

Sulfurization and hydrosulfidation of nanoporous carbon for the preparation of sorbents and solid acid catalysts

Chernenko S. I.¹, Diyuk V. E.¹, Vakaliuk A. V.¹, Grishchenko L. M.¹, Tsapyuk G. G.¹, Mischanchuk A. V.², Mariychuk R.³, Lisnyak V. V.^{1,3}

¹ Taras Shevchenko National University of Kyiv, Volodymyrska Street, 64/13, Kyiv 01601, Ukraine.

E-mail: s.chernenko2020@gmail.com; lisnyak@chem.univ.kiev.ua

² Chuiko Institute of Surface Chemistry of NAS of Ukraine, General Naumov Street, 17, Kyiv 03164, Ukraine.

³ Presov University in Presov, Ul. 17 novembra, 1, Presov 15 080 01, Slovakia.

Today, humanity needs for effective sorbents, carriers, and solid acid catalysts. These catalysts could be prepared by the targeted introduction of heteroatoms, e.g., nitrogen, sulfur, phosphorus, etc., into the surface layer of carbon nanoporous materials. The presence of the heteroatoms, in the surface groups, changes significantly the surface characteristics and is a reason for increasing acidity/basicity and the sorption capacity for heavy metal ions. Nanoporous activated carbons (NACs) with grafted sulfo groups are efficient catalysts for isomerization, hydration, and dehydration. However, the known methods of sulfonation, e.g., with sulfuric acid, oleum, or chlorosulfonic acid, do not give the required concentration of sulfo groups. Sulfur-containing NACs obtained by incomplete carbonation of sulfoaromatic compounds have poor mechanical and structural-sorption characteristics. Therefore, it is promising to create new effective methods of surface acidification.

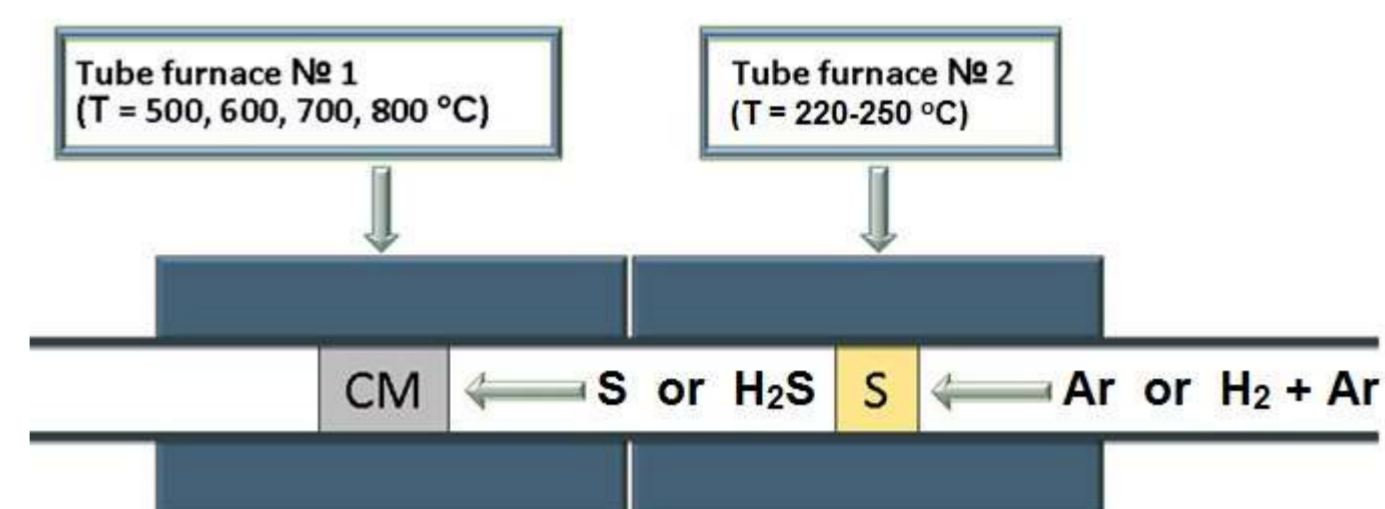


Fig. 1. Synthetic setup for sulfurization or hydrosulfidation.

Preparation of solid acid catalysts

The air-dried, SKN activated carbon (1.5-2.0 g) and sulfur (1.0 g) were placed in a quartz reactor, in a tube furnace #1 and #2, respectively, see Fig. 1. In a flow of argon, the tube furnace #1 was heated to a predetermined temperature and kept at this temperature for 30 minutes. In a given temperature regime, oxygen-containing functional groups were partially removed from the surface. After that, the tube furnace #2 was heated to a predetermined temperature in the range of 220-250 °C and an argon or a mixture of gases H₂-Ar (1: 1) at the flow rate of 100 ml/min was passed to the reactor. In this temperature range, the largest amount of sulfur vapour or hydrogen sulfide is formed. Oxidation of sulfurized and hydrosulfidated NAC samples was carried out to obtain sulfo groups. For oxidative treatment potassium chlorate (6 g) and nitric acid (10 ml) in water (50 ml) were used. Fig. 2 shows the scheme of sulfurization and hydrosulfidation.

