

Removal of carbonaceous matters over alumina supported chromium and platinum chromium catalysts

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Platinum, both alone and with a low and high amount of chromium as an additive supported on alumina, was studied as a catalyst. These catalysts were examined in the removal of the carbonizate as a model material. It was found that the $2\text{Cr}/\text{Al}_2\text{O}_3$ catalyst showed a significant increase in the catalytic activity as compared to $20\text{Cr}/\text{Al}_2\text{O}_3$. An addition of platinum was found to cause a decrease of activity.

Keywords: $\text{Cr}/\text{Al}_2\text{O}_3$, $\text{PtCr}/\text{Al}_2\text{O}_3$, DTA, TG.

INTRODUCTION

As one of the measures taken to protect the natural environment, the EU authorities have introduced limitations on the content of harmful substances, including the diesel soot or the particulate matter, in the vehicle exhaust emissions. The complex physicochemical processes taking place in fuel combustion in diesel engines lead to the formation of soot of different chemical composition. Usually the particulate matter produced, is composed of graphite-like soot with adsorbed hydrocarbons, including the aromatic polycyclic hydrocarbons. The details of the process are presented in the monograph¹ and literature^{2,3}. A few methods for reducing the emission of the particulate matter, one of which is based on the use of catalysts, have been reported on in literature. Our group has been working on heterogenic catalysts for a few years. This paper reports on the study of catalytic oxidation of the carbonizate with the air oxygen over the oxide catalysts containing chromium or platinum-chromium supported on Al_2O_3 , performed by a differential thermal analysis (DTA) and thermogravimetry (TG)⁴⁻⁶.

EXPERIMENTAL

The catalysts were prepared by the method of „incipient wetness” in which the support was saturated with a solution of $\text{Cr}(\text{NO}_3)_3$ (Aldrich) or a solution of $\text{Cr}(\text{NO}_3)_3$ and H_2PtCl_6 (Aldrich) of definite nominal concentrations. The DTA/TG measurements were carried out on the Paulik-Paulik-Erdey OD-102 derivatograph, according to the procedure described earlier⁴⁻⁶.

RESULTS AND DISCUSSION

20mas.% $\text{Cr}/\text{Al}_2\text{O}_3$ and the other two contained the same amounts of $\text{Cr}/\text{Al}_2\text{O}_3$.

The study was performed on four samples of the catalysts; the first two contained 2 and additionally 0.3mas.%Pt. For the sake of comparison analogous measurements were also performed without any catalysts and in the presence of the support (Al_2O_3) type C (Degussa) Moreover, the effect of Pt addition to the chromium catalysts was evaluated relative to the performance of the 0.3mas.% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. The measurements were taken for the carbonizate (Hajnowskie Zakłady Suchoj Destylacji Drewna, Hajnówka, Poland) containing 78.64mas.%C, 1.17mas.%N and 1.34mas.%H, which was well mixed with catalysts in the 29:1 ratio. The total amount of the mixture in each experiment was 600 mg. The

samples were heated at the rate of $13^\circ/\text{min}$ and at the airflow rate of $30\text{ cm}^3/\text{min}$. The mass loss was calculated using the normalized TG curve in the range of exothermic effects.

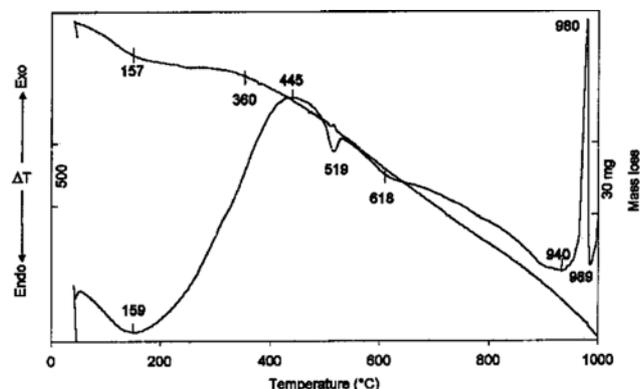


Figure 1. The DTA and TG curves of the carbonizate

Fig.1 presents the DTA and TG curves of the carbonizate. In the whole temperature range studied the mass loss has been evidenced, accompanied by endothermic effects with the minima at 159, 519 and 618°C and the exothermic effects with the maxima at 445, 980°C and a broad one in the range of 618 – 940°C. The exothermic effect at 445°C is very pronounced.

