

The post-carbonization stage of carbon materials synthesis as a factor influencing its thermal stability



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Introduction

Carbon materials are widely used as catalysts [1] and catalyst supports with metal addition [2] in many industrially important processes. The combination of specific properties makes nanostructured synthetic carbon materials (SCM) attractive and competitive compared to nature activated carbons [3]. However, there are a number of industrially important processes that take place under conditions of high temperatures (673-1073 K) [2] and in the presence of an oxidant, in particular oxygen [1], where nanostructured SCM show high activity. Such reaction conditions can be detrimental to carbon materials by contributing to their destruction/burnout. Carbon materials thermal stability can be affected by the concentration of surface defects which also create microporosity and can catalyze carbon gasification and/or the presence of metal particles that also can catalyze carbon gasification [3]. Another challenge to the widespread use of nanostructured SCM is that the methods for obtaining its are often complex and costly. This encourages research into improving existing nanostructured SCM and creating new thermostable ones. **The aim of the work** was to determine the thermal stability of nanostructured SCM produced by template synthesis according to an improved method (with an additional post-carbonization stage) has been investigated. The comparison was carried out with natural activated carbons as well as with and without metal addition.

Results

In general, the synthesized samples have a commensurate specific surface area (S^{BET}) as compared to the natural carbon material and 2.5 times higher total pore volume (V_{Σ}), *Table 1*. The share of micropores ($V_{\text{micro}}^{\text{t}}$) in the total pore volume of **AC** is more than 90 %, that of **SCM1** is 40 %, and **SCM2** is only 16 %. The pore size distribution calculated by the DFT method (*Figure 1*) shows that **AC** is mainly microporous and the synthesized samples **SCM1** and **SCM2** are mainly mesoporous. Thus, an additional carbonization step in the synthesis process contributes to the reduction of the number of micropores in the synthetic samples and, consequently, to the reduction of defects.

Table 1. Parameters of porous structure of the investigated samples

Sample	S^{BET} , m^2/g	S^{t} , m^2/g	$S^{\text{t}_{\text{micro}}}$, m^2/g	$V_{\text{micro}}^{\text{t}}$, cm^3/g	V_{Σ} , cm^3/g	$V_{\text{micro}}/V_{\Sigma}$, %	R , nm
AC	990	16,0	971	0,48	0,51	94	1,0
SCM1	970	517	453	0,49	1,25	39	2,6
SCM2	932	789	143	0,19	1,18	16	2,5

