Gas-phase bromination of carbon materials for the production of surface precursors

Diyuk V. E.[1], Vakaliuk A. V.[1], Tsapyuk G. G.[1], Yatsymyrskyi A. V.[1],

Mariychuk R.[2], Boldyrieva O. Yu.[1], Lisnyak V. V.[1,2]

[1] *Taras Shevchenko National University of Kyiv, Volodymyrska Street, 64/13, Kyiv 01601, Ukraine.*
E-mail: vdiyuk@gmail.com; lisnyak@chem.univ.kiev.ua
[2] *Presov Universirty in Presov, Ul. 17 novembra, 1, Presov 15 080 01, Slovakia.*

The adsorption and catalytic properties of nanocarbons and nanoporous carbon materials (CMs) depend significantly on surface chemistry. Some surface groups are formed during the synthesis and subsequent processing, but the formation of functional groups on the surface is possible only as a result of chemical modification. The most versatile method of modifying is halogenation and the subsequent halogen replacement by other functional groups. This approach allows obtaining the required functional groups at a given concentration on the carbon surface. However, modification using liquid bromine and its solutions caused a low yield of grafted bromine and, because of the high affinity of carbon to oxygen, it is accompanied by significant oxidation of the carbon surface. The treatment with bromine vapor prevents unwanted parallel oxidation and more actively involves the active centers in bromine addition. Activated carbons KAU, SKN1, and SKN2, multi-walled carbon nanotubes (MWCNTs), and carbon black (CB) were subjected to the vapor bromination and examination of chemical properties of the brominated CMs, and evaluation of the concentration of surface functional groups from the thermogravimetry data.
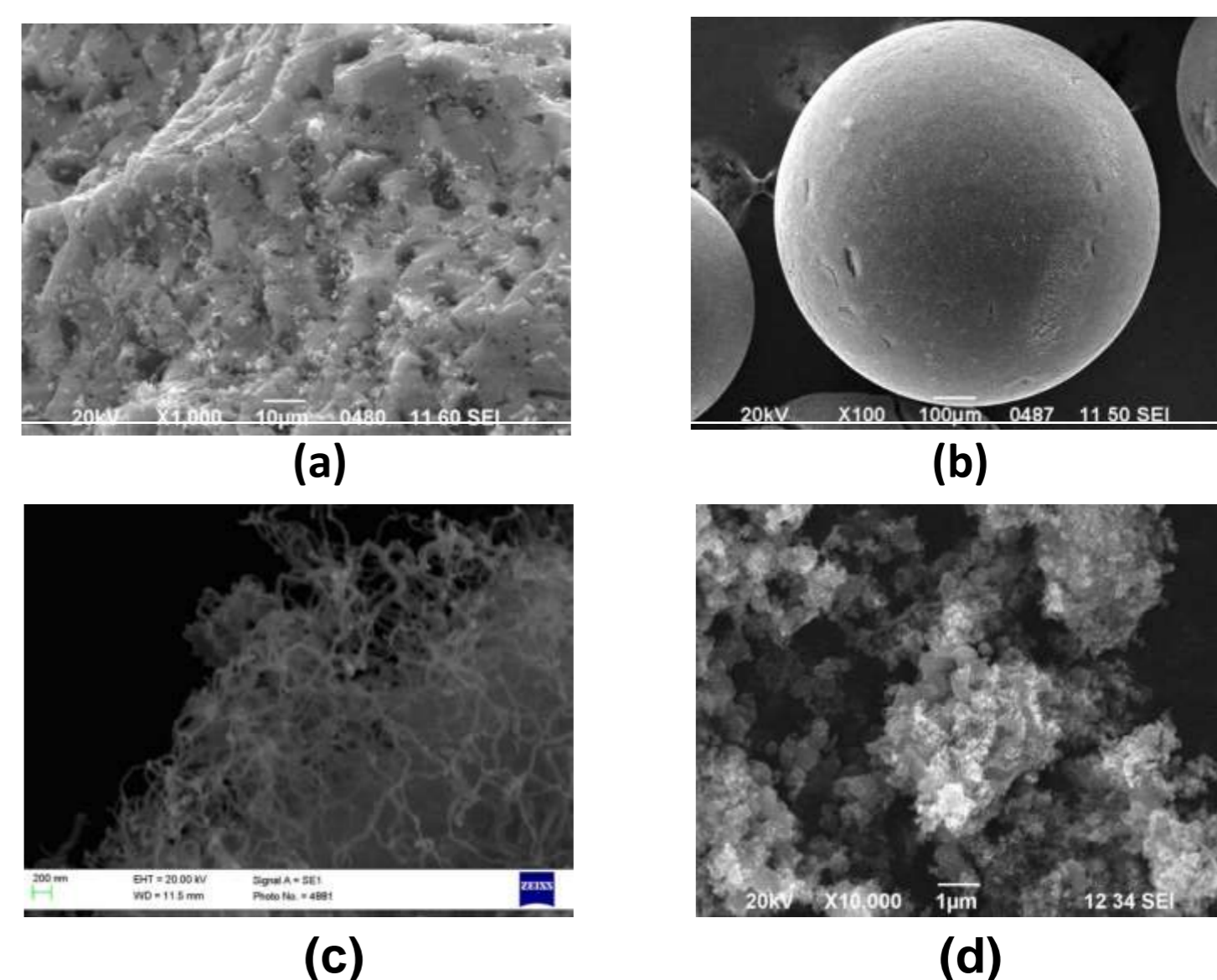

