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STUDY OF GRAPHITE-MANGANESE OXIDE CATALYSTS VIA MODIFIED DTA CURVES

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Modified DTA curves (MDTA) have been used to elucidate the mechanism of oxidation of the graphitized active carbon-manganese oxide catalyst system in a static air atmosphere. It was found that the method is a very useful tool when the DTA curves give disputable results, especially after passing through the exothermic peak. From the DTA curves two different mechanisms of oxidation were proposed, depending on the manganese oxide content.

It has been established that the rate of oxidation of several carbon-containing catalysts depend on the concentration and the chemical nature of the catalysts, as well as on the structure and the chemical properties of the carbon [1, 2]. In the case of the graphite-metal oxide catalysts it is well known that the relation between the rate of oxidation and the metal oxide content is linear only for a low amount of oxide. The mechanism of the oxidation is more complicated in the case of high amounts of oxide.

In this paper, thermal studies on graphitized active carbon impregnated with various amounts of manganese oxide have been carried out in terms of the oxidation reaction in the temperature range from 20 to 1000°.

The modified DTA curves and the data obtained with a derivatograph, have been used to explain the mechanism of the oxidation in the case of samples containing 1.02 to 20.66% of manganese oxide.

Experimental

Material

Active carbon produced by the Polish firm ZEW Racibórz (the trade name of the product is Carbomedicinalis ligni) was graphitized at 2400° for 24 hours. X-ray diffraction analysis with a Cu target indicated that the product obtained has a structure with *d* spacings and line intensities characteristic for graphite. The product was then sieved and the fraction under 80 μm in diameter of particle size was chosen. The surface area of this fraction was calculated by the BET method from the adsorption isotherm of argon at 77.5 K and was equal to 48 m^2/g. Portions of the graphitized carbon were impregnated with aqueous solutions of $KMnO_4$ at 50°. Ethyl alcohol was added to the solutions in order to reduce permanganate ions to manganese oxide. The amounts of ethyl alcohol was sufficient to ensure complete reduction. After sedimentation, the mixture was separated and the clear solution was examined to determine the completeness of the reduction. Finally, dilute HNO_3 was dropped into the stirred mixture to remove the reaction product KOH from the graphite, and the impregnated carbon was washed by decantation until free nitric acid appeared. The samples obtained were dried at 105°. Manganese was estimated as manganese oxide.

Thermal analysis

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: 200 mg; heating rate: 5 deg/min; final temperature: 1000°; reference substance: α-Al_2O_3; static atmosphere: air.The $\Delta T = 0$ line was produced when two sample holders (for both the sample and the inert material) contained α-Al_2O_3. The physicochemical data on the samples are listed in Table 1. The $\Delta T/m_R$ values were calculated at every 5°.

Results and discussion

There is a large exothermic peak in the DTA curves of the investigated samples, with the maximum depending on the manganese oxide content and varying in the temperature range from 580 to 440°. The temperature of the peak maximum of all of the impregnated samples is lower than that of the sample free of manganese oxide (Table 1, Fig. 1). The exothermic peak is accompanied by a distinct weight loss in the TG curves. The characters of the DTA curves of the samples containing 1.02 and 3.75% manganese oxide are different from those of the other samples. In this case, a small but distinct endothermic peak is superimposed on the large exothermic peak, while an inflexion is observed in the DTG curves, which corresponds to a decrease in the reaction rate. The oxidation of the samples involves considerable weight loss, and hence the estimation of thermal changes from the DTA curves at temperatures higher than the peak maximum temperature T_{max} is disputable. Similar difficulties were considered in previous papers [2, 3]. Because of this, the method of modified DTA curves is used; details have been described previously [2, 3]. In this method the modified DTA curves (MDTA) are plotted with the parameter $\Delta T/m_R$ as a function of temperature, where ΔT is the temperature difference taken from the DTA curves and m_R denotes the mass of sample reacting at the given temperature and is taken from the TG curves. The MDTA curves are shown in Fig. 2. It can be seen that the

