PREPARATION OF METAL-DOPED ORGANIC AND CARBON AEROGELS FROM OIL-SHALE PROCESSING BYPRODUCTS

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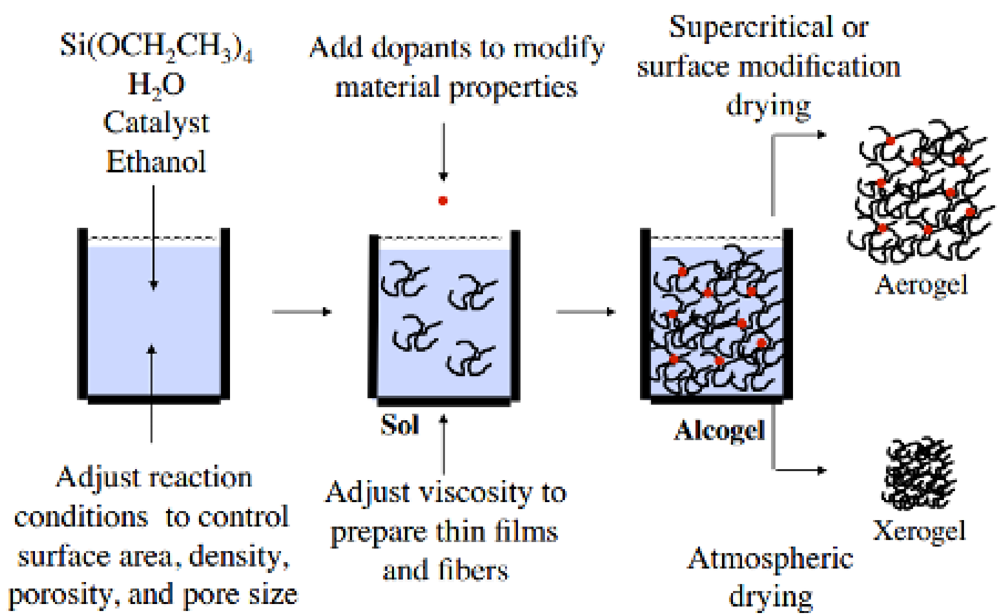
Introduction

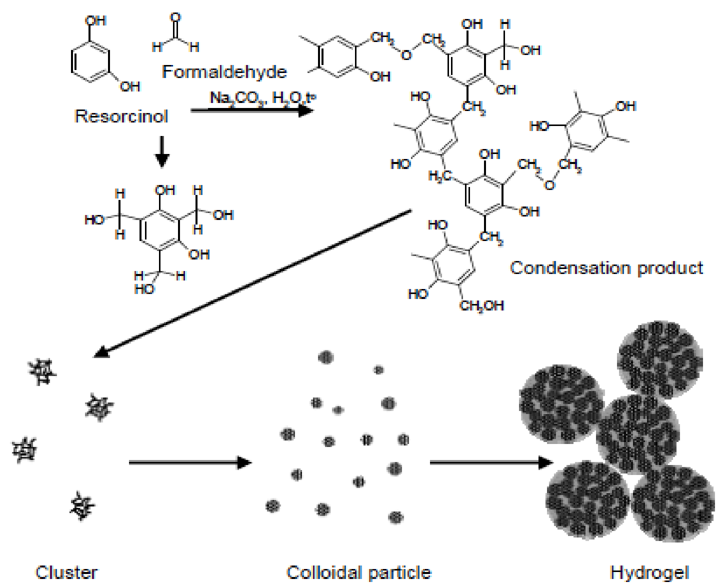
- Aerogels are porous materials which are derived from gel by replacing the liquid component with gas, without collapsing the gel solid network [1]



[1] S.S. Kistler. Coherent Expanded Aerogels and Jellies - *Nature*, 1931, 127, 741.