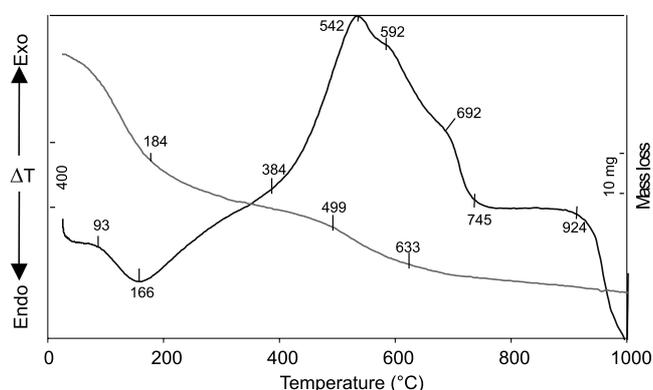


Figure 2. The DTA and TG curves of the carbonizate with Al_2O_3

The DTA and TG curves recorded for the same carbonizate heated together with the Al_2O_3 support (Fig. 2) show the exothermic effects with the maxima at different temperatures than those obtained for the pure carbonizate. The exothermic effect has been shifted from 445°C (Fig. 1) to 542°C. This means that the carbonizate components manifested as the exothermic effects on the rising branch have been transformed.

The descending branch of the exothermic effect is much steeper than the corresponding one, recorded for the carbonizate alone, which means that some of the carbonizate components showing the exothermic effects above 542°C have also been transformed. The changes are the consequence of the presence of Al_2O_3 , which alone does not show any exothermic effects at the temperature studied, see Fig. 3.

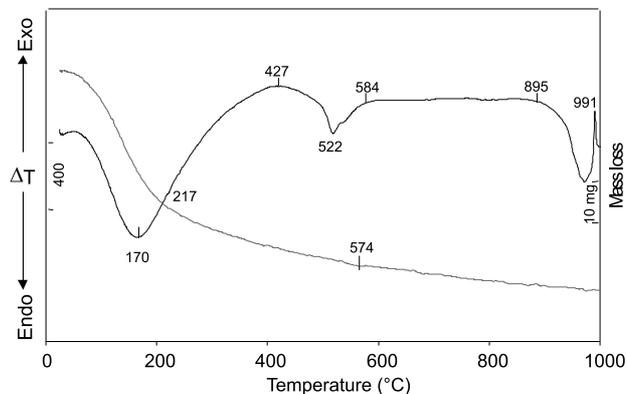


Figure 3. The DTA and TG curves of Al_2O_3

As the main aim of the reaction is the elimination of the carbonizate by its oxidising gasification, the catalytic activity of the samples studied has been assessed on the basis of the mass loss calculations presented in Table 1.

The results obtained for the carbonizate and Al_2O_3 reveal a distinct thermocatalytic effect, however, it does not lead to the gasification of the carbonizate but only to a transformation of some of its components into others. The introduction of Cr^{3+} ions onto the Al_2O_3 support results in the gasification of the carbonizate. As follows from Table 1, their presence can lead to a mass loss of the carbonizate by over 30 mg/g.

Table 1. The carbonizate mass loss on oxidation

Catalyst	Mass loss (mg/g)
Al_2O_3	0
2%mas. $\text{Cr}/\text{Al}_2\text{O}_3$	31
20%mas. $\text{Cr}/\text{Al}_2\text{O}_3$	34
0,3%mas $\text{Pt}/\text{Al}_2\text{O}_3$	25
0,3%mas. $\text{Pt} - 2\%$ mas. $\text{Cr}/\text{Al}_2\text{O}_3$	27
0,3%mas. $\text{Pt} - 20\%$ mas. $\text{Cr}/\text{Al}_2\text{O}_3$	20