Table 1 Physicochemical properties of the samples

Sample	MnO_2 content, %	DTA exotherm, T_{max}, °C	DTA endotherm, T_{min}, °C	Ignition temperature from DTA curves T_{im}, °C	Ignition temperature from DTA curves T_i, °C
0	0.00	700	–	610	600
1	1.02	520 580 main	540	460	450
2	3.75	460 540 main	500	370	380
3	4.93	460	–	350	350
4	10.04	440	–	310	320
5	15.18	440	–	270	270
6	20.66	440	–	260	270

MDTA curves initially run almost parallel to the temperature axis. This corresponds to the reactions being governed by the chemical reactivity of the samples [1, 3–5] and the $\Delta T/m_R$ values do not exceed 0.05. In this temperature region the catalysts begin to sorb oxygen, mainly on the outer surfaces of the grains. This process is accompanied by solid-state diffusion into the carbon mass and also by some degree of desorption of carbon-oxygen complexes from the surfaces [6]. The reactions in this temperature region are controlled by 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 catalyst grains, the temperature is raised, which is reflected as a gentle increase in the MDTA curves. Finally, the increase in the temperature in the reaction zone results in ignition of the catalysts, as indicated by a sharp rise in the MDTA curves. The ignition temperatures T_i were taken as the extrapolated onset of the DTA and the MDTA curves, just as in the previous papers [2, 3]. As seen in Table 1, the ignition temperature T_i and the DTA peak maximum T_{max} decrease when the manganese oxide content increases. With further increase in the temperature, the burning undergoes an acceleration, which is indicated by increases in the DTA and the MDTA curves. Simultaneously, the commencement of weight loss is observed in the TG and the DTG curves. The DTA peak maximum T_{max} corresponds to the curvature in the MDTA plot and may be attributed to the highest reaction rate [7].

The MDTA curves were used to explain why the DTA curves for the samples containing 1.02 and 3.75% manganese oxide differ from the others and exhibit a small endothermic peak superimposed on the main exothermic peak.

Suppose that the exothermic peak corresponds to the oxidation of carbon, among others, according to the following equation:

