

Hydrosulfidation of nanoporous carbon for the preparation of solid acid catalysts

Diyuk V. E.¹, Horodetska D. S.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: d.horodetska@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.

Preparation of solid acid catalysts

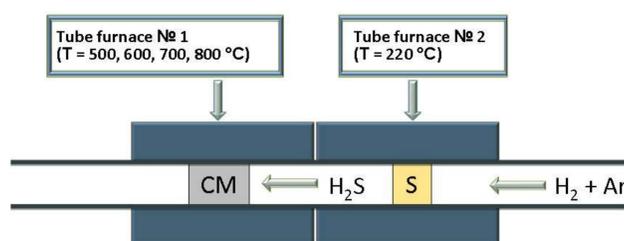


Fig. 1. Synthetic setup for hydrosulfidation.

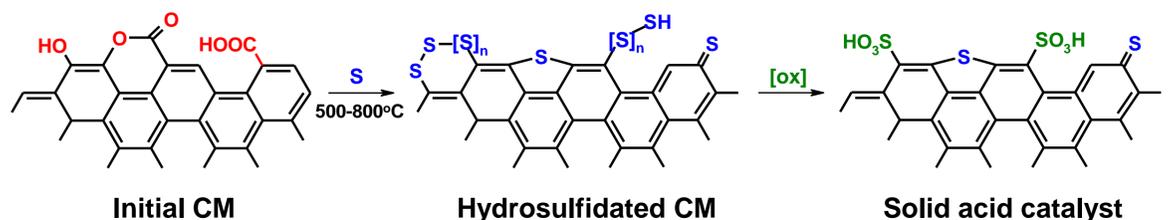


Fig. 2. Schematic diagrams of surface hydrosulfidation and oxidation.

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, a mixture of gases H₂-Ar (1: 1) at the flow rate of 100 ml/min was passed to cool the reactor, and the tube furnace #2 was heated to a predetermined temperature. For efficient synthesis, the optimal operating temperature for the tube furnace #2 is in the range of 220-250 °C. In this temperature range, the largest amount of hydrogen sulfide is formed. Fig. 2 shows the scheme of hydrosulfidation.

Oxidation of CM samples was carried out to obtain sulfo groups. For oxidative treatment, two different oxidizing mixtures dissolved in protic solutions were used: potassium chlorate (6 g) and nitric acid (10 ml) in water (50 ml) (ox1) and hydrogen peroxide (30%) in acetic acid (ox2). The oxidative treatment time was 24 hours. After oxidation, the samples were washed with water and Na₂CO₃, to alkaline pH, and then again with water. The resulting samples to restore the acidic form of sulfo groups were immersed in a solution of 3% hydrochloric acid, kept for 2 h, then thoroughly washed with water (until neutral pH), and then dried at 130 °C.