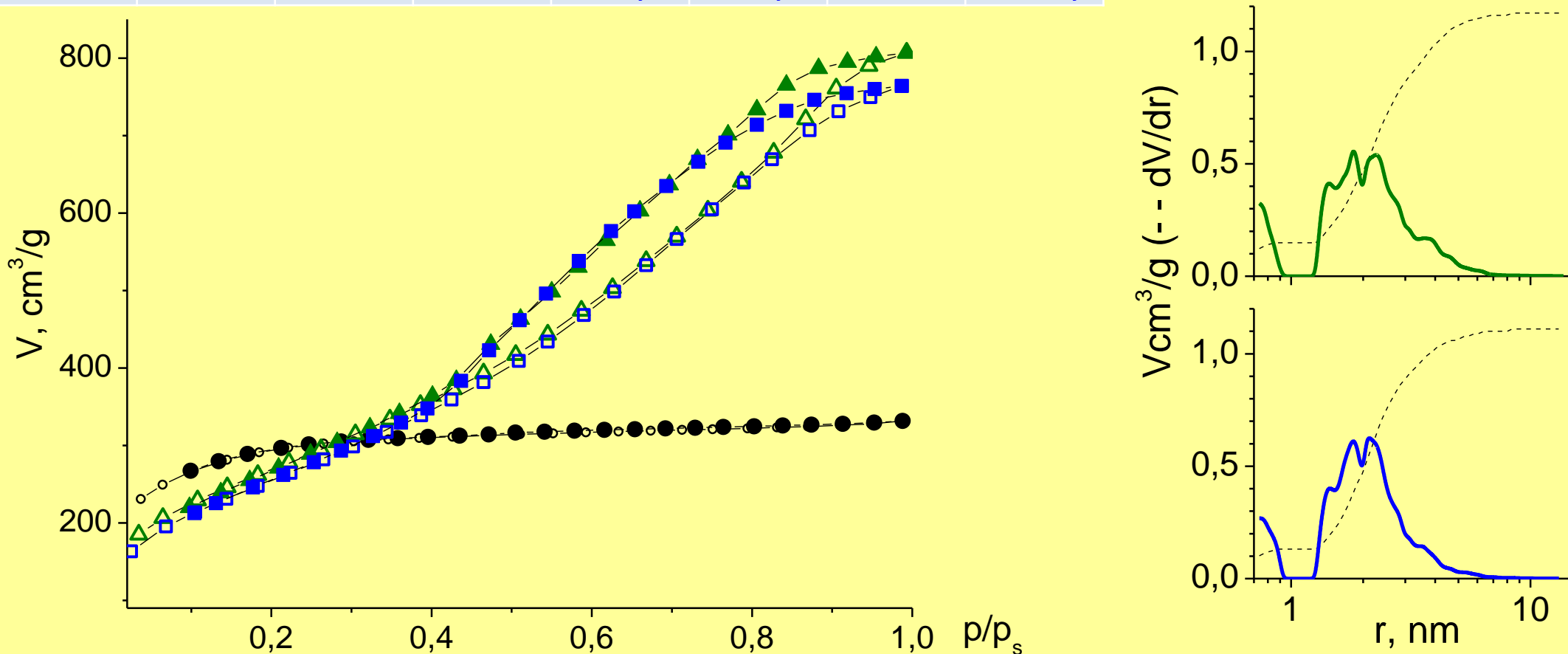


Figure 1. Low-temperature ad(de)sorption isotherms of nitrogen (left) and pore size distribution (right) of the investigated samples

The most common and simple way to investigate the temperature resistance of carbon material is thermogravimetric analysis. The mass loss of the test samples (*Figure 2*) is due to combustion processes indicated by exothermic effects (DTA curves). The initial mass loss (TG, DTG curves) of 10 % for **AC**, as for the sample **SCM1**, is reached at 823 K, whereas for **SCM2** it is at 853 K (30 K higher). The higher temperature resistance to oxidation in air of the sample with the additional carbonization stage is indicated by the maximum mass loss rate temperatures (903 and 923 K for **SCM1** and **SCM2** samples) compared to **AC** (863 K).

