Three-Dimensional Mesoporous Carbon aerogels: Ideal Catalyst Supports for Enhanced H2S Oxidation

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1. Experimental

1.1 Preparation of carbon aerogels

Gels were prepared by the aqueous sol-gel polymerization of phenol, melamine and formaldehyde using sodium hydroxide as basic catalyst. In a typical procedure, 6.02 g phenol (64 mmol) and 10.4 g formaldehyde (37 wt%, 128 mmol) were dissolved in 20 ml of 0.2 M NaOH solution (10 mmol). The mixture was stirred at 70 °C for 40min. A clear and light red solution was obtained. Then, 3.22 g melamine (25.6 mmol) and 6.2 g formaldehyde (76.8 mmol) were added to the above solution to react for 30 min with consecutive agitation until the solution became clear. Finally, the pH value of the solution was adjusted by 1 M NaOH solution, and then the solution was diluted to 100 ml with deionized water. The diluted solution was decanted to five glass ampoules (20 ml capacity each), which were sealed by gas torch and placed in a water bath at 85 °C for gelation/aging. After a five-days cure, the wet gels were removed from ampoules and immediately immersed in excess of methanol bath to displace water at 45 °C for 3 days with fresh methanol exchanged everyday. The methanol displaced gels called alcogels hereinafter were placed in an autoclave which was filled up with petroleum ether (boiling range 30–60 °C), and then the autoclave was heated to 240 °C

with a heating rate of 1 $^{\circ}$ C /min, while the pressure was adjusted to 7.0 MPa by a modulating valve. The autoclave was isothermally depressurized to atmospheric pressure at a rate of 0.1 MPa/min after at 240 $^{\circ}$ C and 7.0 MPa for 1 h. Then the autoclave was cooled to room temperature and the crack-free, cylindrical organic aerogels were obtained. Carbon aerogels were obtained by pyrolysis of organic aerogels at 800 $^{\circ}$ C for 3 h with a heating rate of 5 $^{\circ}$ C / min under protection of nitrogen.

1.2 Preparation of catalysts

The obtained carbon aerogels were ground to 550-830 μ m sieve fractions. Then, the CA were dipped into a proper amount of 6% Na2CO3 solution and well mixed for ca. 30 min, which has been described in detail elsewhere.¹

1.3 Characterization

The thermogravimetric analysis (TA Instrument Q600 Analyser) of samples was carried out at a nitrogen or air flow rate of 100 ml/min. The samples were heated to 1000 $^{\circ}$ C with a rate of 5 $^{\circ}$ C /min.

Elemental analysis was carried out using Elemental Vario EL III. The carbon (C), hydrogen (H), and nitrogen (N) contents of the carbon aerogels were determined directly using the thermal conductivity detector. The total sulfur content was tested with the oxidation titration method.

The elemental sulfur, sulfate, and sulfide contents of the exhausted samples were determined following the method described by M. J. Martin et al.² In all case, the content of elemental sulfur is up to 95 %.

The morphologies of samples were observed under scanning electron microscopy (SEM, FEI Q-300) and transmission electron microscopy (TEM, JEOL 2100F).

The N₂ adsorption-desorption isotherms of carbon aerogels were measured using a Micromeritics ASAP 2020M analyzer. The BET surface areas (S_{BET}) were analyzed by Brunauer-Emmett-Teller method. Micropore volumes (V_{mic}), micropore surface areas (S_{mic}) and external surface areas (S_{ext}) were obtained by t-plot method. Mesopore volumes (V_{mes}) and average mesopore sizes (D_m) were obtained by Barrett-Johner-Halendar (BJH) desorption model. The mesopore size distributions were calculated from the analysis of the desorption branch of the isotherms in the pore range of 1.7–300 nm using the BJH method.

