

PREPARATION OF METAL-DOPED CARBON AEROGELS FROM OIL SHALE PROCESSING BY-PRODUCTS

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Abstract. Carbon aerogels are nanostructured porous carbon materials, which can be produced from locally available phenolic compounds. A method for the preparation of metal-doped carbon aerogels from oil shale processing by-products 5-methylresorcinol and 2,6-dihydroxy-4-methylbenzoic acid was developed. Aerogels doped with Ni, Co and Cu were characterized by atomic absorption spectroscopy, nitrogen adsorption, transmission electron microscopy and X-ray diffraction.

The resulting materials exhibited pore diameters in microporous and mesoporous regions, high surface areas and pore volumes. The metal content in aerogels was found to be dependent on the amount of ion-exchange moiety and metal content as high as 14.5 wt% was achieved in carbon aerogels, where also metal nanoparticles had formed.

Keywords: aerogel, organic aerogel, carbon aerogel, 5-methylresorcinol, 2,6-dihydroxy-4-methyl benzoic acid, supercritical drying, oil shale, ion-exchange, metal-doped, nanoparticles.

1. Introduction

Nanoporous materials, due to their unique surface, structural and bulk properties, have attracted a lot of interest and acquired many important applications in several areas. Aerogel, as an example of a nanoporous material, is a low density material with high surface area and porosity. There are various types of aerogels which are prepared from different precursors.

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Carbon aerogels are made by pyrolysing organic aerogels. For example, Pekala was the first to obtain organic aerogels by supercritically drying gels, which were made through sol-gel polymerization by using resorcinol (R) and formaldehyde (FA) as precursors [1, 2].

Previously, the preparation of aerogels from 5-methylresorcinol (MR) and 2,6-dihydroxy-4-methylbenzoic acid (dHMBA), has been studied in our laboratory. MR is a good alternative to resorcinol. Besides MR being a by-product of oil shale industry and therefore a locally available precursor, gels prepared from MR have also shown faster gelation times compared to gels prepared from resorcinol [3–5]. The preparation of aerogels from MR and dHMBA together showed that the structure and properties of aerogels are dependent on the molar ratio of MR to dHMBA. dHMBA differs from MR by being a bifunctional monomer and, in addition to being a monomer, also acts as a catalyst due to its acidic properties [6]. dHMBA can be synthesized from MR.

Doping of carbon aerogels prepared from MR and FA with palladium by using impregnation in supercritical CO₂ has been previously carried out, but to the authors' knowledge no attempt to dope aerogels prepared from dHMBA has been made before [5].

There is on-going activity to expand potential aerogel applications with the modification of carbon aerogels (CA) through the incorporation of metal species into carbon frameworks. Doping of carbon aerogels with metals modifies their structure, conductivity and catalytic activity [7–12]. There are different methods for preparing metal-doped carbon aerogels, which can roughly be divided into three categories, as was done by Moreno-Castilla and Maldonado-Hódar [13]. First, the metal precursor can be added to the initial mixture before gel formation, secondly, the metal precursor can be deposited onto the already existing organic or carbon aerogel and lastly, the ion-exchange method can be used [13].

The ion-exchange method for preparing metal-doped aerogels was first studied by Baumann et al. [12]. Carbon aerogels were prepared in which instead of resorcinol the researchers used the potassium salt of 2,4-dihydroxybenzoic acid (dHBA) in the sol-gel process, producing K⁺-doped hydrogels. This meant that each repeat unit of the gel contained a binding site for metal ions. The desired metal ion was deposited by exchanging the potassium ion in an ion-exchange process. A common carbon aerogel treatment process for gel drying and carbonization was used to generate metal-doped carbon aerogels.

Over the years, several studies on ion-exchange deposition have been reported [12, 14–20]. In these researches, the effect of different metals, pyrolysis temperature and different applications have been described. Recently, a paper was published in which the ion-exchange capacity of gels was altered by using together dHBA (ion-exchange moiety containing monomer) and resorcinol [21].

The goal of this work is to modify the preparation of aerogels from precursors MR and dHMBA, so that metal-doped carbon aerogels could be

obtained. The doping of materials with metals will be carried out similarly to the ion-exchange method developed by Baumann et al. [12], though in the current case two resorcinol derivatives (MR and dHMBA) will be used for aerogel preparation. Since only dHMBA has an ion-exchange moiety (carboxylic group), then the possibility of preparing aerogels with different metal contents, by changing the MR to dHMBA molar ratio, will be discussed. The process for preparation of metal-doped carbon aerogels from MR and dHMBA will be developed and properties of the obtained materials determined.