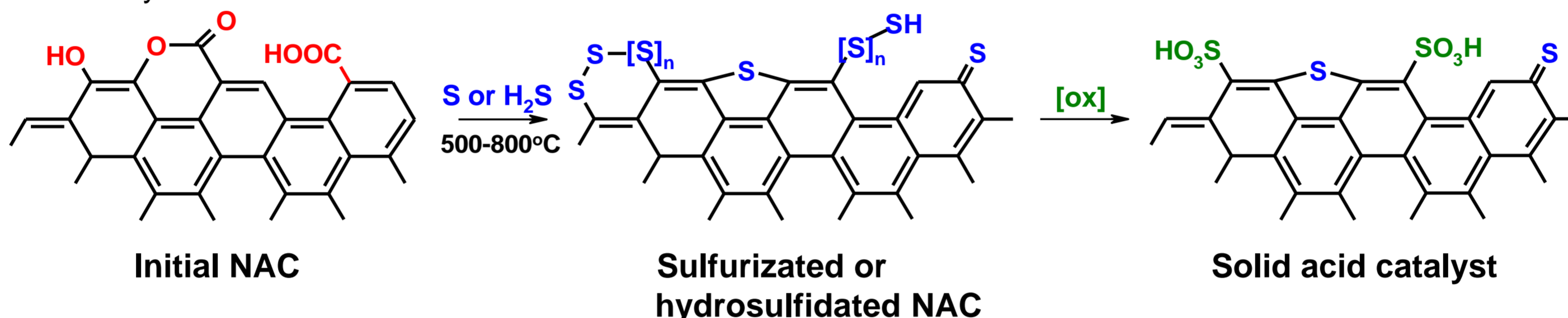


Fig. 2. Schematic diagrams of surface sulfurization, hydrosulfidation and oxidation.

Characterization of sulfurized and hydrosulfidated NACs and solid acid catalysts

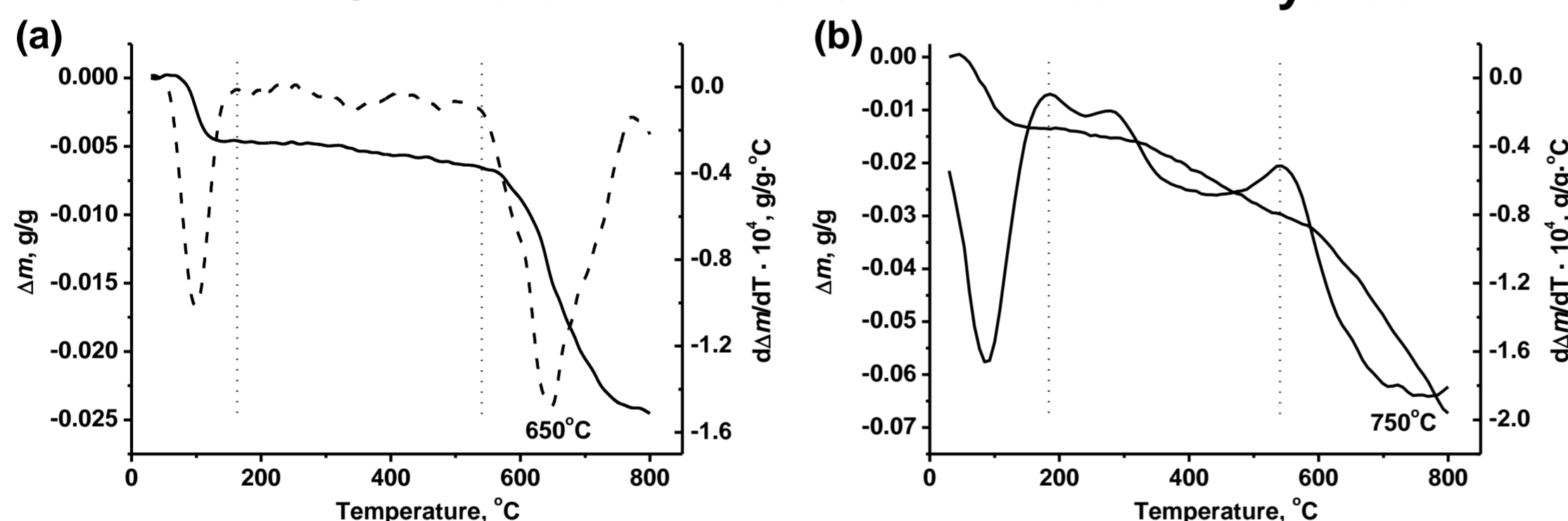


Fig. 3. Typical TG/DTG data for (a) hydrosulfidated and (b) sulfurized NACs.