Organic and carbon aerogels

- Resorcinol-formaldehyde organic aerogels are the most studied



Carbon aerogels are obtained by pyrolysing organic aerogels

Carbon aerogel properties:
consist almost entirely of carbon, have high surface areas (up to 3200 m^2/g), continous porous structure and can be electrically conductive

Applications: catalyst support, adsorbent, materials for electrodes

5-methyresorcinol as a local alternative

- Produced by extraction from oil shale retort liquid
- 5-methylresorcinol (MR) is an appropriate compound for preparing organic aerogels [2].
  - faster gelation times than resorcinol
  - gelation at room temperature
- Organic aerogels prepared by using MR as a precursor, have
  - densities as low as 0.1 g/cm^3
  - surface areas higher than 350 m^2/g.
  - carbon aerogel surface areas up to 2000 m^2/g

[2] F. Perez-Caballero, A.-L. Peikolainen, M. Uibu, R. Kuusik, O. Volobujeva, M. Koel. Preparation of carbon aerogel from 5-methylresorcinol-formaldehyde gels - *Microporous and Mesoporous Materials*, 2008, 108, 230-236.

Metal-doped aerogels

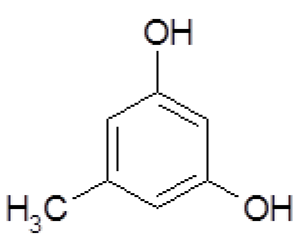
- Doping carbon aerogels with metals enables to modify the structure of the materials, catalytic activity and electrical conductivity.
- Methods that have been used for doping aerogels with metals can be divided roughly into three categories [3]:
  - Adding the metal precursor before gelation into the sol
  - The ion-exchange method [4]
  - Immersing aerogels in metal precursors

[3] C. Moreno-Castilla, F.J. Maldonado-Hódar. Carbon aerogels for catalysis applications - *Carbon*, 2004, 43, 3, 455-465.

[4] Baumann, T. F., Fox, G. A., Satcher, J. H., Yoshizawa, N., Fu, R., Dresselhaus, M. S. Synthesis and characterization of copper-doped carbon aerogels. *Langmuir*, 2002, **18**, 7073-7076.