Fig. 1. SEM images of initial carbon materials:
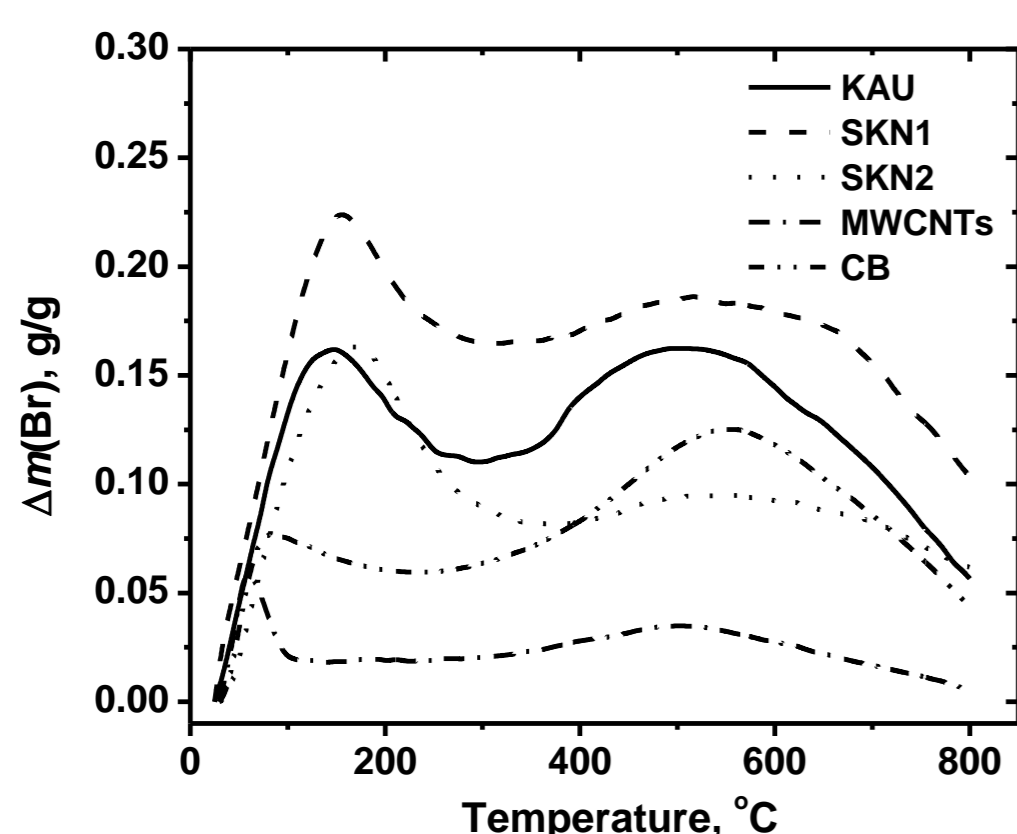(a) – KAU, (b) – SKN1, (c) – MWCNTs, and (d) – CB.