$$C + O_{2(air)} \longrightarrow CO_2 + \Delta Q_1 \tag{1}$$

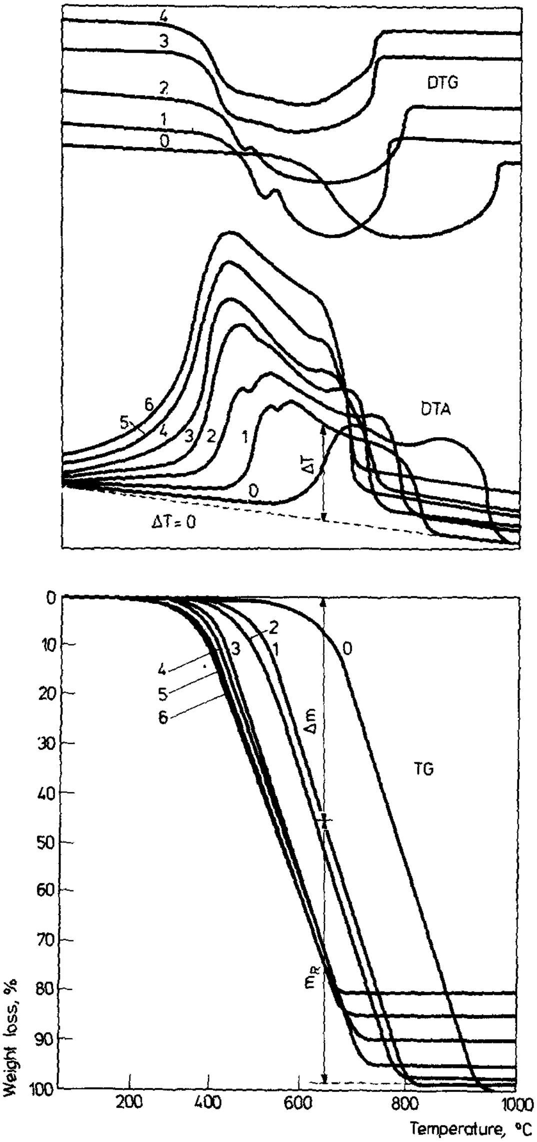

Fig. 1 TG, DTG and DTA curves of the samples

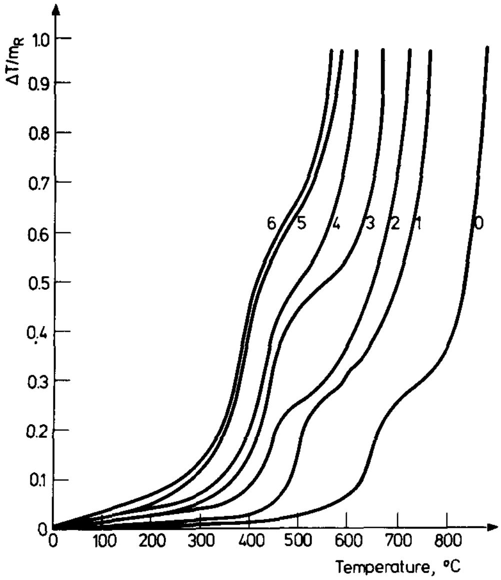

Fig. 2 Modified DTA curves of the samples

whereas the endothermic reaction of the manganese oxide decomposition occurs as follows [8]:

$$4\,MnO_2 \longrightarrow 2\,Mn_2O_3 + O_2 - \Delta Q_2 \qquad (2)$$

As things now stand, the decrease in the reaction rate at the temperature of manganese oxide decomposition may be elucidated via the temperature decrease in the reaction zone following the decrease in the air diffusion rate. Thus, the endothermic peak results from Eq. 2, which is opposite to reaction 1. This interpretation is supported by the MDTA curves. At the temperature of the DTA endothermic peak an inclination towards the temperature axis is observed, which clearly indicates that the reaction zone temperature decreases.

It is more interesting that the DTA curves of the samples containing over 3.75% manganese oxide do not exhibit the endothermic peak. This phenomenon is difficult to elucidate by the above mechanism. On the other hand, it is beyond any doubt that manganese oxide reduction occurs in the considered temperature range. This contradiction may be resolved when the following features are taken into account. Firstly, manganese oxide present in the catalysts is catalytically active, as revealed by the decrease in the ignition temperature when some oxide is present (Table 1, Figs 1–3). In the case of the catalysts containing over 3.75% manganese oxide reduction (according to Eq. 2) is so considerable that the endothermic effect may be partially compensated by heat liberated in the reaction between carbon and air. Secondly, it

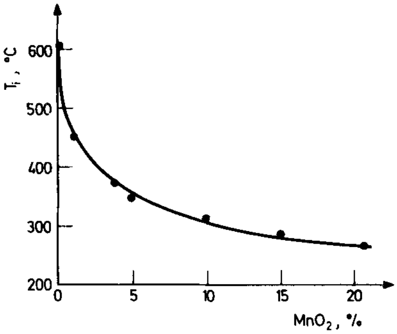

Fig. 3 Sample reactivity by ignition temperature as a function of catalyst content

should be emphasized that the reaction of Eq. 2 for the samples mentioned above occurs at about 500° (small inflexion in the DTG curves), i.e. after the maximum in the DTA curves. Accordingly, the small endothermic effect might be difficult to record when the DTA curves incline towards the temperature axis. This leads to the conclusion that the DTA curves are not useful in the case when T_{max} is overstepped. For the interpretation of the mechanism it is more useful to take into consideration the changes in the parameter $\Delta T/m_R$ as a function of temperature. In Fig. 2 the inflexion may be seen at a temperature higher than T_{max}, which may be attributed to a decrease in the reaction heat. This heat diminution becomes smaller and smaller as the oxide content increases. On this basis it may be accepted that the endothermic reaction of Eq. 2 does not play a significant role in the overall reaction. The considered changes may be better described by the following equations:

$$C + O_{2(air)} \longrightarrow CO_2 + \Delta Q_1 \qquad (1)$$

$$4\,MnO_2 + 2\,C + O_{2(air)} \longrightarrow 2\,Mn_2O_3 + 2\,CO_2 + \Delta Q_3 \qquad (3)$$