1.4 Catalyst test

The experimental setup is given in S Fig. 1. Catalysts were packed in a glass tube with the diameter of 4 mm and the height of 20 mm. A simulated mixture (99 % of N₂ and 1% O₂ at 25 °C) containing 0.1 % (1000 ppm) of H₂S (with 80 % moisture) was passed through the column of the catalysts with a flow rate of 150 mL/min. The gas flow rates were controlled by a mass flow controller system (ZF-MFC-1, Shanghai Zufa Co.). The reaction temperature was controlled by a K-type thermocouple in the furnace and monitored by another K-type thermocouple axially centered in the reactor tube. The concentrations of the exhaust gases from the reactor were monitored using Sulfur Microcoulomb Analyzer and gas chromatography (GC, Shimadzu) with a pulsed flame photometric detector (FPD) permitting the detection levels as low as 0.5 ppm. The test was stopped at the point that the elution concentration is approximately equal to the inlet concentration, and it does not change with time any more. To such time the adsorption gets the equilibrium state. For each sample, the test was repeated at least twice. No other gaseous sulfur species (SO₂, COS) but H₂S were detected during the oxidation experiments, suggesting the selectivity of oxidation H₂S to element sulfur was referenced to be near 100 %.



Fig. S1 Schematic diagram of experimental system

1-cylinder of N_2 ; 2-cylinder of O_2 and N_2 ; 3-cylinder of H_2S and N_2 ; 4-pressure regulator; 5-mass flow controller; 6-triple valve; 7-humidifier; 8-reactor; 9-cyclic water bath; 10-H₂S analyzer; 11-computer; 12-NaOH solution.

Adsorption/removal capacities, x/M (g H₂S/g of catalyst), were then calculated by

integrating the corresponding breakthrough curves and by applying the following equation

$$\frac{x}{M} = \frac{QM_W}{wV_M} (C_0 \times t_s - \int_0^{t_s} C(t) dt)$$

where Q is the total inlet flow rate (m³/s), w is the weight of catalysts introduced into the column (g), M_W is the molecular weight of H₂S, V_M is the molar volume, C_0 is the inlet gas H₂S concentration (ppmv), C(t) is the gas outlet concentration (ppmv), and ts is the bed breakthrough/saturation time (s).

Table S1 Porosity parameters of raw carbon aerogels (CA), impregnated carbon aerogels

Sample	$\mathbf{S}_{\text{BET}}^{a}$	S _{ext} ^b	S _{mic} ^c	V_t^{d}	$V_m^{\ e}$	${D_{BJH}}^{\mathrm{f}}$
	m ² /g	m ² /g	m ² /g	cm ³ /g	cm ³ /g	nm
CA-1	631	411	220	2.35	2.39	25
CA-2	543	386	157	1.72	1.72	18
CA-3	618	409	209	1.47	1.42	12
CA-1-I	416	334	78	2.01	2.04	25
CA-2-I	430	334	96	1.57	1.54	18
CA-3-I	509	362	146	1.32	1.30	12
CA-1-E	29	29	/	0.23	0.24	27
СА-2-Е	41	41	/	0.28	0.28	20
СА-3-Е	69	71	/	0.35	0.35	15

(CA-I) and exhausted catalysts (CA-E).

^aBET surface area; ^bexternal surface area calculated by t-Plot method; ^c micropore area calculated by t-Plot method; ^dtotal pore volume; ^eBJH desorption cumulative volume; ^fBJH desorption average pore diameter.

 $\begin{array}{c} \textbf{Table S2} \ H_2S \ breakthrough \ capacity \ and \ saturated \ capacity \ of \ the \ impregnated \ carbon \\ aerogels \end{array}$

Samples	Na ₂ CO ₃ loading	Breakthrough capacity	Saturated capacity				
	wt. %	g/g catalyst	g/g catalyst				
3018-JT ^a	6-8	0.31	0.35				
CA-3	8.1	1.44	1.62				
CA-2	8.2	1.75	1.95				
CA-1	8	2.55	2.91				
CA-1	0	0.056	0.06				
CA-1	4.1	0.89	0.98				
CA-1	14.7	3.14	3.45				
^a Commercially available catalyst							



Fig. S2 TG and DTG curves of the exhausted carbon aerogels in N_2 atmosphere. For all samples, one intensity peak appeared at the temperature range between 200 and 350 °C, which should be assigned to the removal of element sulfurs from the inter-particle mesopores or macropores. A new poor peak appeared at about 350-450 °C, which should be attributed to the removal of sulfurs from the intra-particle micropores.³



Fig. S3 Representative TEM images of exhausted carbon aerogels. The sulfurs with sizes ranging from tens nanometers up to several micrometers can be found.