Gas-phase bromination of CMs

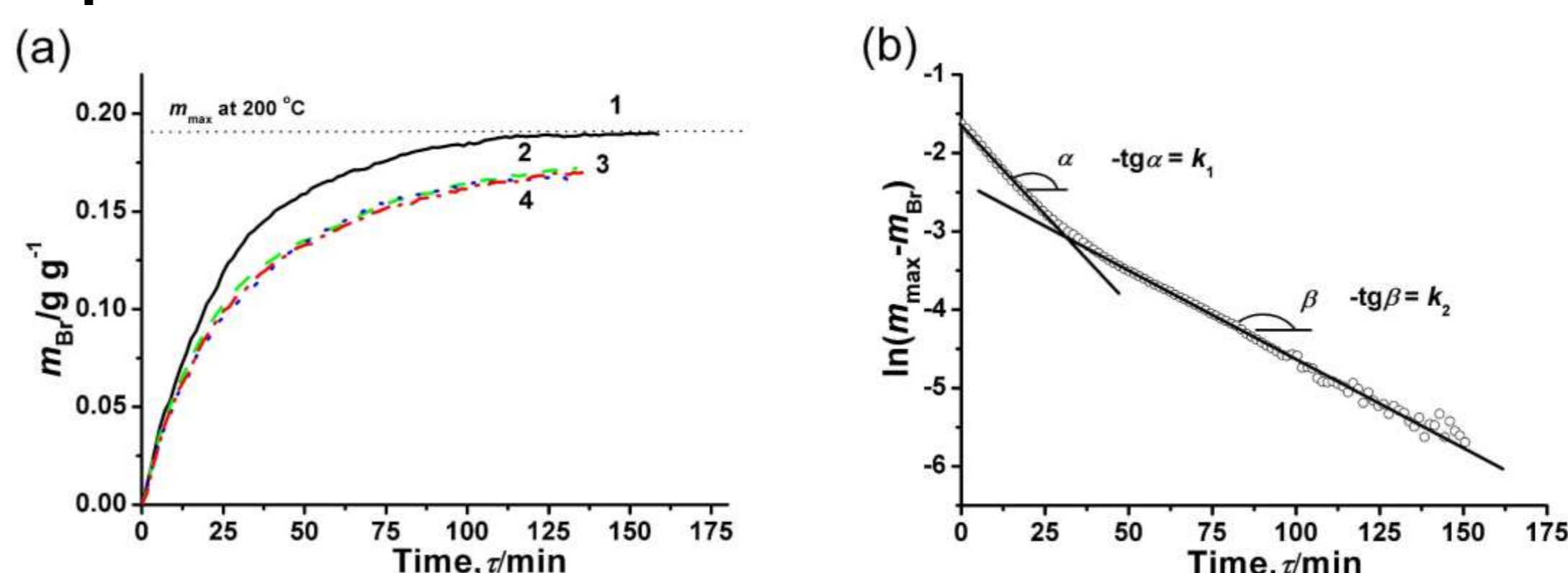**Fig. 2.** Kinetic curves for the non-isothermal bromination of CMs (heating rate of 3 °C/min).

Fig. 3. Kinetic TG profiles of the bromination of the KAU samples for the temperature: 1 – 200 °C; 2 – 300 °C; 3 – 400 °C; 4 – 500 °C; **b** The linearization of the TG profiles in the semilogarithmic coordinates.

