Universal approach to prepare effective solid acid catalysts from the surface-brominated nanoporous activated carbons

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Activated nanoporous carbon (NAC), due to its high surface area, developed porous structure and chemical resistance in various media, is a promising material for adsorption and catalysis. The formation of N- and S-containing functional groups is often based on a common synthetic approach, which involves the introduction of an active halogen atom into the molecule, followed by the substitution of this halogen for the desired functional groups. For the grafting of bromine-containing groups one often uses quite aggressive and difficult to perform methods of plasma-chemical treatment of samples of carbon materials, which require special equipment and complex installations [1,2]. In this paper, we consider a fairly simple method of introducing bromine-containing groups on the NAC surface, which consists in treatment of the samples with bromine reagents at room temperature. In the work we used activated carbon GSGD (hemosorbent granulated deligandizing), with particle sizes of 0.5 mm and a specific surface area of 2000 m^2/ g.

The grafting of acidic groups was carried out by treatment the carbon with liquid bromine and an aqueous solution of bromine in potassium bromide, followed by replacement of bromine with sulfur-containing groups. Modification with sulfur-containing compounds was performed by treatment the pristine and brominated samples with solutions of sodium mercaptoacetate (method S1) and sodium sulfide (method S2), followed by hydrolysis and oxidation of mercaptogroups to sulfogroups. The S1′ method was used when the hydrolysis and oxidation steps were combined using a mixture of acetic acid and hydrogen peroxide and the S1″ method for which the hydrogen peroxide oxidation step was performed without preliminary acidic hydrolysis.

Methods:

- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Chemical Analysis (C.A.)
- Thermogravimetric analysis (TGA)
- Thermoprogrammed desorption with IR registration of products (TPD IR)
- Thermoprogrammed desorption mass-spectrometry (TPD MS)

Table 1. Total mass loss (Δm), temperature range (Δt), maximum temperature (t_{max}) and concentration (c_{Br}) of bromine, by the TGA and chemical analysis, concentrations of carbon oxides (c_{CO}) and (c_{CO_2}), determined by TPD IR

Sample	Δm, g/g	Δt,°C	t_{max},°C	c_{Br}, mmol/g		c(CO), mmol/g	c(CO_2), mmol/g
				TGA	C.A.		
GSGD	0,03	-	-	-	-	0,14	0,02
GSGD/KBr_3	0,08	150-420	280	0,22	0,44	1,17	0,12
GSGD/Br_2	0,10	165-430	280	0,23	0,45	1,63	0,18

Table 2. The residue of bromine in samples NAC (Δ_{Br}) after treatment (40 min) with bases.

Sample	Base	c_{Br}, mmol/g	Δ_{Br}, %
GSGD/Br_2	$Na_2S_2O_3$	0,45	58
GSGD/KBr_3	$Na_2S_2O_3$	0,44	55
GSGD/Br_2	$MeNH_2$	0,45	56
GSGD/Br_2	SuEn	0,45	60

Table 3. Total mass loss, temperature range and temperature of thermal decomposition maxima (t_{m1}, t_{m2}) of acid groups, total SO_2 concentration, concentration of low- (c_L) and high-temperature (c_H) forms of SO_2-centers, concentration of carbon oxides for S-containing samples based on brominated NAC and maximum propylene yield temperature

Sample	Δm, g/g	Δt, °C	t_{m1}, t_{m2}, °C	c(SO_2)	c_L, c_H	c(CO)	c(CO_2)	$t_{100\%}$, °C
				Concentration, mmol/g				
GSGD/S1	0,058	195-620	295, 395	0,13	$8\cdot10^{-5}$; $7\cdot10^{-5}$	0,44	0,16	265
GSGD/S1′	0,059	145-570	265, 380	0,12	$6\cdot10^{-5}$; $6\cdot10^{-5}$	0,86	0,28	260
GSGD/KBr_3/S1	0,095	205-570	310, 395	0,12	$5\cdot10^{-5}$; $7\cdot10^{-5}$	0,67	0,20	260
GSGD/KBr_3/S1′	0,091	130-500	225,370	0,13	$5\cdot10^{-5}$; $8\cdot10^{-5}$	1,08	0,35	255
GSGD/Br_2/S1	0,088	180-500	290, 370	0,17	$8\cdot10^{-5}$; $9\cdot10^{-5}$	0,67	0,25	250
GSGD/Br_2/S1′	0,090	145-550	240, 300	0,16	$9\cdot10^{-5}$; $8\cdot10^{-5}$	0,84	0,55	250
GSGD/Br_2/S1″	0,088	175-570	320, 390	0,11	$6\cdot10^{-5}$; $5\cdot10^{-5}$	1,69	0,44	275
GSGD/Br_2/S2	0,116	130-540	210, 340	0,29	$7\cdot10^{-5}$; $8\cdot10^{-5}$	1,44	0,49	225

