to the DTA ones (Figs 1 and 2). It is beyond any doubt that the diffusion of oxygen down the pores depends on the porosity spectrum. In the present paper attempts were made to investigate the influence of the volume of pores having various radii on the oxidation process in the diffusion region. Figure 3 shows a comparison of the  $\Delta T/m_R$  values (chosen arbitrarily for  $750^\circ$ ) with the ratio of the pore volume in the radius range from 75 to 7500 nm to the total porosity determined by helium adsorption, as functions of the nickel content. Both the  $\Delta T/m_R$  and the  $V_2 + V_3/V_{He}$  functions follow the same trend with increase of the nickel content. This comparison allows the finding that the modified DTA curves produced during oxidation of the active carbon-nickel catalysis would yield an intermediate assessment of the sample reactivity in the

diffusion region. Figure 2 shows that the  $\Delta T/m_R$  curves do not lie on a common line below the ignition temperature. This feature may be helpful in predicting the trends in the oxidation process leading to ignition of the catalysts.

In conclusion it may be emphasized that the modified DTA curves prove to be very useful in the investigation of active carbon – nickel catalysts. With the present method it was simple to ascertain that the oxidation of the examined catalysts in a static air atmosphere is a two-stage process.

It was found that the reaction in the low-temperature region was governed by the chemical reactivity of the samples leading to ignition, whereas the reaction in the high-temperature region was controlled by gaseous diffusion, depending on the participation of several pores. This finding is in accordance with the conclusions by Walker et al. [7] and those presented in papers [1, 8].

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RÉSUMÉ — Les courbes ATD et TG fournies par un Dérivatographe lors de l'étude de l'oxydation des catalyseurs à base de charbon actif-nickel en atmosphère d'air statique, ont été utilisées pour tracer les courbes ATD modifiées, définies comme  $\Delta T/m_R$  ( $m_R$  étant la masse réactive du prélèvement). Les tracés de  $\Delta T/m_R$  entre 200 et 850° ont permis de prouver que le processus d'oxydation suivait une réaction en deux étapes. On a établi que la réaction dépend, dans la région de diffusion, du volume des pores, pour des rayons allant de 75 à 7500 nm. On présente les variations de la température d'ignition en fonction de la teneur en nickel des échantillons.

ZUSAMMENFASSUNG — Die DTA und TG-Kurven der derivatographischen Untersuchungen zur Oxidation der Aktivkohle-Nickel Katalysatoren in statischer Luft-Atmosphäre wurden verwendet um die modifizierten DTA-Kurven, definiert als  $\Delta T/m_R$  (wobei  $m_R$  die reaktive Masse der Probe ist) aufzuzeichnen. Die Funktionen  $\Delta T/m_R$  gestatteten im Bereich von 200 bis 850° die Aussage des Oxidationsvorganges als eine Zweistufenreaktion. Es wurde festgestellt, daß die Reaktion im diffusen Bereich von den Porenvolumina mit Radien von 75 bis 7500 nm abhängt. Die Änderungen der Entzündungstemperatur in Abhängigkeit von dem Nickelgehalt der Proben wurden beschrieben.

Резюме — Кривые ДТА и ТГ, полученные при дериватографическом изучении окисления катализаторов типа активированный уголь — никель в статической атмосфере воздуха, использовались для извлечения видоизмененных кривых ДТА, обозначаемых как  $\Delta T/m_R$  и где  $m_R$  — реакционная масса образца. Графики  $\Delta T/m_R$  в области от 200 до 850° позволили установить, что процесс окисления является двухстадийной реакцией. Отмечено, что реакция в диффузной области зависит от объема пор с радиусом от 75 до 7500 нм. Представлены изменения температуры воспламенения в зависимости от содержания никеля.