2. Experimental

2.1. Materials

5-methylresorcinol with a reported purity of > 99% was provided by AS VKG, Estonia and 2,6-dihydroxy-4-methylbenzoic acid, with a purity of > 99%, was provided by Carboshale OÜ, Estonia. Sodium acetate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$), with a purity of 99.7%, was obtained from Fisher Scientific, UK. The water used was purified using a Milli-Q water system. Acetonitrile, HPLC purity, was obtained from Rathburn Chemical Ltd., Germany. Formaldehyde (37 w/w solution in water) was purchased from Sigma-Aldrich. CO_2 (99.8%) was obtained from Eesti AGA AS.

The supercritical extraction system with a double clamp autoclave, 100 ml in volume, was constructed by NWA analytische Meßgeräte GmbH, Germany.

The MTF 12/38/400 pyrolysis oven with a maximum temperature of 1200 °C was from Carbolite, England.

2.2. Sample preparation

The gels were prepared by adding dHMBA and MR (MR:dHMBA molar ratio 1:1, 3:1 or 9:1) to the solvent (70 wt% acetonitrile and 30 wt% distilled water). The molar ratio of solvent (SOLV) to aromatic monomers (AM) was 35:1. The moles of aromatic monomers (AM) were calculated by adding up the moles of MR and dHMBA and the moles for the solvent were calculated by adding up the moles of acetonitrile and water. To the solution of aromatic monomers and solvent a stoichiometric amount of sodium acetate (NaOAc) to dHMBA was added (NaOAc:dHMBA molar ratio 1:1) to obtain the sodium salt of dHMBA. After that formaldehyde (FA) was added (AM:FA molar ratio 1:2) and, finally, another amount of NaOAc was added as a catalyst (AM:NaOAc molar ratio 50:1).

Glass molds containing the solutions were sealed and the mixture was allowed to gel and cure at 40 °C for 7 days. The obtained Na^+ -doped gels were orange and transparent. The gels were then soaked for 3 days in 0.1 M aqueous solutions of CuCl_2 , $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, respectively. Each time the solution was renewed after 24 hours. After that the

gels were washed by soaking them in water for 24 hours, followed by acetone exchange which lasted 4 to 5 days. Acetone was changed every 24 hours. The gels were dried with supercritical CO₂. A more detailed description of the drying method has been published elsewhere [6]. Carbonization was performed in N₂ atmosphere by raising the temperature to 700 °C (2.5 °C/min), then to 900 °C (5 °C/min) and was kept at 900 °C for 1 hour.

2.3. Characterization

The bulk densities of carbon aerogels were calculated by measuring the dimensions and mass of each monolithic sample. Elemental analyses were performed by a Spectra AA 220F flame atomic absorption spectrometer (Australia). Nitrogen adsorption analyses were performed using a KELVIN 1042 Sorptometer (Costech International, Italy). Helium was used as a carrier gas, nitrogen as the adsorptive gas. Nitrogen adsorption data was taken at relative pressures from 0 to 1 and at liquid nitrogen temperature. The specific surface area (S_{BET}) was calculated according to the Brunauer-Emmett-Teller theory. The specific micropore volume (V_{mic}) was determined via the t-plot and the pore size distributions were determined using the Barrett-Johner-Halendar (BJH) method from the desorption branch. The X-ray diffraction (XRD) pattern was recorded with a Rigaku Ultima IV diffractometer using the D/teX Ultra line detector (USA). Cu-K_α radiation was used with a Ni filter for removing K_β radiation. The recorded diffractograms were analysed by Rigaku PDXL software. Energy-filtered transmission electron microscopy (TEM) was carried out with the Leo 912 Omega microscope (Zeiss, Germany) at 120 kV, using a LaB₆ gun.

3. Results and discussion

In the previously developed method for the preparation of aerogels from MR and dHMBA, it was suggested that dHMBA, in addition to being a monomer, also acted as an acidic catalyst [6]. The method developed in this work involved, during gel preparation, the addition of NaOAc, which can also act as a catalyst. Therefore the role of dHMBA as a catalyst is not clear in the present case.

The method developed by Baumann et al. employed potassium carbonate to neutralize the solution and as a catalyst, but in the current work a stronger gel was obtained by using sodium acetate instead. This resulted in a slightly acidic solution (pH 5.5) due to the formation of acetic acid and, hence, incomplete neutralization of the solution.

