Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 867-875

STABILITY AND REACTIVITY OF THE ACTIVE ASSEMBLIES IN MODIFIED GRAPHITES CHARACTERIZED BY TPD AND TPH

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(Received January 22, 1997; in revised form June 9, 1998)

Abstract

Synthetic graphites, as prepared and modified by sulphonation or acetylation, were doped by Fe-, Co-, Ni- and Ca-nitrates. Temperature Programmed Desorption (TPD) and Temperature Programmed Hydrogenation (TPH) were applied to characterize thermal stability and reactivity of the active assemblies formed on the matrix surface. The functional groups lowered the reactivity of the graphites. Thermally less stabile carboxylic groups decomposed with formation of secondary groups giving more reactive material. Fe containing as well as sulphonated graphites showed a much lower reactivity than the others. Synergistic effects of Co/Ca and Ni/Ca were confirmed in the graphite materials.

Keywords: active assemblies, carbon materials, hydrogenation, synergistic effects, synthetic graphite, TPD, TPH

Introduction

The 3-D macromolecular structure of condensed aromatic and hydroaromatic layers joined together by aliphatic and etheric bridges has been accepted as the model of natural coals [1]. There are also smaller organic molecules encapsulated inside the empty spaces of the loose macromolecular structure. These molecules can undergo decomposition and/or desorption during thermal treatment and reactions, or they may be extracted during the processes with organic solvents, e.g. liquefaction [2]. In the course of coal pyrolysis or hydropyrolysis, the remaining organic molecules can react easily, masking the specific reactivity of the 3-D macromolecular structure. Moreover, the reactivity depends strongly

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1418–2874/99/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

on the kinds and number of functional groups and heterocyclic rings present in the natural coals [3]. For these reasons the studies on defined graphite materials, as model compounds, seems to be of great value to characterize the specific reactivity of 3-D macromolecular structure in abstraction from the properties of smaller molecules.

In our previous paper [4] the synthetic electrode graphite modified by Fe-, Co-, Ni- and Ca-nitrates was used as a model material in studies of the catalytic hydrogenation of carbon. In these studies the synergistic effects of Ca additives as well as of CO_2 and O_2 preadsorption were found.

This was the impulse to implant functional groups into pure and inactive synthetic graphite. The obtained material should allow verifying the introductory hypothesis that metal–functional groups are the active assemblies that catalyze the hydrogenation of graphite matrix more efficiently than metal catalysts alone. The temperature-programmed methods, desorption (TPD) and hydrogenation (TPH), were applied as convenient tools to characterize the thermal stability and reactivity of there assemblies.

Experimental

Samples

All the samples were prepared from pure synthetic graphite powder manufactured by Polgraph SA, Nowy Sącz, Poland. The original graphite contained only very small amounts of metal impurities (Ti:66.0 ppm, Si:37.1 ppm, V:12.6 ppm, Ca:6.0 ppm, other metals:below 2.0 ppm). The total ash content was equal to 375 ppm and the BET surface area was about 100 $m^2 g^{-1}$.

The original material was modified in order to introduce the surface functional groups into graphite. One part of the original material was treated with acetyl chloride in CCl_4 solution, in presence of $AlCl_3$ as the catalyst (like the standard Friedel-Crafts acetylation). Then it was washed thoroughly with distilled water. Another part of graphite was sulphonated in reaction with concentrated H_2SO_4 at temperature 180–190°C for 3 h. Then it was cooled in ice, washed thoroughly with distilled water and dried in vacuum.

Metal catalysts (Ni, Co, Fe, Ca) were introduced by incipient wetness (dry impregnation) technique using methanol solution of nitrates. Then all the samples were dried for 1 h at 120°C. Concentrations of the metal catalysts in the samples were equal to 0.5 wt%. The surface area of the impregnated samples decreased to about 2 $m^2 g^{-1}$, probably due to closing of pores by metal nitrates during impregnation.