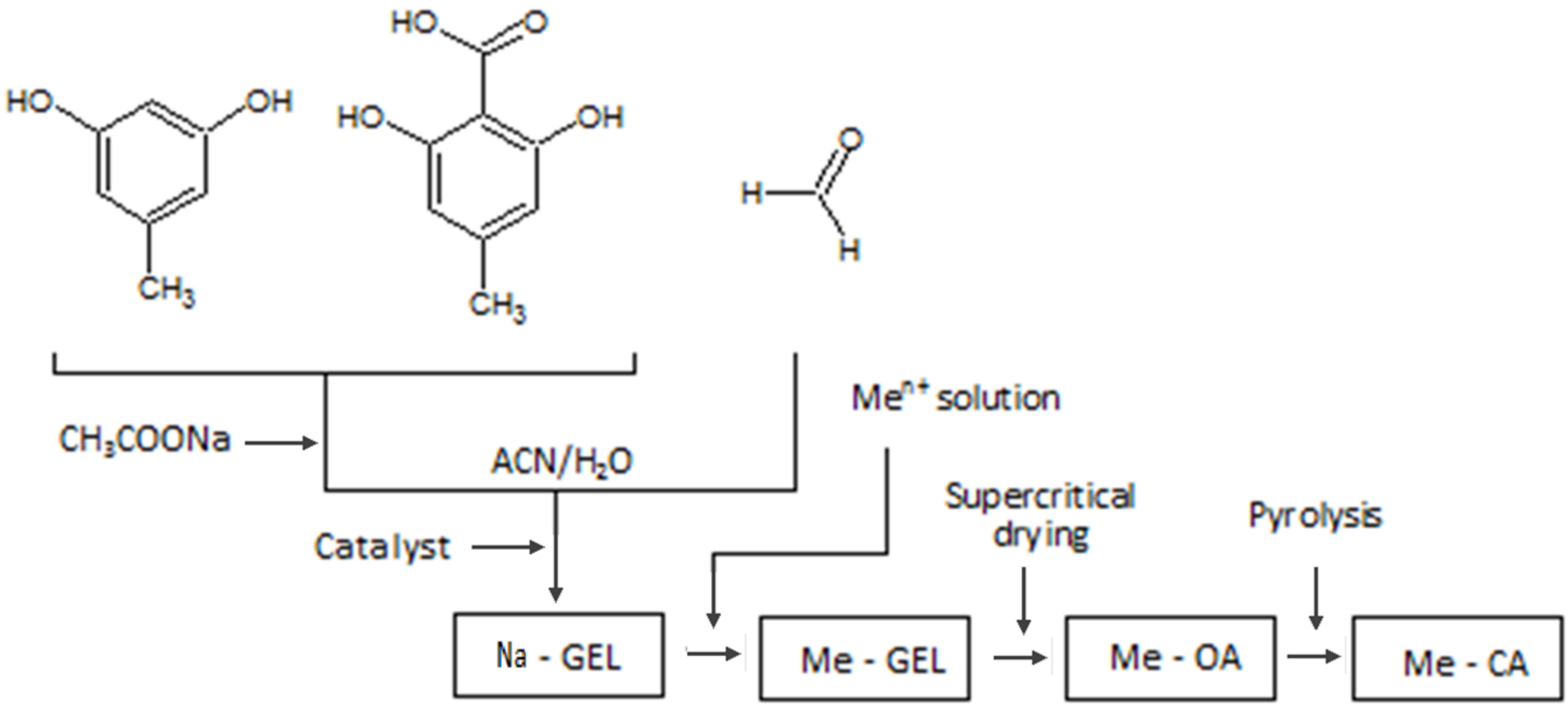
My research

- Preparation of metal-doped carbon aerogels from 5-methylresorcinol (MR) and 2,6-dihydroxy-4-methylbenzoic acid (dHMBA).
- Metal ions are introduced through the ion-exchange process and reduced during pyrolysis.
- Testing of prepared aerogels for new applications



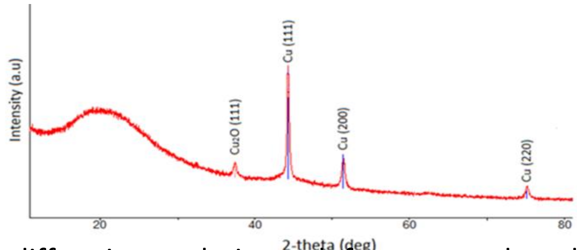
Copper-doped carbon aerogels

The ion-exchange method



Carbon aerogels doped with Cu, Ni, Co

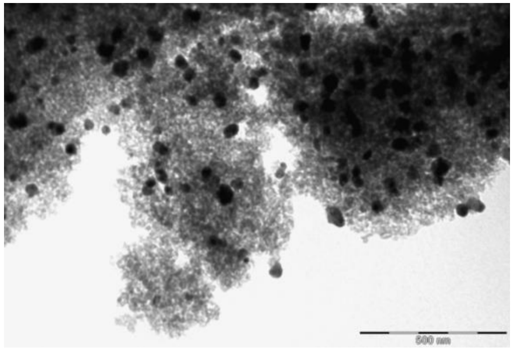
- Surface areas of aerogels are up to 520 m^2/g and pore volumes up to 610 mm^3/g.
- Metal ions are reduced during carbon aerogel preparation.



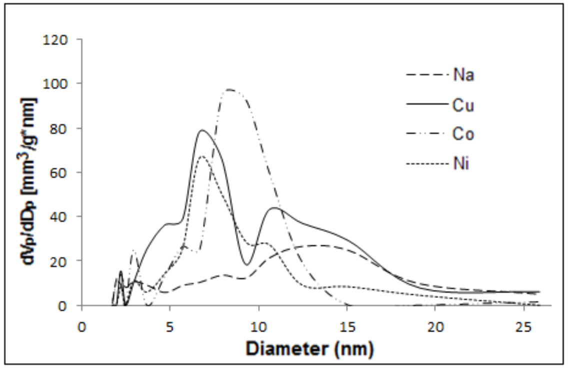
X-ray diffraction analysis result for copper–doped carbon aerogel

- By changing the molar ratio of MR and dHMBA, the metal content can be varied from 1% to 20%, depending on the metal used.

- Carbon aerogels contain metal nanoparticles.



Transmission electron microscope picture of a cobalt-doped carbon aerogel.



Pore size distribution analysis results

Kreek, K., Kulp, M., Uibu, M., Mere, A., Koel, K. Preparation of metal-doped carbon aerogels from local oil shale processing by-products. *Oil Shale*, 2014, 31(2), 185-194.