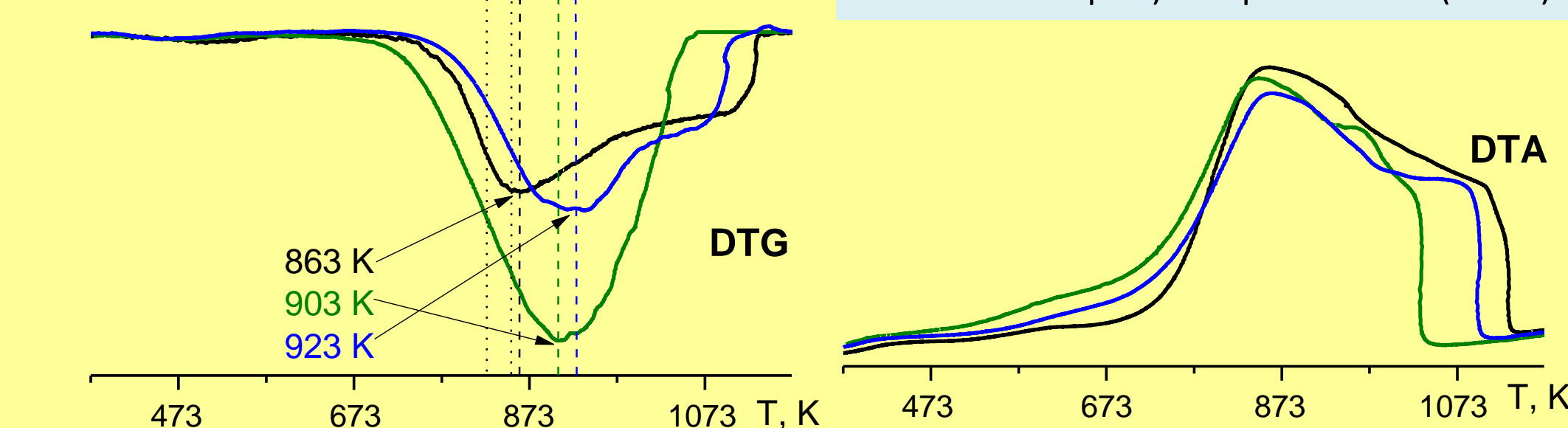
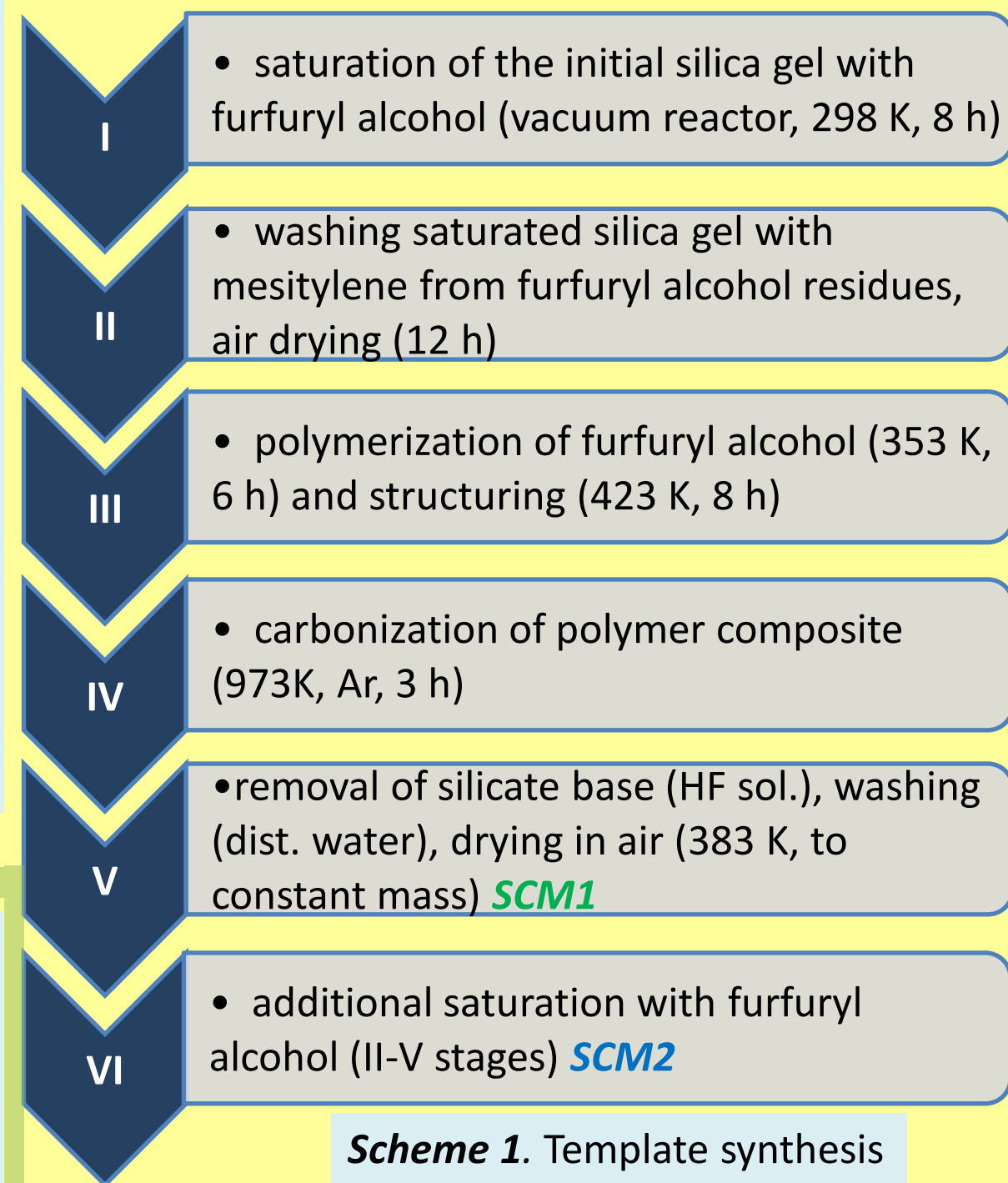


Figure 2. Thermogravimetric analysis of the investigated samples

Experimental methods



Scheme 1. Template synthesis

The method of template carbonization allows obtaining carbon materials with a controlled structure and a relatively narrow distribution of pores in size. Consequently the nanostructured SCM was obtained by template synthesis according to the method [4], *Scheme 1*.

Isotherms of low-temperature ($T = 77 \text{ K}$) nitrogen ad(de)sorption were measured on a Quantachrome® NOVA-1200e automatic sorbtometer after in situ evacuation at 473 K (5 h). The NovaWin 11.04 software was used to calculate the parameters of a porous structure (*Figure 1*, *Table 1*).

The carbon materials thermal stability were characterized on a derivatograph type Q1500D made by MOM (in the air, 10 K/min). The comparison synthesized samples was carried out with natural activated carbon (**AC**) as well as with and without metal addition.

Thermal stability can also be affected by the presence of metals on the carbon material, which can catalyze carbon oxidation and lower the combustion temperature. In order to establish this effect, Ni was applied to the samples in amounts of 1 and 4 % by mass and their thermal stability was investigated.

The weight loss of the Ni-contained samples, like the original samples, is due to combustion processes (DTA curve). The initial mass loss (10 %; TG and DTG curves) when Ni is introduced and as the amount of Ni is increased it shifts towards lower temperatures for **AC** from 823 to 763 K, for **SCM1** and **SCM2** from 823 and 853 to 683 K, respectively. The same temperature shift occurs for the maximum mass loss rate up to 783 K for **AC**, 683 K for **SCM1** and **SCM2** (*Figure 3*).