Table 1. Sulfur content in the sulfurized and hydrosulfidated NACs

Sample	C(S), mmol/g	Sample	C(S), mmol/g
NAC-S500	6.38	NAC-H ₂ S500	4.30
NAC-S600	4.76	NAC-H ₂ S600	2.34
NAC-S700	3.00	NAC-H ₂ S700	0.51
NAC-S800	3.24	NAC-H ₂ S800	0.38

The model reaction of gas-phase isopropyl alcohol dehydration

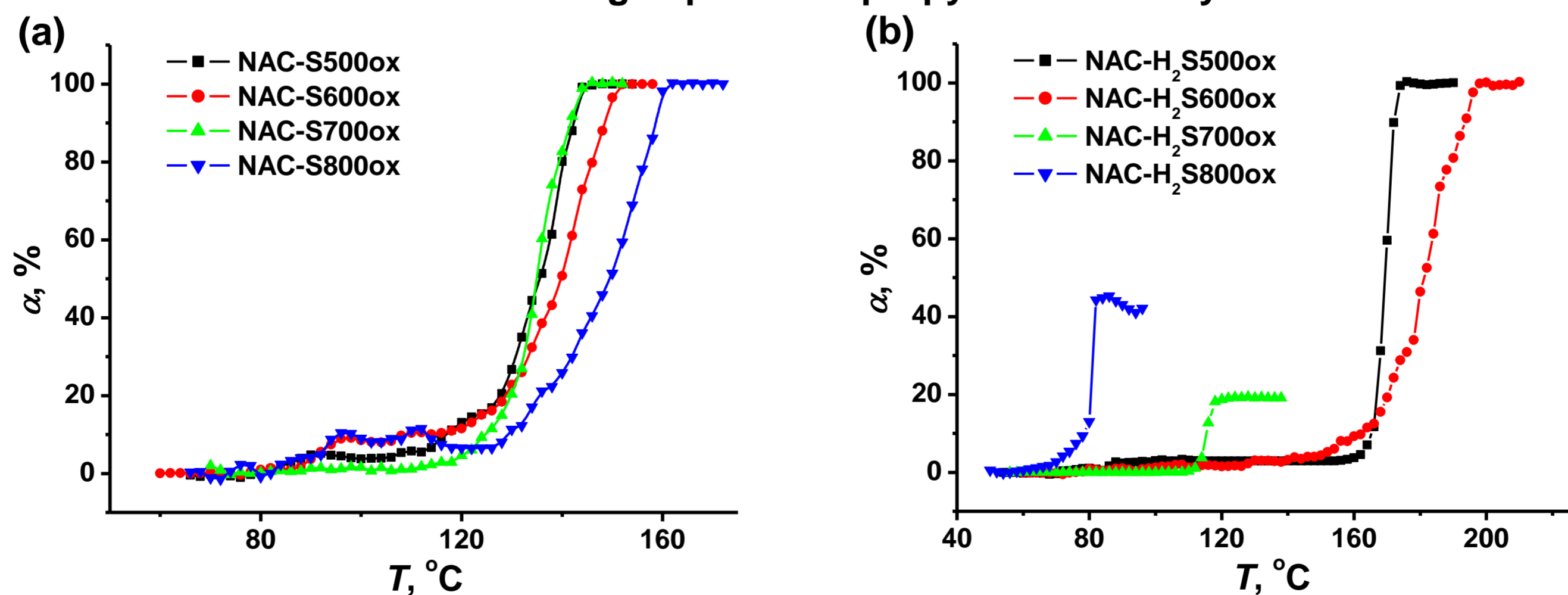


Fig. 4. Temperature dependences of propylene yield in the catalytic reaction of isopropyl alcohol dehydration.

Conclusions. By modifying the activated carbon with sulfur or hydrogen sulfide, in the temperature range of 500-800 °C, one can introduce into the surface layer of up to 6.4 mmol/g of sulfur, in the form of various functional groups. Thermogravimetric analysis showed that chemisorbed sulfur is thermally stable in the temperature range 30-550 °C. The highest content of chemisorbed sulfur can be achieved by sulfurization and hydrosulfidation at medium-high temperatures (500-600 °C). When the temperature increases, the sulfur content decreases because of desorption from the surface of activated carbon. When one treats ACs after hydrosulfidation with strong oxidants, i.e., KClO₃ sulfo groups are formed. The obtained oxidized samples have high catalytic activity in the isopropanol dehydration reaction. The 100% conversion of isopropanol to propylene on the most active samples is observed at 145-200 °C. So the proposed method can be used to obtain solid acid catalysts.