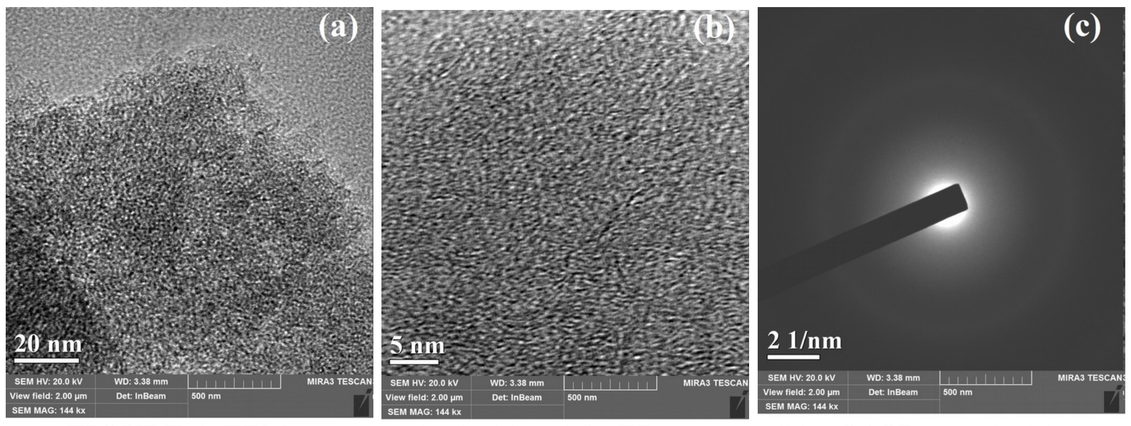

FIGURE 1. TEM micrographs (a, b) and SAED pattern of the GSGD sample (c).

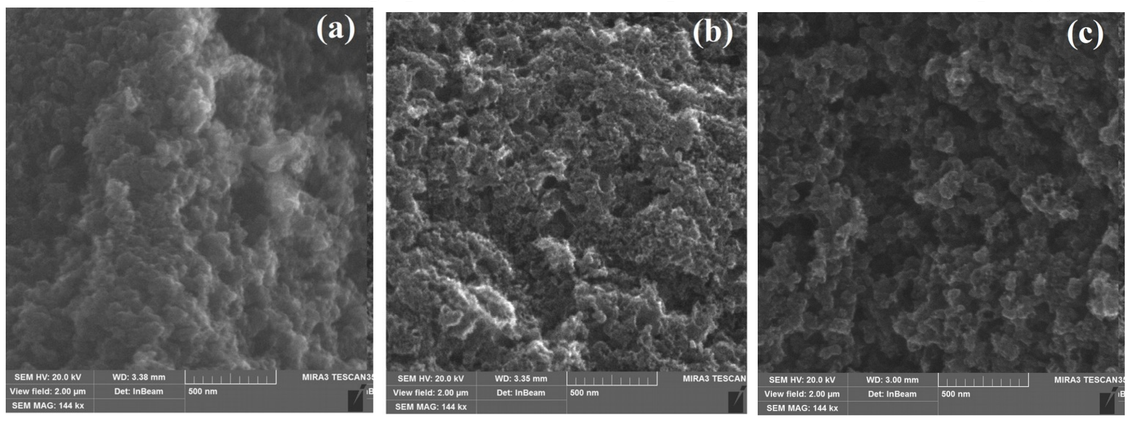

FIGURE 2. SEM micrographs: (a) GSGD, (b) GSGD/Br_2, (c) GSGD/Br_2/S1.