Experiments

Thermal stability and reactivity of the samples were investigated using the microreactor system presented in Fig. 1. The sample (about 50 mg) was placed in

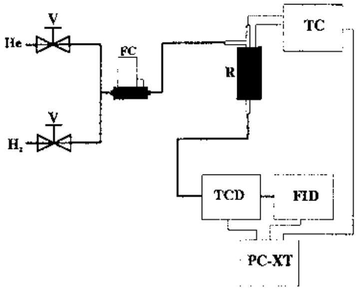

Fig. 1 Scheme of the experimental system for temperature programmed desorption and hydrogenation (V – toggle valve, FC – mass flow controller, R – microreactor with oven, TC – temperature programmer, TCD – thermal conductivity detector, FID – flame ionization detector)

a tubular quartz glass microreactor (7 mm ID) located inside a vertical oven equipped with a digital temperature programmer. The temperature of the sample was measured using a thermocouple placed in a quartz capillary inside the reactor. The gas supply system enabled feeding the reactor with pure helium or hydrogen. The flow rates of both gases were controlled by electronic mass flow controllers (ERG 100). The outlet of the reactor was connected directly with two gas chromatographic detectors (VARIAN GC 3400CX) connected in series: thermal conductivity detector (TCD) and flame ionization detector (FID), operating simultaneously. The voltage signals from the detectors and the reactor thermocouple were collected on-line by the computer every 4 s. Both detectors were calibrated by injections of pure CH_4 into the flow of both H_2 and He.

Additionally, the controlling experiments of evolved gas analysis (EGA) were performed using a quadrupole mass-spectrometer (VG-SX 200).

Two types of experiments have been performed:

1. TPD: the samples were heated in flow of helium (40 ml min^{-1}) up to 850°C with constant heating rate 10°C min^{-1}.
2. TPH: the samples were heated in flow of hydrogen (40 ml min^{-1}) up to 850°C with constant heating rate 10°C min^{-1}.

Results

Employing two chromatographic detectors of different sensitivity to organic and inorganic compounds allowed us to discriminate between these two types of products in our experiments. The TCD signal represented a measure of the total concentration of reaction products in the outlet gases, while the signal of the specific FID was generated by the organic products only. It should be noted that in the conditions under study several gaseous compounds could be formed so that quantitative separation of individual reaction products was not possible, therefore a simplified method of interpretation of results was used. Calibration data obtained using injections of pure methane enabled us to recalculate signals of both detectors in a semi-quantitative way, assuming that CH_4 was the only product of the reaction. It was evidently a simplification (valid only for TPH experiments); however, it enabled us expressing the signals as approximate specific reaction rates.

TPD

The profiles of TPD from the original (G), acetylated (GA) and sulphonated (GS) graphites are presented in Fig. 2. There are traces of gases evolved from the original graphite, though with visible maximum of CH_4 evolution at 435°C (Fig. 2B). The sulphonated graphite produces more CH_4 molecules, but less than the acetylated sample. The position of the CH_4 maxima does not change with the applied modifications of graphites.

The observed substantial evolution of inorganic compounds in course of TPD from acetylated graphite (Fig. 2A), is obviously from the decomposition of the surface groups. In case of sulphonated graphite, the evolution of inorganic products is smaller, but still much higher than in the original graphite.

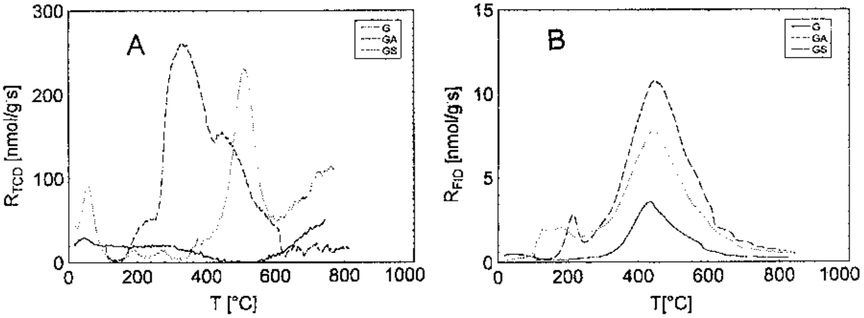

Fig. 2 TPD profiles of the 'as prepared' graphites (G – non modified, GA – acetylated, GS – sulphonated)