After immersing the gels containing Na⁺ ions in the copper ions containing solution, the Na content in organic aerogels was measured and found to be about 0.005%. In comparison, the Na content in the aerogel, which had not been immersed in the solution containing copper ions, was 6.40%. It confirms that the exchange of sodium ions for copper ions takes place.

The authors studied which effect dHMBA has on the metal content in aerogels. Gels at MR to dHMBA molar ratios of 1:1, 3:1 and 9:1 were prepared and dried. The results are shown in Figure 1. It can be seen that with increasing dHMBA content in aerogels their metal content also increases. Therefore changing the MR to dHMBA molar ratio is an easy way to control the metal content in aerogels. Previously a study was performed where the ratio between the two phenolic compounds used (R and dHBA) was changed, to evaluate the ion-exchange capacity. Though it was also noted that at lower relative mole fractions of the ion-exchange monomer the ion-exchange capacity decreased, a change in metal content to the same extent as in the current case was not shown [21].

Subsequently, carbon aerogels at an MR:dHMBA molar ratio of 1:1 were prepared (Table). The metal content in carbon aerogels was about twice as high as in the organic aerogel. It can be explained by the decomposition of organic matter during pyrolysis.

The Table also presents data on the density, specific surface area and pore volume of metal-doped carbon aerogels. The density of organic aerogels ranged from 0.45 to 0.62 g/cm³ and that of carbon aerogels from 0.83 to 1.26 g/cm³, which is higher than for metal-doped carbon aerogels prepared from dHBA [16]. This may be explained by that in the present case the authors used higher solids content to prepare aerogels, which is known to cause higher densities [22]. Also, the diameter of gels decreased about 20% during the immersion of gels in metal ion solutions and during solvent exchange.

Nitrogen adsorption/desorption isotherms for metal-doped carbon aerogels are shown in Figure 2. The Table presents the specific surface areas and pore volumes of carbon aerogels doped with different metals. While comparing carbon aerogels that were doped with transition metals (Co, Cu, Ni) to the blank sample (Na containing), it was found that both specific surface areas and pore volumes were larger for the transition metal containing samples. The same effect has been observed before for aerogels prepared from dHBA (the blank sample contained potassium) [12, 16].

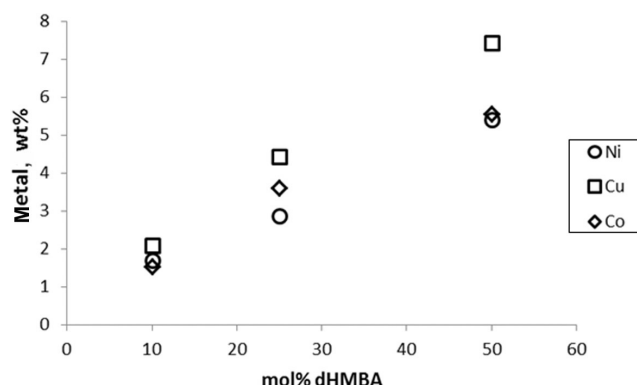


Fig. 1. Metal content in organic aerogels.

Table. Properties of metal-doped carbon aerogels

Sample	$\rho(\text{OA}),$ g/cm^3	$\rho(\text{CA}),$ g/cm^3	$S_{\text{BET}},$ m^2/g	$S_{\text{non-mic}},$ m^2/g	$S_{\text{mic}},$ m^2/g	$\%S_{\text{mic}},$ $\%$	$V_{\text{TOT}},$ mm^3/g	$V_{\text{mic}},$ mm^3/g	$\%V_{\text{mic}},$ $\%$	Metal, $\%$ OA	Metal, $\%$ CA
Na	0.58	0.83	286	153	133	46.5	429	47	11.0	6.40	-
Cu	0.45	1.01	464	173	291	62.7	607	103	17.0	7.43	14.5
Co	0.62	1.03	519	166	353	68.0	610	124	20.3	5.50	10.7
Ni	0.59	1.26	379	106	273	72.0	446	96	21.5	5.50	11.0

All the samples were prepared at an MR:dHMBBA molar ratio of 1:1. OA is organic aerogel and CA is carbon aerogel. All the parameter values obtained apply to carbon aerogels, unless otherwise noted. ρ is the calculated density, S_{BET} is the BET surface area, S_{mic} is the microporous surface area, $\%S_{\text{mic}}$ is the percent of microporous surface area, V_{TOT} is the total pore volume, V_{mic} is the volume of micropores, $\%V_{\text{mic}}$ is the percent of microporous volume, metal % is the weight percent of metal in aerogels.