Overall reaction:

$$4\,MnO_2 + 3\,C + 2\,O_{2(air)} \longrightarrow 2\,Mn_2O_3 + 3\,CO_2 + \Delta Q_4 \qquad (4)$$

It is seen that the overall reaction is exothermic. The reaction of Eq. 3 involves carbon oxidation and simultaneous reduction of manganese oxide. Since the reduction of manganese oxide takes place on the carbon—manganese oxide—air interface, carbon dioxide is formed by simultaneous reaction of carbon with atmospheric oxygen as well as with oxygen liberated in the manganese oxide decomposition. Because of this, it would be expected that the amount of heat liberated will be proportional to the manganese oxide content. Indeed, the results illustrated in Fig. 2 confirm this expectation. However, the shape of the MDTA curves shows that this relation is not linear, especially for the samples containing 15.18 and 20.66% manganese oxide. This may be interpreted, among others, by assuming that the amount of ash formed on the carbon grains becomes higher and higher as the manganese content increases. Accordingly, the penetration of air into the carbon is restricted and the rate of the reaction decreases. The influence of the ash formed on the reactivity of the samples is shown in Fig. 3. The increase in catalytic reactivity is seen to be less significant over 10% manganese oxide content. Further, it is necessary to take into consideration that a slight part of the manganese oxide does not interact with the carbon grains according to Eq. 4, but decomposes in the reaction of Eq. 2.

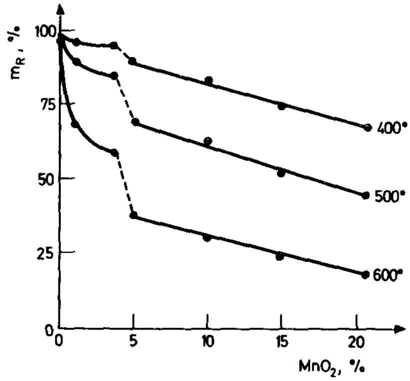

Fig. 4 Sample reactivity by reactive mass as a function of catalyst content

The results obtained show that the MDTA curves can serve as a very useful tool in the investigation of graphite–manganese oxide catalysts. With the present method it was simple to ascertain that the oxidation of the catalysts in the low-temperature region is governed by the chemical reactivity of the samples proceeding to ignition, whereas the reaction in the high-temperature region is controlled by the gaseous diffusion of air. Moreover, it was very interesting to ascertain that oxygen liberated in the manganese oxide decomposition plays an important role in the oxidation process. Using the MDTA method, it was possible to note that the oxidation of the graphite–manganese oxide catalysts occurs according to two different mechanisms, depending on the manganese oxide content, as is shown in Fig. 4.

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Zusammenfassung — Modifizierte DTA-Kurven (MDTA) wurden zur Aufklärung des Mechanismus der Oxydation von aus graphitisierter Aktivkohle und Mangandioxid bestehenden katalytischen Systemen in statischer Luftatmosphäre herangezogen. Es wurde festgestellt, dass die vorgeschlagene Methode in den Fällen nützlich ist, bei denen die DTA-Kurven, insbesondere die Bereiche nach dem exothermen DTA-Peak, keine eindeutigen Schlussfolgerungen zulassen. Basierend auf den MDTA-Kurven wurden, abhängig vom Mangandioxidgehalt, zwei verschiedene Mechanismen für die Oxydationsreaktion vorgeschlagen.

Резюме — Модифицированные ДТА-кривые (МДТА) были сделаны для обьяснения механизма окисления в статической воздушной атмосфере катализаторной системы графитизированный активный углерод — окись марганца. Установлено, что представленный метод очень полезный в случае, когда ДТА-кривые дают спорные результаты, особенно после прохождения через экзотермический пик. На основании МДТА-кривых было предложено два различных механизма реакции окисления в зависимости от содержания окиси марганца.