TPD curves obtained for Fe-containing graphites (Fig. 3) are similar to those obtained for the graphites without any introduced metals. However, there are some differences. The most important one is the appearance of two low-temperature peaks (below 100°C and about 200°C) common for all the graphites impregnated by nitrates (Fig. 3A). The other differences concern more complex and intensive evolution of organic gases in the presence of Fe, especially in case of GA (Fig. 3B).

More distinct changes arise from Co- and Ni-doping. TPD from Co-doped graphites are presented in Fig. 4. Apart from the low-temperature maxima one can notice sharp peaks at 600°C for Co(N)/G and at 700°C for Co(N)/GA (Fig. 4A). Also the TPD spectra of organic compounds (Fig. 4B) are more intensive and complex than in the Fe-containing graphites.

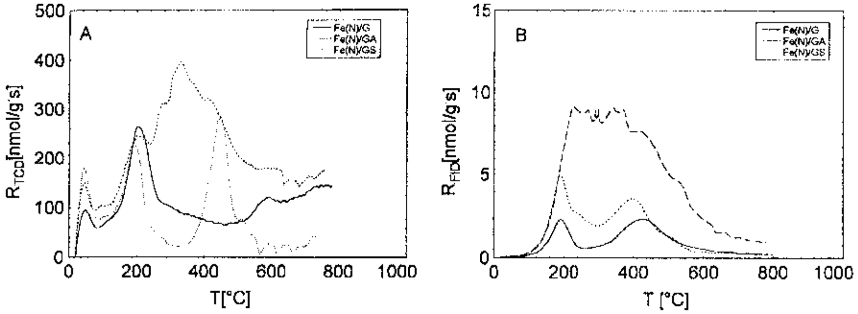

Fig. 3 TPD profiles of the 'as prepared' graphites (G – non modified, GA – acetylated, GS – sulphonated) impregnated with $Fe(NO_3)_3$

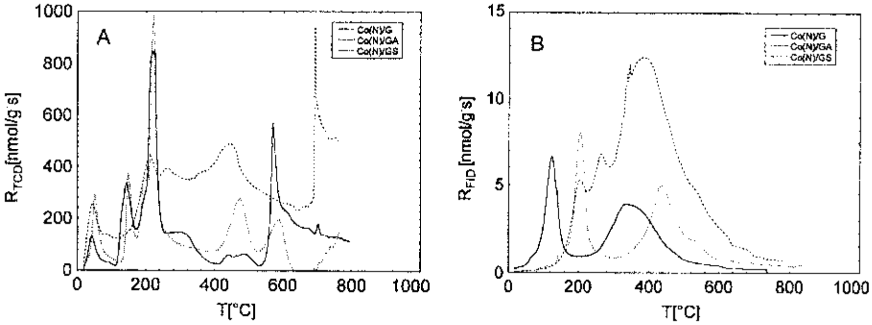

Fig. 4 TPD profiles of the 'as prepared' graphites (G – non modified, GA – acetylated, GS – sulphonated), impregnated with $Co(NO_3)_2$