Characterization of hydrosulfidated CMs and solid acid catalysts

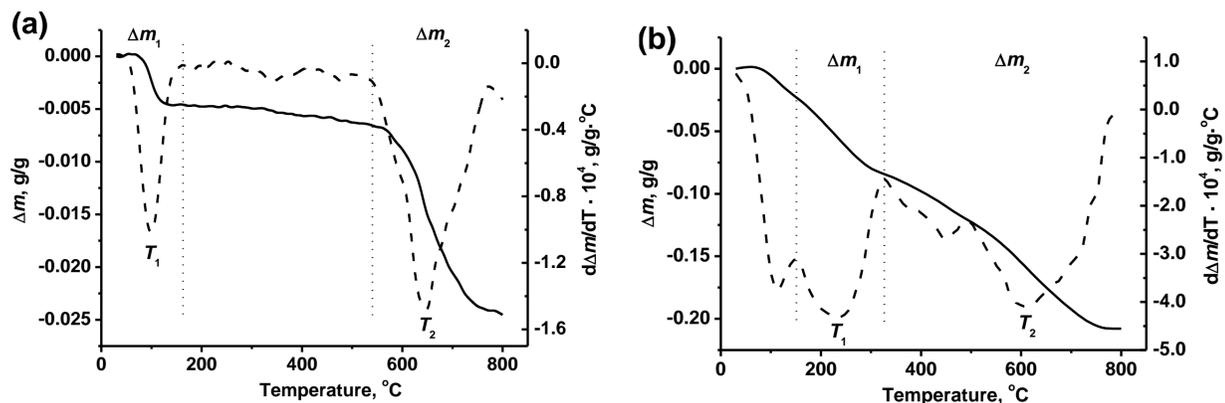


Fig. 3. Typical TG/DTG data for (a) hydrosulfidated SKN600 and (b) solid acid catalyst SKN600ox1.

Table 1. C.A. and TG/DTG

Sample	C(S), mmol/g	T ₂ , °C	Δm ₂ , g/g
SKN500	4.30	690	0.027
SKN600	2.34	652	0.019
SKN700	0.51	772	0.020
SKN800	0.38	792	0.002

Table 2. C.A. and TG/DTG

Sample	C(S), mmol/g	T ₁ , °C	Δm ₁ , g/g	T ₂ , °C	Δm ₂ , g/g
SKN500ox1	3.25	232	0.061	608	0.124
SKN600ox1	1.86	204	0.073	604	0.143
SKN700ox1	0.10	195	0.076	676	0.157
SKN800ox1	0.12	168	0.088	572	0.160
SKN500ox2	4.15	185	0.020	683	0.035
SKN600ox2	2.10	199	0.010	681	0.031
SKN700ox2	0.34	172	0.012	690	0.037
SKN800ox2	0.43	196	0.016	680	0.036

The model reaction of gas-phase isopropyl alcohol dehydration

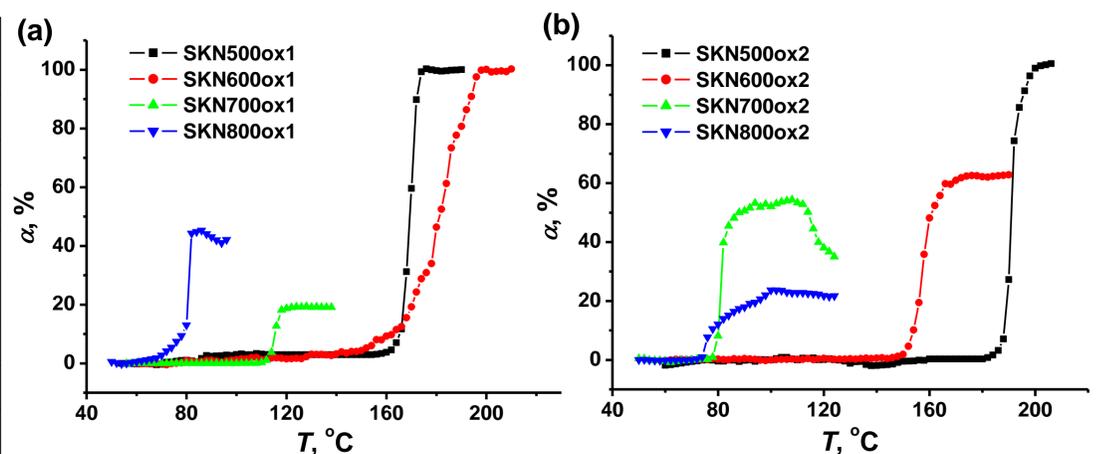


Fig. 4. Temperature dependences of propylene yield in the catalytic reaction of isopropyl alcohol dehydration.

Conclusions. By modifying the activated carbon with hydrogen sulfide, in the temperature range of 500-800 °C, one can introduce into the surface layer of up to 3.25 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 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 or H₂O₂, sulfo groups are formed. KClO₃ is a more effective oxidant than H₂O₂. 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 175-200 °C. So the proposed method can be used to obtain solid acid catalysts.