Fig. S4 N_2 adsorption and desorption isotherms and BJH pore size distribution of the raw CA-3 and the exhausted CA-3 without the Na₂CO₃ impregnation. After sulfurs deposition, the t-plot microporous surface area of CA-3 was significantly decreased from 220 to 6 m²/g, whereas the external surface area was approximately equivalent before and after the oxidation of H₂S, which indicated that only micropore was filled by sulfurs. The results suggested that micropore play dominantly catalytic role on the oxidation of H₂S and storage the sulfur at the absent of Na₂CO₃.



Fig. S5 XRD patterns of raw carbon aerogels (CA-1), impregnated carbon aerogels (CA-1-I) and exhausted catalysts (CA-1-E). No obvious differences between the XRD patterns of raw carbon aerogels and impregnated carbon aerogels were detected, although the impregnated carbon aerogels contain 8 % Na₂CO₃. This result indicates Na₂CO₃ with very small crystalline size were highly dispersed on the surface of carbon aerogels that can not be discerned by XRD. After the oxidation of H₂S, the exhausted carbon aerogels exhibit lots of intensity peaks, some of them are ascribed to the polysulfides with S8 form and crystal Na₂SO₄.



Fig. S6 TG and DTG curves of the raw CA-3, the impregnated CA-3 with 8 % Na₂CO3 and the commercial desulphurization catalyst 3018-JT (the Na₂CO₃ impregnated activated carbon) in air atmosphere. Results show that the burn-off of the impregnated CA-3 starts at a temperature of between 300 and 400 °C, which is much smaller than that of the raw carbon aerogels. However, this temperature range is slightly superior to that of the 3018-JT catalyst, which is widely used for low-temperature H₂S removal in industrial plants. Therefore, no risk of self-ignition of the impregnated carbon aerogels was expected to take place during the study of the low-temperature oxidation of H₂S.



Fig. S6 High-resolution O 1s spectra of carbon aerogels.

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Sampla	531.1	532.3	533.3	534.2	536.1
Sample	C=O	C-OH,R-O-R	R-O-C=O	С-ООН	H2O
CA-1	28	24	14	16	18
CA-2	29	25	13	15	18
CA-3	28	25	14	16	17

STable3 Results of the curve fitting of the O 1s region, values given in %

High-resolution O 1s spectra of carbon aerogels, corresponding to binding energies between 522.5 and 542.5 eV, were given. The optimum curve fitting of the O 1s peak was achieved, and four different O functionalities as well as a contribution of chemisorbed water were identified, as reported in the studies of Zielke et al.. The peak at 531.1 eV corresponds to the carbonyl oxygen atoms; the peak at 532.3 eV to the carbonyl oxygen atoms in esters, amides and anhydrides as well as oxygen atoms in hydroxyls or ethers; the peak at 533.3 eV to the ether oxygen atoms in esters and anhydrides; and the peak at 534.2 eV to the oxygen

atoms in the carboxyl groups. The contribution of water was located at 536.1 eV. The results of the curve fitting of the O 1s region were listed in STable 3. No obvious changes were observed for these carbon aerogels, indicating these carbon aerogels have the same surface chemistry.

Supporting references

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2 A. Ros, M. A. Montes-moran, E. Fuente, D. M. Nevskaia, M.J. Martin. Dried sludges and sludge-based chars for H2S removal at low temperature: influence of sewage sludge characteristics. Environ. Sci. Technol. 2006, 40, 302-309.

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