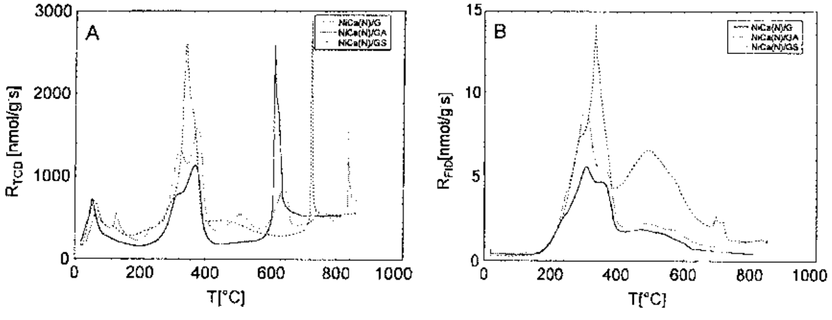

Fig. 5 TPD profiles of the 'as prepared' graphites (G – non modified, GA – acetylated, GS – sulphonated), impregnated with $Ni(NO_3)_2$ and $Ca(NO_3)_2$

Additional increase in the evolution of the inorganic gases is caused by $Ca(NO_3)_2$ doping. The response curves for the original and modified graphites doped mutually by $Ni(NO_3)_2$ and $Ca(NO_3)_2$, are presented in Fig. 5. In the range 300–400°C the highest gas evolution is observed for the acetylated graphites

(Fig. 5A). The high-temperature peak is moved from 600 up to 850°C in case of the sulphonated graphite.

TPH after TPD

The results obtained during the temperature-programmed hydrogenation (TPH) of the samples after proceeding TPD, show disappearance of all low-temperature peaks (Figs 6–8). The residual evolution of inorganic gases below 500°C is higher for Fe-containing graphite (Fig. 6A) than for the others. During the TPH, performed after TPD experiments, the high-temperature hydrogenation of graphites is clearly noticeable.

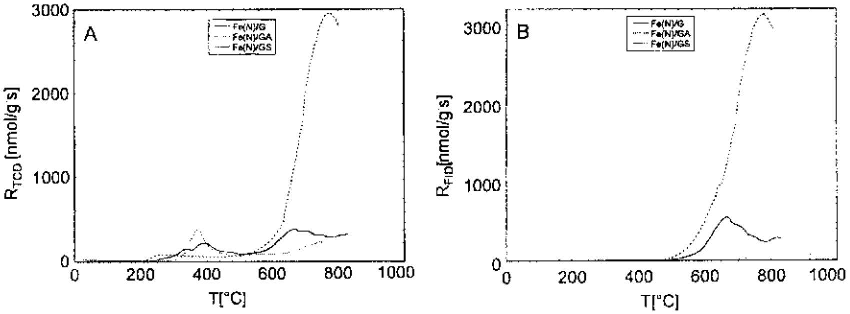

Fig. 6 TPH profiles of the graphites (G – non modified, GA – acetylated, GS – sulphonated), impregnated with $Fe(NO_3)_3$, obtained in TPH following TPD

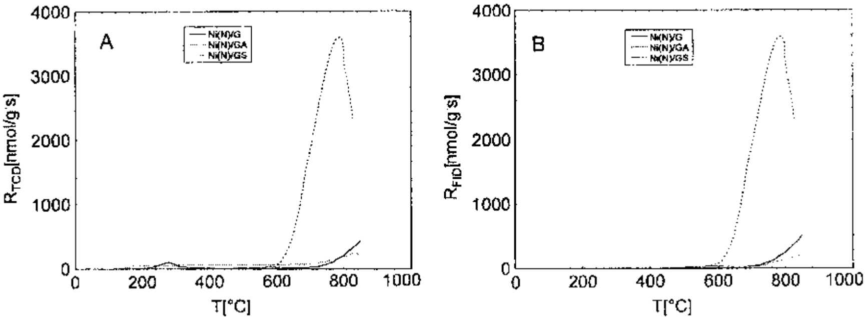

Fig. 7 TPH profiles of the graphites (G – non modified, GA – acetylated, GS – sulphonated), impregnated with $Ni(NO_3)_2$, obtained in TPH following TPD

The acetylated graphites are the most reactive one. Among them, the Ni-containing one shows the highest hydrogenation rate (Fig. 7). In this case methanation of carbon material takes place, as nearly 100% of CH_4 was found in the evolved gases within the high-temperature peaks.