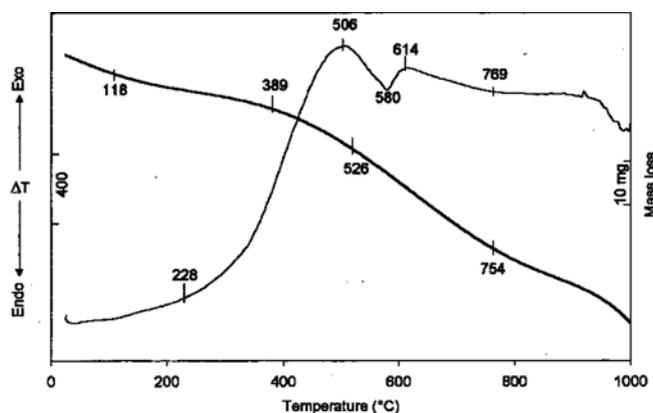


Figure 4. The DTA and TG curves of the carbonizate with 2mas. % $\text{Cr}/\text{Al}_2\text{O}_3$

Figs. 4 and 5 present the changes in the course of the DTA and TG curves caused by the presence of Cr^{3+} ions. In the DTA curve the exothermic effect maximum is shifted from 445°C for the carbonizate without the catalyst to 506°C for the carbonizate with the catalyst containing 2mas.% $\text{Cr}/\text{Al}_2\text{O}_3$. An

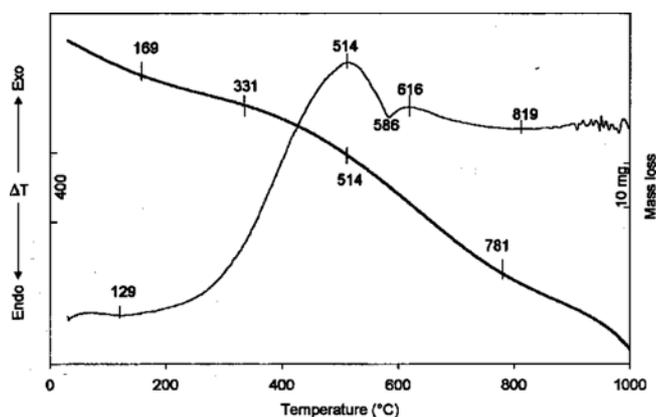


Figure 5. The DTA and TG curves of the carbonizate with 20mas. % $\text{Cr}/\text{Al}_2\text{O}_3$

increase in the Cr concentration to 20mas.% has no significant effect on the catalytic activity (Table 1). The results show that the carbonizate components undergoing the oxidising gasification are those that correspond to the exothermic effects below 506°C, in the presence of 2mas.% $\text{Cr}/\text{Al}_2\text{O}_3$ (Fig.4) and below 514°C, in the presence of 20 mas.% $\text{Cr}/\text{Al}_2\text{O}_3$ (Fig.5). The effects are only a consequence of the presence of chromium groups. As follows from the data presented in Table 1, an addition of 0.3mas.% platinum to the samples already containing chromium leads to a decrease in the gasification of the carbonizate by 16% relative to that obtained in the presence of 2 mas.% $\text{Cr}/\text{Al}_2\text{O}_3$ and by 41% relative to that obtained in the presence of 20mas.% $\text{Cr}/\text{Al}_2\text{O}_3$. It has been shown that the activity of the 0.3mas.% $\text{Pt}/\text{Al}_2\text{O}_3$ system in the gasification of the carbonizate is much lower than that of $\text{Cr}/\text{Al}_2\text{O}_3$. However, it should be emphasised that the presence of 0.3mas.% of platinum alone supported on Al_2O_3 strongly increases the gasification of the carbonizate relative to that in the presence of Al_2O_3 only. The course of the DTA curve of the carbonizate in the presence of 0.3mas.% $\text{Pt}/\text{Al}_2\text{O}_3$ (Fig.6) is similar to those presented in Figs. 4 and 5.