Aerogels doped with lanthanides

- Lanthanides are widely used as catalysts in organic synthesis. Aerogels are good candidates for catalyst carriers, because of their high surface area and continuous porosity.

- Support or entrapment of lanthanides or lanthanide species in aerogels has been scarcely studied though

- This paper presents the preparation of lanthanide (La, Ce, Pr, Nd) doped organic and carbon aerogels, using the ion-exchange method. Since in organic aerogels the lanthanides are bound ionically to the aerogel matrix, the use of these OAs as supported ion-exchange resins will be discussed.

K. Kreek, K. Kriis, B. Maaten, M. Uibu, A. Mere, T. Kanger, M. Koel· Journal of Non-Crystalline Solids, 2014, In Press

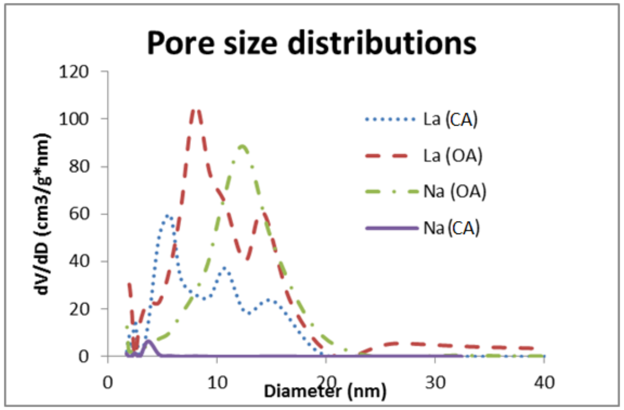
Specific surface area and porosity

Table 1. Densities, metal content and N_2-adsorption analysis results for organic aerogels (OA) and carbon aerogels (CA).

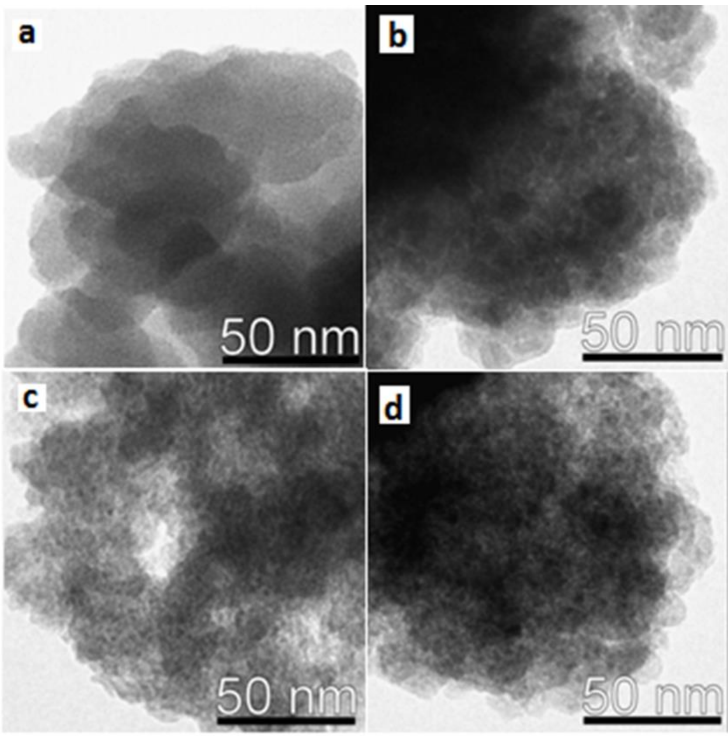
	ρ(OA), g/cm³	ρ(CA), g/cm³	S_{BET} (OA), m²/g	V_{TOT} (OA), mm³/g	V_{mic} (OA), mm³/g	S_{BET} (CA), m²/g	V_{TOT} (CA), mm³/g	V_{mic} (CA), mm³/g	$V_{mic\%}$ (CA), %	Metal% (OA), %	Metal% (CA), %
La	0,54	1,16	429	889	2	321	477	58	12	11,0	22
Ce	0,52	1,03	393	734	2,5	368	533	78	14,6	10,7	21
Pr	0,53	1,14	371	721	3,1	255	302	55	18,2	11,5	21
Nd	0,53	1,08	378	659	2	257	301	52	17,3	11,3	22
Na	0,58	0,83	221	643	0	30	19	9	47,0	6,4	---

ρ is calculated density, S_{BET} is the BET surface area, V_{TOT} is total pore volume, V_{mic} is the volume of micropores, $V_{mic\%}$ is the percent of microporous volume and metal (%) is the weight percent of metal in aerogels.

