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DTA, TG STUDIES OF CATALYTIC OXIDATION OF CARBON PARTICLES OVER $M_2^{III}O_3$ (M^{III}=Al, Cr, Fe, Ni)

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Abstract

Carbonizate as a model soot has been submitted to oxidation using Al_2O_3, Cr_2O_3, Ni_2O_3 and Fe_2O_3 as catalysts in the temperature range from RT up to 1000°C. The results obtained indicate that Fe_2O_3 is the most active catalyst in soot oxidation. However, all the catalysts examined are active in transformation of carbonizate components. It has been shown that DTA and TG methods can be used as fast methods testing the carbonizate oxidation.

Keywords: carbonizate, catalysts, DTA, oxidation, TG

Introduction

Mean emission of particulate matters and dust by a Diesel motor reaches ~1–10 g kg^{-1} of combusted fuel, while the corresponding emission of a spark motor with a threeway catalyst is only 0.05–0.3 g kg^{-1}. Some of the pyrolysis products including polycyclic aromatic hydrocarbons, heavy metals, sulphates, sulphuric acid and water are strongly adsorbed on the porous surface of soot. This process takes place mainly in the exhaust system. The chemical composition and physical properties of the emitted particulate matter depend mainly on the conditions of the engine work. The dark colour of exhaust gases emitted from the exhaust system suggest a soot content over 100–130 mg m^{-3}, while the emission of black smoke usually means that the soot content is higher than 600 mg m^{-3}. Removal of the particulate matter with adsorbed polycyclic aromatic hydrocarbons is the problem of great concern in view of the established carcinogenic and mutagenic effects of these hydrocarbons. One of the methods proposed to decrease the level of particulate matter emission is based on the use of the oxidation catalysts.

Experimental

In the study the performance of the following oxide catalysts was tested: Al_2O_3, Cr_2O_3, Ni_2O_3, Fe_2O_3 and a carbonizate made by Gryfskand (earlier known under the

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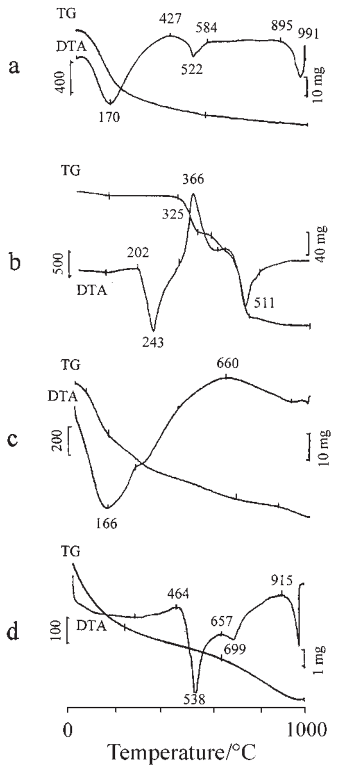

Fig. 1 DTA and TG curves of catalysts: a – Al_2O_3, b – Cr_2O_3, c – Ni_2O_3 and d – Fe_2O_3

name of the Hajnowskie Zakłady Suchej Destylacji Węgla), Hajnówka, Poland. The tests were conducted in a derivatograph OD-102 of the system made by Paulik –Paulik–Erdey (Hungary). A portion of well-homogenised mixture of the catalyst and carbonizate at the mass ratio 1:29 was placed in a ceramic crucible and heated to 1000°C at the rate of 13° min^{-1}, in air blown at the rate of 30 cm^3 min^{-1} [2, 3]. The differential thermal analysis (DTA) and thermogravimetry (TG) curves were recorded. Analogous measurements in the same conditions were performed for the catalysts (Fig. 1) and the carbonizate (Figs 2a and 3a) separately. The carbonizate was subjected to elemental analysis on Euro Vector model EA 300 (Italy) and FT-IR study on a Perkin Elmer apparatus [4]. The deconvolution was performed with the use of the program Origin I Gaussian function I Fit Multi-peaks.

Results and discussion

According to the results of the elemental analysis the carbonizate contains 78.64 m/m% C, 1.34 m/m% H and 1.7 m/m% N, the contents of the other components were not determined. Its IR spectrum revealed bands characteristic of polycyclic aro-

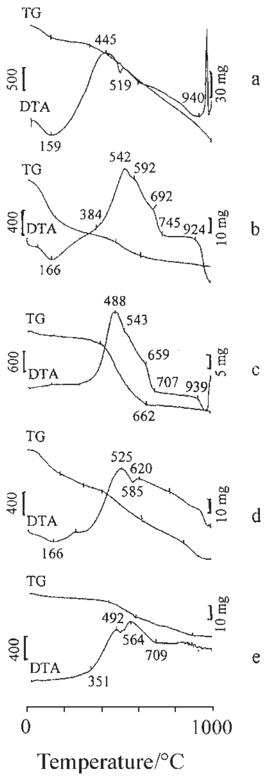

Fig. 2 a – DTA of α-carbonizate and TG curves of carbonizate and mixture of carbonizate with the following catalysts: b – Al_2O_3, c – Cr_2O_3, d – Ni_2O_3 and e – Fe_2O_3

matic hydrocarbons. In view of the above the carbonizate was assumed as relatively well simulating the particulate matters produced in Diesel motors.