The optimum bromination temperature is in the range of 300-600 °C (Fig. 2). For all CMs, in the temperature range of 200-500 °C, the formation of two chemisorbed bromine forms is observed (Fig. 3). The amount of chemisorbed bromine referred to 1 g of CMs increases in the sequence: MWCNTs <SKN2 <CB <KAU <SKN1. In contrast, the reactivity of the surface increases as follows: SKN2 <KAU <SKN1 <MWCNTs <CB. Probably, the higher reactivity of the surface of CB and MWCNTs is explained by the higher number of reactive and accessible boundary C = C bonds in graphene planes.
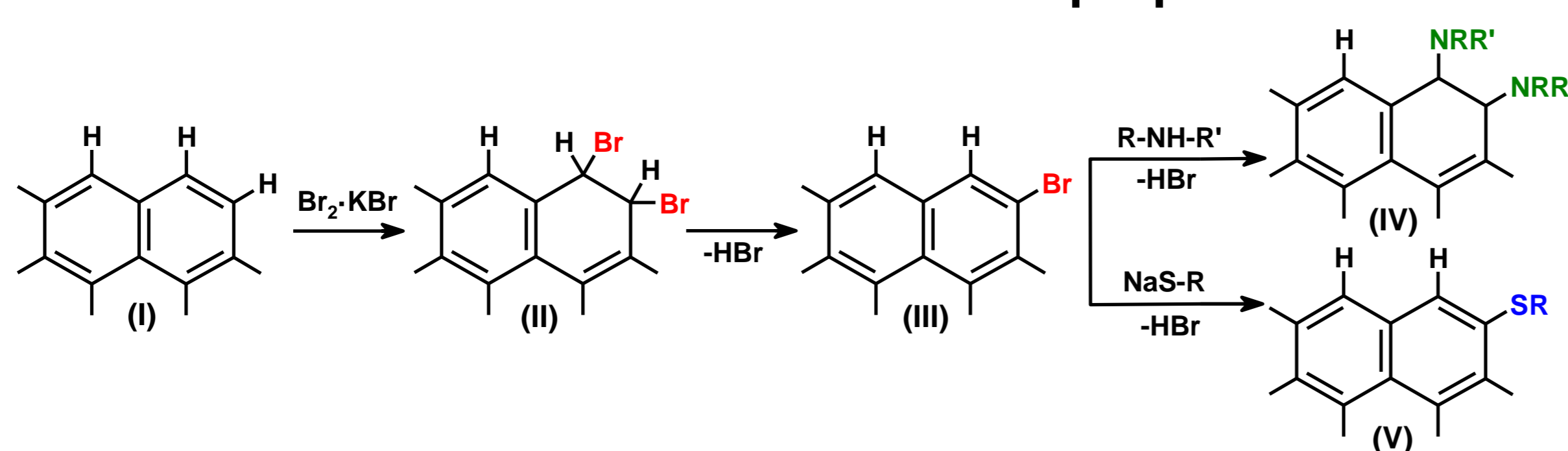
Thermal and chemical properties of brominated CMs