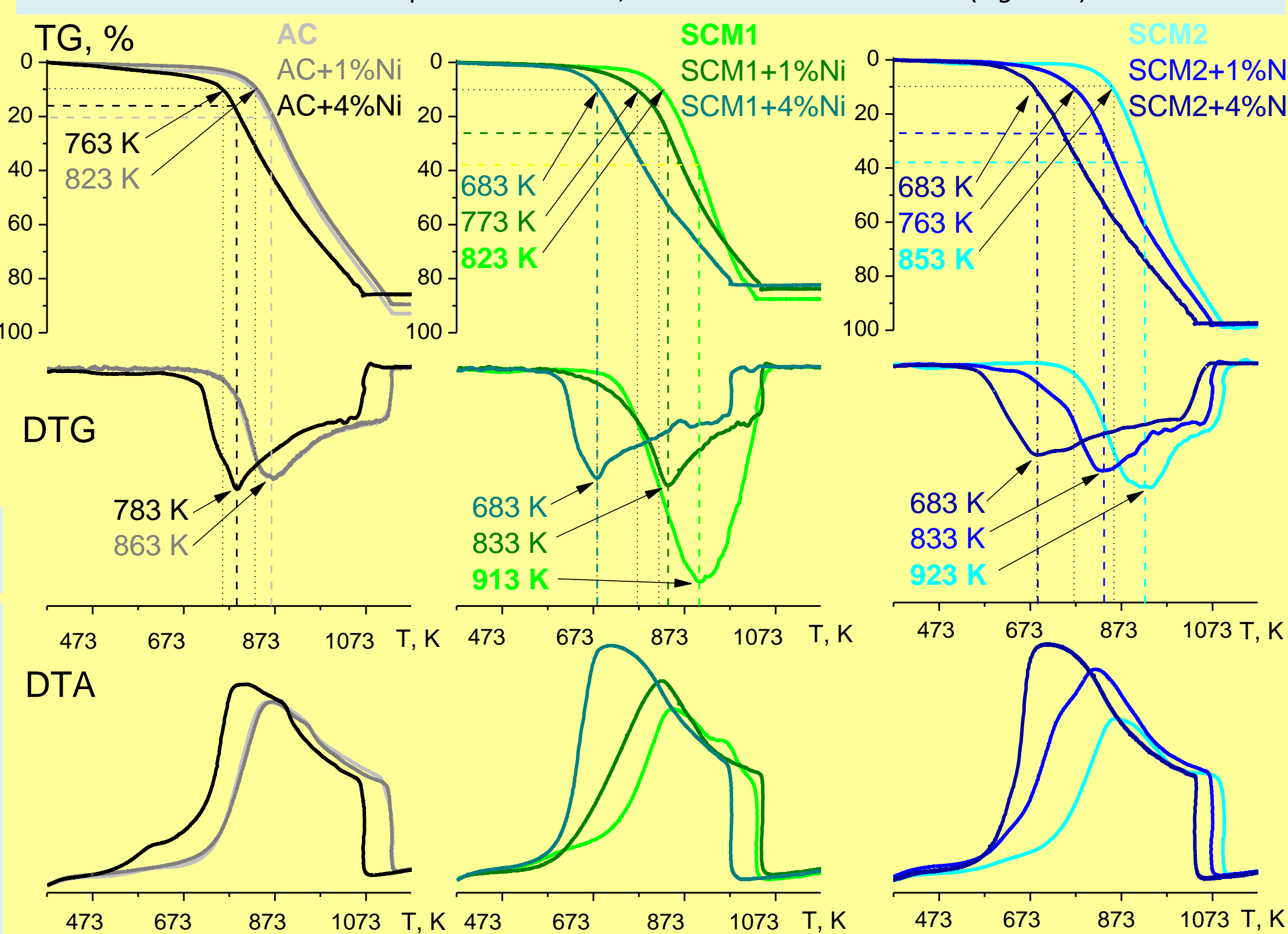


Figure 3. Thermogravimetric analysis of the investigated samples with applied Ni

Conclusion

An additional carbonization step in the synthesis of the carbon material reduces the number of structural defects and increases their thermal stability, which makes such materials promising for replacing natural carbon in liquid-phase catalytic processes. Regardless of the nature of the carbon material, the application of metal negatively affects to the thermal stability of the carbon material by catalyzing its oxidation. The dependence of heat resistance on the amount of applied metal is anti-bat. An additional carbonization step can increase the heat resistance of carbon materials or correct it for metal-containing carbon catalysts.

References

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