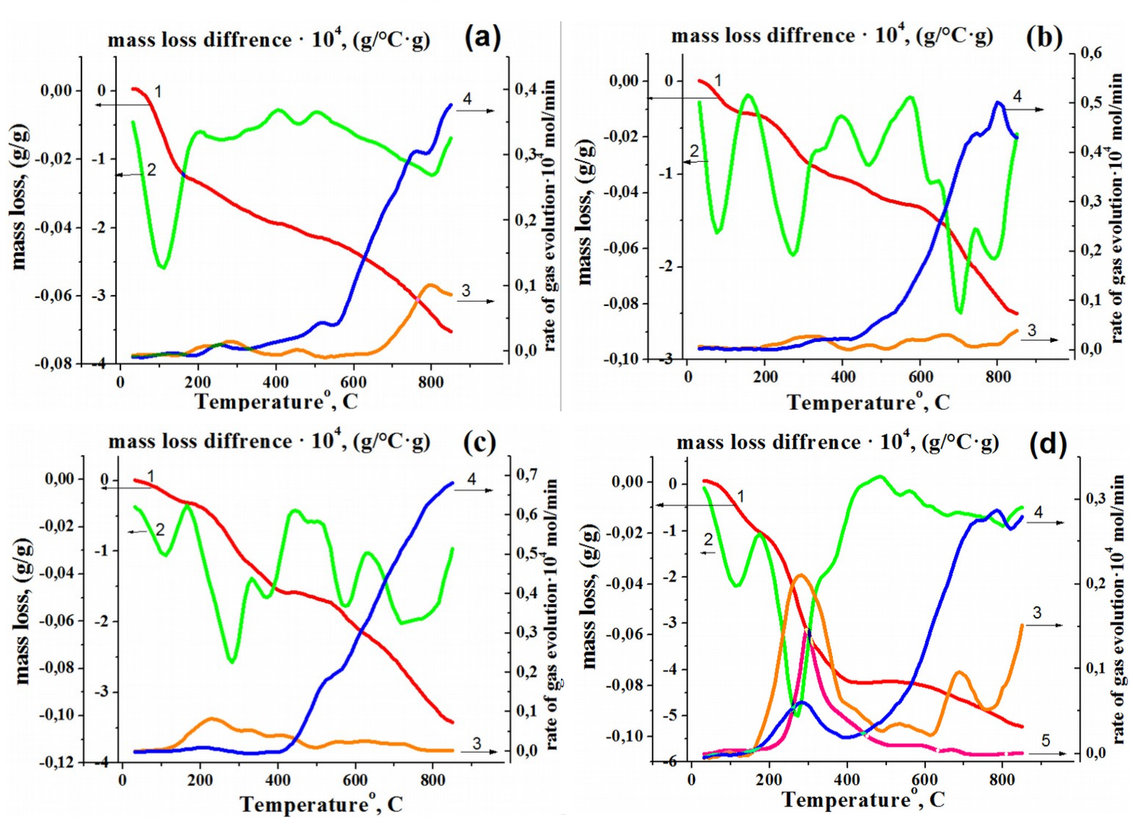

FIGURE 3. TGA: (1) TG and (2) DTG, (3) CO_2, (4) CO, (5) SO_2 for (a) GSGS, (b) GSGD/KBr_3, (c) GSGD/Br_2, (d) GSGD/Br_2/S1.

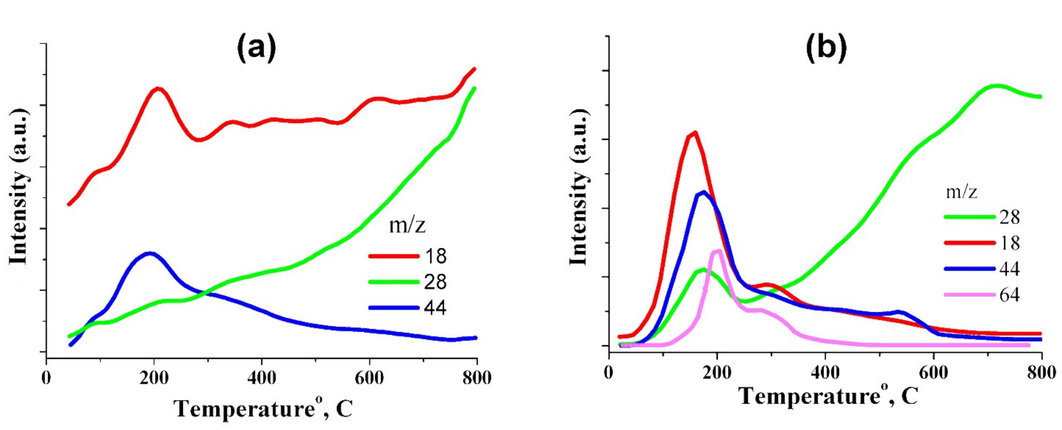

FIGURE 4. TPD MS profiles for GSGD (a) and GSGD/Br_2/S1 (b).

Conclusions

1. In this work, bromination of activated carbon samples under mild conditions was performed and active bromine-containing precursors have been obtained in which bromine is capable of being substituted for other types of functional groups. The concentration of bromine in the obtained samples is up to 0.5 mmol / g.
2. It is shown that when treatment of brominated samples with sulfur-containing reagents with subsequent oxidation, it is possible to obtain carbon samples that are catalytically active in the dehydration reaction of isopropyl alcohol in the gas phase.
3. It was found that the use of bromine-containing precursors, in comparison with the pristine NAC, allows obtaining catalysts with higher activity in the dehydration reaction of isopropanol - the temperatures of the dehydration reaction are reduced by 10-40ºC.

References

1.T. M. Bezugla et al., Mol. Cryst. Liq. Cryst. 661 (1), 58 (2018).
2. Friedrich J.F., Wettmarshausen S., Hanelt S. at al. Carbon. 48. 3884 (2010).