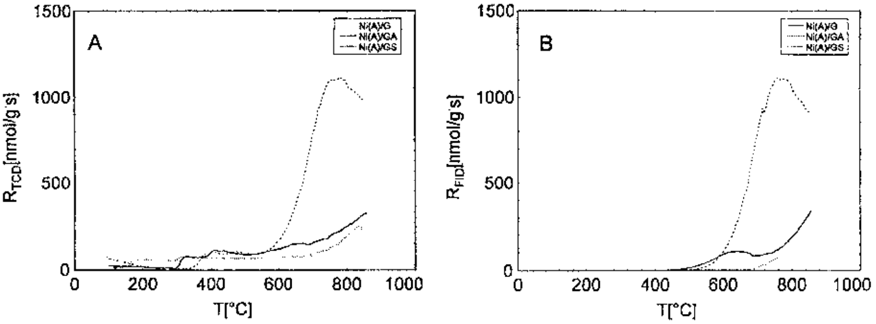

Fig. 8 TPH profiles of the graphites (G – non modified, GA – acetylated, GS – sulphonated), impregnated with Ni(acac)$_2$, obtained in TPH following TPD

The further modification applied and tested was the replacement of the M-nitrates by the M-acetyloacetonates. This modification suppresses visibly the catalytic activity of any transition metal. In Fig. 8, the case of Ni(acac)$_2$ is presented, as an example.

TPH of the 'as prepared' graphites

The TPH curves obtained for the original and modified graphites, without the previous TPD, are similar to the TPD curves from the same graphites. As an example, the results obtained with no-metal graphites (Fig. 9) and with the graphites impregnated by Co(NO$_3$)$_2$ (Fig. 10) are presented.

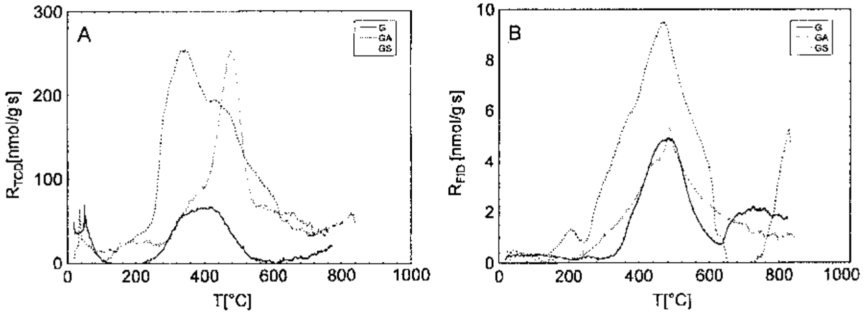

Fig. 9 TPH profiles of the 'as prepared' graphites (G – non modified, GA – acetylated, GS – sulphonated)

There are, however, some differences. The obvious one is that hydrogenation (into nearly 100% to CH$_4$) is taking place above 500°C. In case of TPD there was no hydrogen to proceed with this reaction.

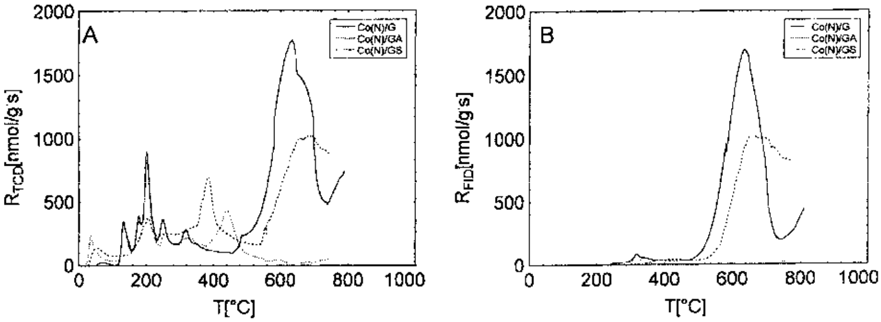

Fig. 10 TPH profiles of the 'as prepared' graphites (G – non modified, GA – acetylated, GS – sulphonated), impregnated with $Co(NO_3)_2$