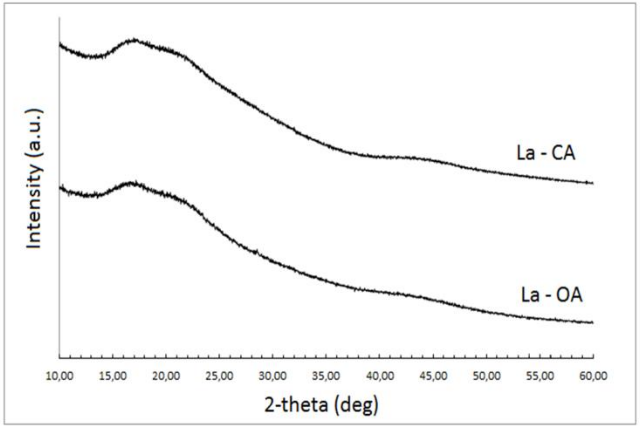
Pore size distributions of OAs and CAs



Morphology of aerogels



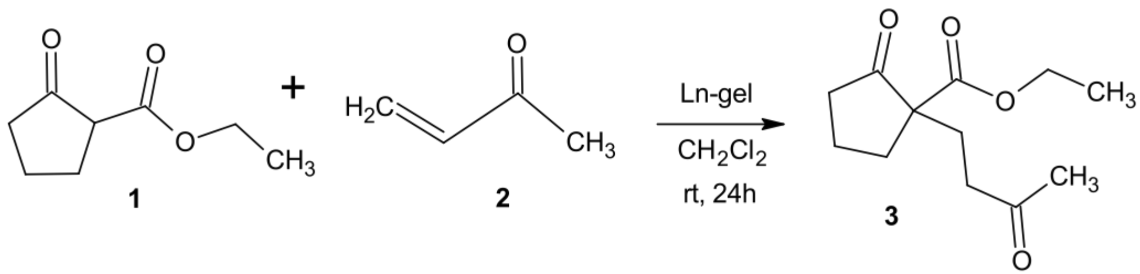
Transition electron microscopy pictures of aerogels: (a,b) La-doped organic aerogel; (c,d) La-doped carbon aerogel



X-ray diffraction analysis results for La-doped carbon and organic aerogel

Application as catalysts in Michael reaction

Michael reaction of ethyl 2-oxocyclopentanecarboxylate **1a** with 3-buten-2-one **2a** in the presence of Ln-aerogels as catalysts [a]



Element	Conversion (%)	
	OA	CA
La	84	49
Ce	82	---
Nd	97	92
Pr	91	32

Table 2. Conversion of 2-oxocyclopentanecarboxylate to 3-buten-2-one in 24 h for Ln-doped organic and carbon aerogels.

Reaction conditions: 0.006 mmol of catalyst (3mol% Ln with respect to the limiting regent), 0.2 mmol of **1**, 0.6 mmol of **2** in 0.4 ml of CH_2Cl_2 at room temperature 24 hours. [b] Conversion of product **3** was determined by GC. For organic aerogels (OA) catalyst loading 7.5 mg and for carbon aerogels (CA) 4.0 mg was used. For La OA and CA the result shown in table is the average of three separate tests.

Co-and Fe-doped nitrogen containing carbon aerogels as catalyst materials for oxygen reduction reaction