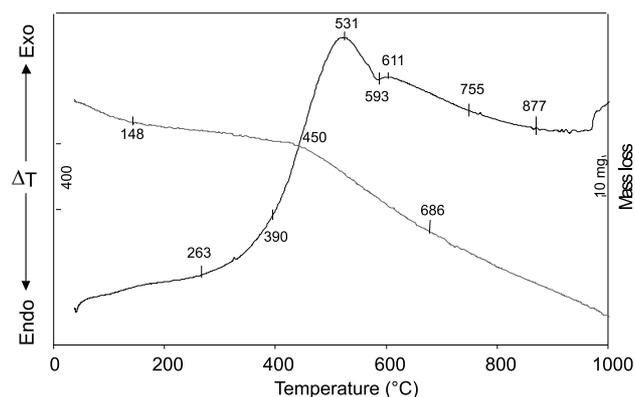


Figure 6. The DTA and TG curves of the carbonizate in the presence of 0.3 mas.% $\text{Pt}/\text{Al}_2\text{O}_3$

The only difference in the oxidising gasification of the carbonizate is the effectiveness leading to the elimination of the carbonizate components corresponding to the exothermic maxima below 531°C. The course of the DTA curves for the carbonizate in the presence of the catalysts of 0.3 mas.% $\text{Pt} - \text{Cr}/\text{Al}_2\text{O}_3$ (Fig. 7 and 8) demonstrates only small differences in the positions of the extremes, while their shape is similar to those in Fig. 4 and 5.

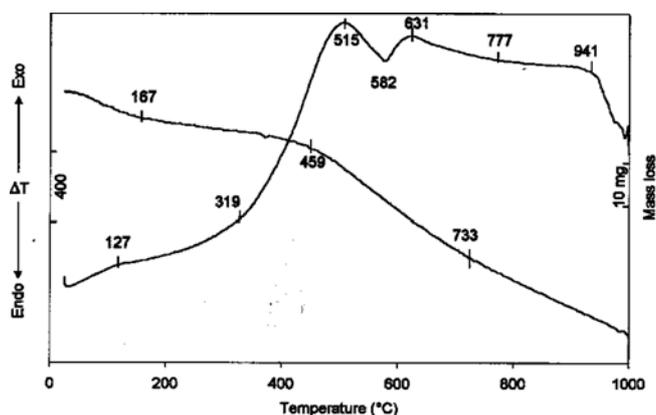


Figure 7. The DTA and TG curves of the carbonizate in the presence of 0.3mas. % Pt – 2mas. % Cr/Al₂O₃

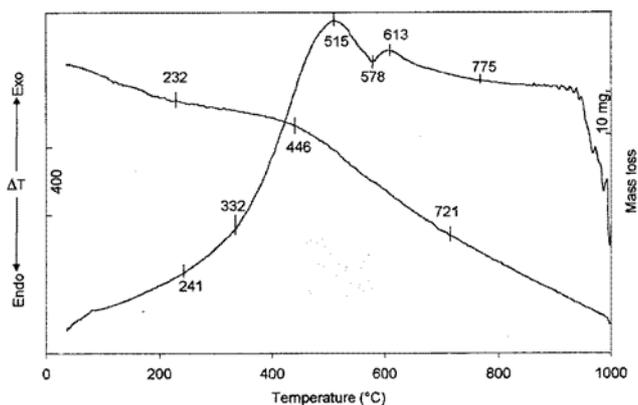


Figure 8. The DTA and TG curves of the carbonizate in the presence of 0.3mas. %Pt – 20mas. % Cr/Al₂O₃

CONCLUSION

As follows from the above presented results, an introduction of a small amount (2%mas.) of chromium (III) ions onto the surface of Al₂O₃ results in a significant increase in the catalytic gasification of the carbonizate, while the introduction of the ten times greater amount of these ions causes only a small further increase in this process. The results obtained after the introduction of 0.3mas.% Pt into the Cr/Al₂O₃ systems were rather surprising. An addition of platinum was found to cause a relatively great reduction in the gasification of the carbonizate, which may be related to the formation of less active surface catalytic centres. It should be noted that in the presence of platinum alone supported on Al₂O₃ the catalytic activity of this system in the carbonizate gasification is much greater than that of Al₂O₃. The presence of the support stimulates only the transformation of some components of the carbonizate without its gasification.

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