Discussion

By sulphonation and acetylation are implanted functional groups into synthetic graphite surfaces. They, however, undergo partial decomposition just during drying in vacuum. Hence the FTIR spectra [5] have given evidences for the presence of –OH groups, in majority from sulfonic ones in the sulphonated graphites. In the acetylated graphites either methyl and carboxylic groups have been found in the FTIR spectra.

The temperature-programmed procedures TPD as well as TPH of modified graphites (as prepared) cause further decomposition of the surface groups, and desorption of organic molecules (mostly CH_4) and inorganic ones (CO_2, SO_2, H_2O), as it was proved by EGA.

In spite of these decomposition and desorption, the residual surface is much more active in case of the acetylated graphites. The initial surface groups must have be transformed into highly active ones, especially in presence of Ni or Co. The synergistic effect of surface groups and metal additives supports the hypothesis on the active assemblies enabling fast hydrogenation.

There is however one exception. If Ca is introduced to the acetylated graphite and these samples have undergone the TPD procedure just before the TPH, a visible inhibition of hydrogenation is noticed. The nature of this effect is unclear.

Usually just the opposite effect is observed. The synergistic of Ca improves the catalyst effectiveness. CH_4 is formed with higher rate and the observed catalytic activity is more stabile. It may be explained by protecting the metal crystallite against sintering, as it was proposed by Baker and Sherwood [6].

The alternative explanation assumes stabilization of the secondary surface groups by basic Ca. Zoheidi and Miller [7] postulated formation of very active secondary groups from the initial oxide groups in active carbons which groups are stabilized by potassium.

The higher catalytic activities observed for the transition metals introduced as nitrates in comparison with those found for acetyloacetonated (Figs 6–8) can be explained by oxidative activation of the graphite matrix by NO_x formed during the thermal treatment. Formation of basic groups in carbon material activated with HNO_3 was proposed by Nemerovets *et al.* [8]. These basic groups may be similar to those present in natural coals – pyrone [9] and chromene [10]. As it was proved later the basic groups are extremely stabile. They are removed from the coals above 1000°C [11].

The TPD curves (Figs 3 and 4) exhibit similar maxima to the thermal decomposition of pure $Fe(NO_3)_3 \cdot 9H_2O$ [11] or $Co(NO_3)_2 \cdot 6H_2O$ [12]. The literature data on the thermal decomposition of $Ni(NO_3)_2 \cdot 6H_2O$ are different from the TPD curve obtained for NiCa(N)/G (Fig. 5). This discrepancy can be understood taking into account that the drying procedure is at 120°C, very close to the temperature of $Ni(NO_3)_2$ decomposition, what suppose at least partial decomposition of $Ni(NO_3)_2$ before starting the TPD programme.

One more phenomenon needs some comments. The sharp peaks about 600–700°C on TPD curves of the transition metal doped graphites (Figs 4 and 5) should be ascribed to the reduction of metal oxides by the graphite matrix. After integration of the TPD signal the reduction degree of the metal oxide could be determined. In most of the cases the reduction degree is very close to 100%. There are however two cases with a reduction degree higher than 100%. They were obtained for NiCa(N)/G and NiCa(N)/GA samples. Maybe NO_x from the decomposition of nitrates oxidizes the graphite matrix with the formation of CO_2 which in turn reacts with CaO forming $CaCO_3$. This carbonate decomposes at temperature 550°C [12], so in vicinity of the TPD peak ascribed to NiO reduction by carbon matrix (Fig. 5).

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This work was supported by KBN (the Committee for Scientific Research, Poland) under contract No. PB 0568/P4/93/05.

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