Table 1 presents the carbonizate mass loss expressed in mg/g of the catalyst, obtained as a sum of the mass loss taking place during the heating of catalyst with carbonizate taking into account the mass contribution of the catalyst used in preparation of the mixture with the carbonizate. The calculations were performed on the basis of the TG curves, Figs 1 and 2.

Table 1 Carbonizate mass loss during the catalytic oxidation

Catalyst	Mass loss/mg g^{-1}
Al_2O_3	0
Cr_2O_3	2
Ni_2O_3	20
Fe_2O_3	25

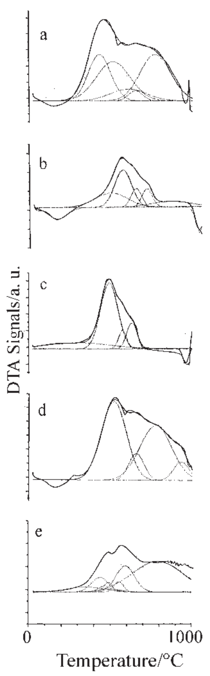

Fig. 3 a – deconvolution of α-carbonizate, b – Al_2O_3, c – Cr_2O_3, d – Ni_2O_3 and e – Fe_2O_3

Assuming that the activity of the oxidation catalyst is measured as the carbonizate mass loss on its heating in a mixture with the catalyst, expressed in *mg* of the carbonizate per *g* of the catalyst, the catalysts studied can be arranged in the following series according to decreasing activity: $Fe_2O_3 > Ni_2O_3 > Cr_2O_3 > Al_2O_3$.

However, during the catalytic decomposition of the carbonizate in the conditions of the programmed temperature increase, the original components of the carbonizate are observed to gradually disappear giving way to formation of new components as a result of the catalytic transformation.

Figure 2a apart from the TG shows also the DTA curve with the characteristic temperatures marked. The DTA curve was subjected to the a procedure of deconvolution getting five component curves (dotted lines), Fig. 3a.

When Al_2O_3 is used as a catalyst the maximum on the DTA curve is shifted to 542°C (Fig. 2b), which means that the carbonizate components characterised by the exothermic effects occurring below 542°C, have been oxidised. Simultaneously, the wide exothermic effect characterising the carbonizate and occurring above 745°C (Figs 3a, b) is observed to disappear. The number of the carbonizate components after the reaction catalysed by Al_2O_3 remains the same as without the catalyst. In view of the fact that no carbonizate mass loss is observed (Table 1), it seems that only a transformation of the carbonizate components has occurred. When the catalyst Cr_2O_3 is used (Figs 2c and 3c) the exothermic effect with a maximum at 490°C becomes much narrower relative to that recorded for pure carbonizate. When this catalyst is used, the exothermic effects in temperatures up to 350 and above 700°C disappears. Some of the carbonizate components have undergone transformation and only 2% of the carbonizate have been oxidised (Table 1). A much greater catalytic activity leading to the oxidation of ~20 m/m% of the carbonizate was observed when the catalyst used was Ni_2O_3. In this case the exothermic effect corresponds to the presence of four carbonizate components (Figs 2d and 3d). The carbonizate components giving signals in temperatures up to ~350°C (Figs 2a and 3a) disappear. The greatest catalytic activity in the oxidation of the carbonizate was observed for Fe_2O_3 (Table 1). Relative to the data obtained for pure carbonizate (Figs 2a and 3a) the exothermic effects are shifted to the temperatures 492 and 564°C (Fig. 2d), which means that the pure carbonizate components giving earlier signals below 330°C have disappeared, (Fig. 3d). However, for this catalyst, the carbonizate was found to undergo a relatively deep transformation leading to formation of seven components.

The above presented results have proved that the introduction of metal oxides into the carbonizate leads to its catalytic transformations. The carbonizate is observed to partly disappear as a result of oxidation (except when Al_2O_3 is used) and partly undergo transformation of its components. The positions of the effects corresponding to the carbonizate components indicate that a certain amount of the carbonizate has undergone transformation. The catalytic transformation can be related to a degradation of particular components of the carbonizate into those of lower number of molecules, however, a transformation into more complex systems cannot be excluded.

Conclusions

The results of DTA and TG study have shown that the compounds Fe_2O_3 and Ni_2O_3 are active catalysts in oxidation of the carbonizate, while Al_2O_3 and Cr_2O_3 have not been active in the process. The catalysts used are also responsible for a transformation of the carbonizate in less or more complex forms. The methods DTA and TG have been shown to be fast and effective techniques in assessment of the catalytic activity in the carbonizate oxidation.

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