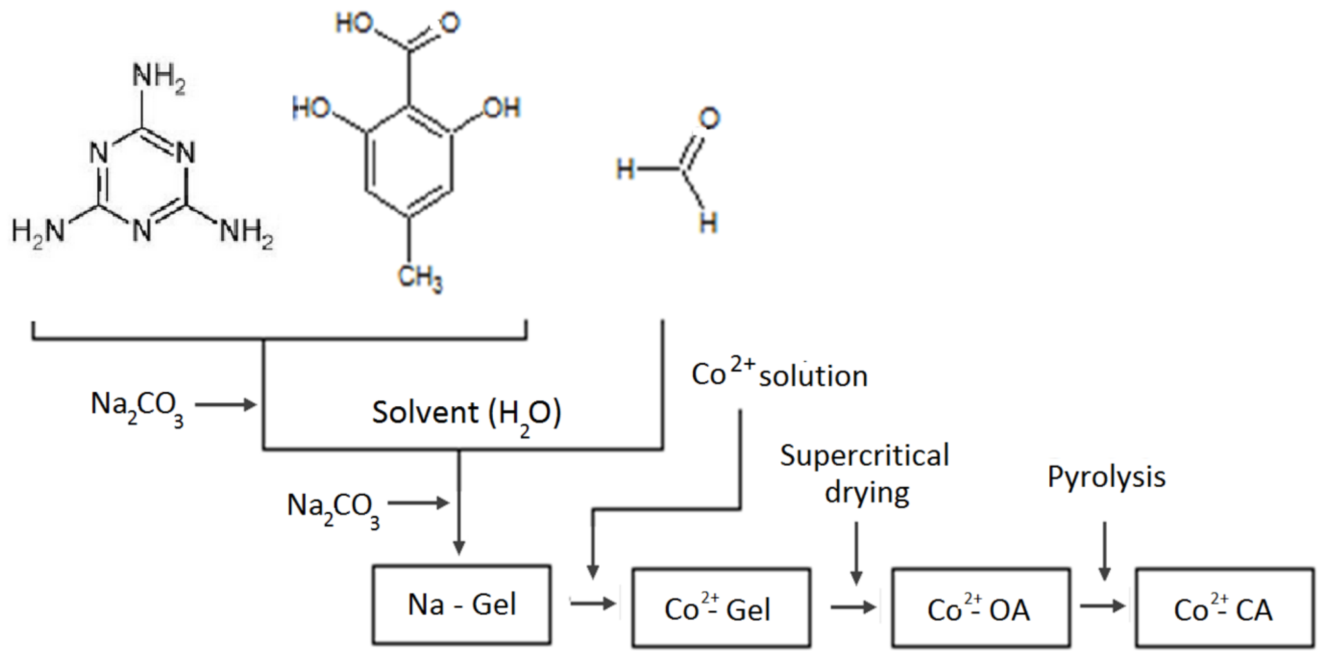
N-doped carbon materials have been reported as good catalysts for oxygen reduction reaction [5]. Melamine has a high nitrogen content and has been used before for making N-doped carbon aerogels [6].

The incorporation of non-precious metals such as cobalt or iron into the catalyst would further increase the catalytic activity [7].

We hereby propose a new method for preparing cobalt/iron and nitrogen containing organic aerogel (OA) and carbon aerogels (CA) by using the ion-exchange method for doping with cobalt.

[5] Wang, H., Maiyalagan, T., Wang, X. ACS Catalysis,Vol. 2, 2012, p. 781-794.
[6] Wei, Y., Shengzhou, C., Weiming, L. Int. J. Of Power Energy, Vol. 37, 2012, p. 942-945.
[7] Bezerra, C., Zhang, L., Lee, K., Liu, H., Marques, A., Marque, E., et al. Electrochim Acta, Vol. 53, 2008, p. 4937-4951.

The method used for aerogel preparation



Initial results

- Electrochemical testing of resulting materials by thin film rotating disk electrode technique revealed their high activity and stability in alkaline solution.
- The most active catalysts were pyrolysed at 800 ^{o}C.
- Co-containing aerogel showed slightly better performance than Fe-containing material and the aerogel not containing transition metals was considerably less active.
- Koutecky-Levich analysis indicated nearly four-electron reduction of O_2 on metal-containing carbon aerogels.
- The non-precious metal catalysts studied could be used as cathode materials for alkaline membrane fuel cells.

Conclusion

- Estonian oil shale production by-products 5-methylresorcinol and 2,6-dihydroxy-4-methyl benzoic acid are good precursors for organic and carbon aerogel preparation.
- The method enables to prepare carbon aerogels with high surface areas and to easily control the metal content in aerogels.
- Prepared aerogels are promising materials for several applications.

Acknowledgements

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