Fig. 4. Surface chemistry changes after bromination, amination and sulfurization of CMs.
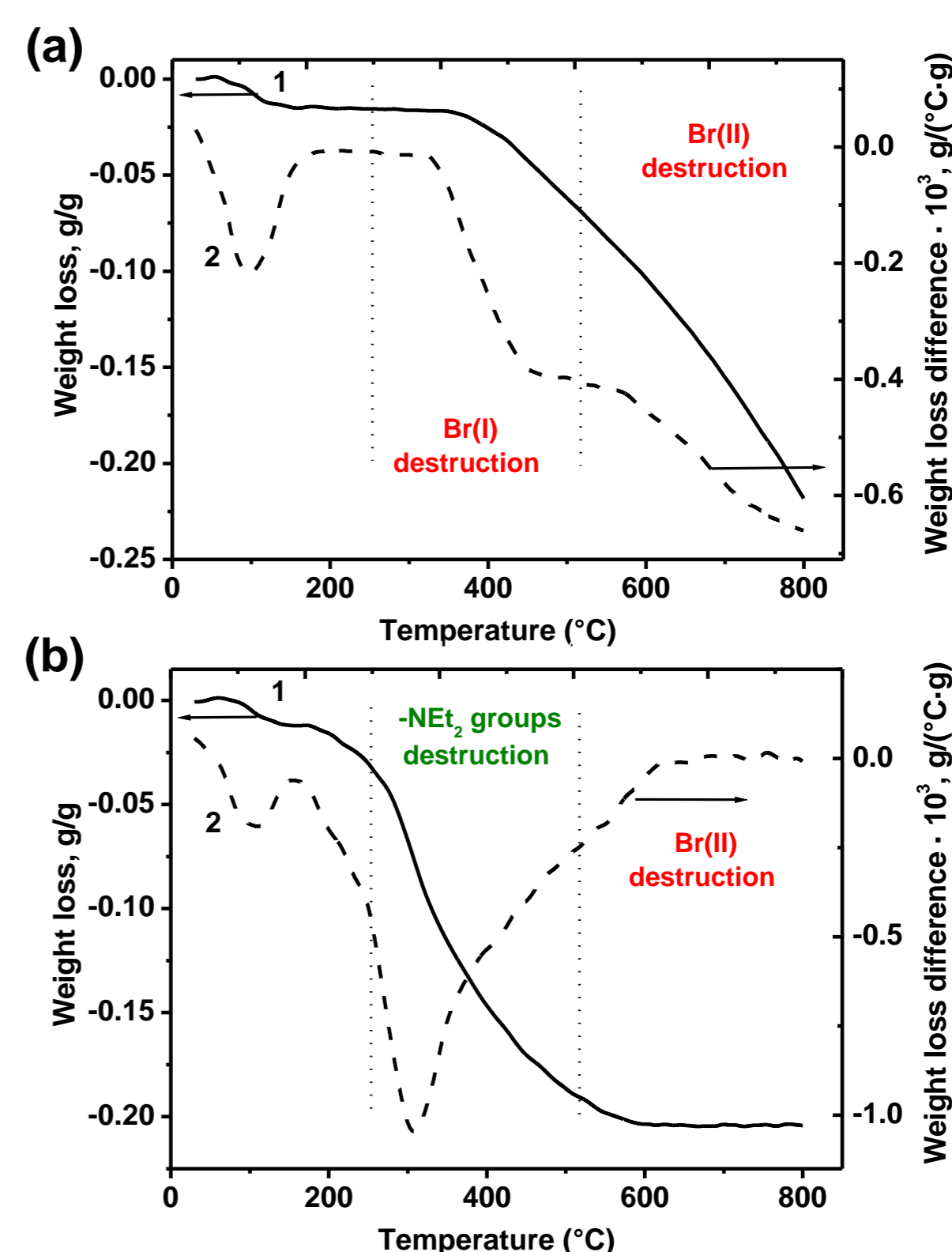

Fig. 5. Temperature dependences of mass change in the integral (1) and in the differential (2) forms for the samples: a – SKN1-Br(400), b – SKN1-Br(400)-NEt$_2$.

Conclusions. It was found that the gas-phase bromination in the temperature range of 200–500 °C is a simple and effective method of the CMs functionalization. Under the stated conditions, the mentioned above CMs can chemisorb the maximal quantity of bromine, up to 2.2 mmol/g. The almost complete bromination of active sites of the surface is realized within the time interval of 1.5–2.5 h. The kinetics of the CMs bromination depends significantly on the textural characteristics of the initial CMs. The chemical reactivity of the CMs in the bromination is determined by the presence of double C=C bonds, which are reacted with the active bromine. The surface bromine is characterized by high reactivity, and it can be replaced with up to 1.7 mmol/g of NEt$_2$ groups by amination. According to TG data, the surface-functionalized NEt$_2$ groups are characterized by high thermal stability. The maximal thermal decomposition rate of them is registered at 305±10 °C. The obtained aminated CMs have potential as selective adsorbents in the industrial separation of environmental contaminants, such as Hg ions or NO$_2$ and CO$_2$ gases.