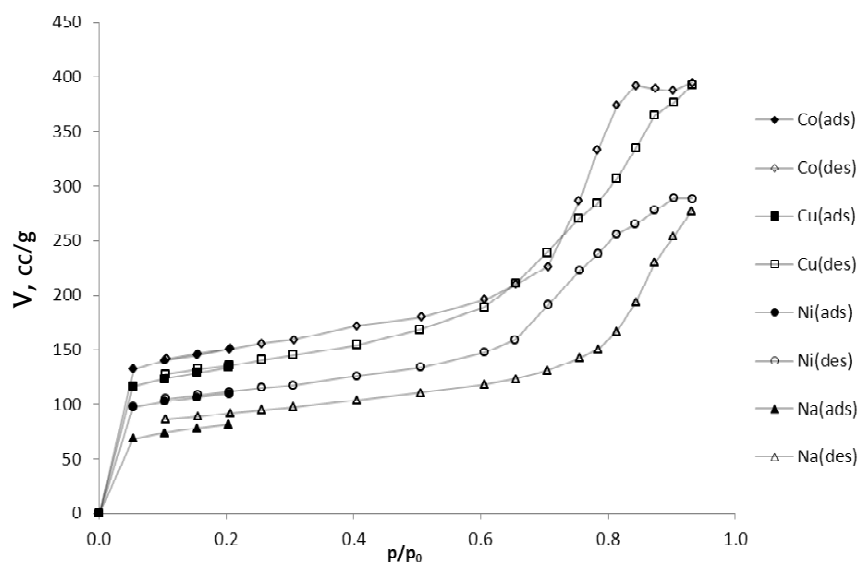


Fig. 2. Results of adsorption/desorption analysis of nitrogen; (ads) – adsorption isotherm, (des) – desorption isotherm.

Transition metal containing aerogels showed higher values of microporous surface area and microporous pore volume compared to the Na containing sample, the respective percentages being almost twice as high for the aerogels. The increase in micropore volume could be attributed to the transition metals favouring the formation of new microporosity or causing a stronger shrinkage of mesopores, which become micropores during carbon aerogel preparation as a result. The increase in pore volume of transition metal containing aerogels was due not only to the increase in microporosity, but also to the fact that the non-microporous volume of Cu and Co containing carbon aerogels was larger.

From Figure 3 it can be seen that the peak of pore size distribution (PSD) of the Na containing aerogel is at a pore diameter of 10–15 nm, whereas the peak for all the other doped aerogels is at 5–10 nm. This indicates that for carbon aerogels the addition of transition metals resulted in the reduction of pore diameter. This result is different from those obtained in a previous study, which showed that in case of carbon aerogels made from dHBA, incorporation of transition metals had no significant effect on pore size distribution [16].

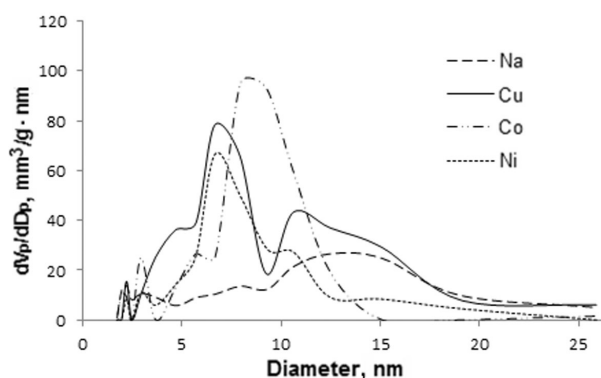


Fig. 3. Pore size distribution of metal-doped carbon aerogels (MR:dHMBA molar ratio 1:1).

The results of X-ray diffraction analysis of carbon aerogels are shown in Figure 4, revealing the presence of peaks corresponding to metals (oxidation state 0). This suggests that metal ions must have been reduced during carbon aerogel preparation. For the copper-doped carbon aerogel there is also a peak corresponding to copper(I)oxide, whose presence could have been caused by either incomplete reduction during pyrolysis or oxidization of copper afterwards. The diffractogram for nickel-doped carbon aerogel has also peaks corresponding to graphite (marked C in the figure). However, no graphitic structures were observed in TEM pictures, possibly due to low resolution.

TEM pictures of aerogels were taken to visualize metal nanoparticles in samples. Figure 5a shows an organic aerogel, which before drying was soaked in the solution of cobalt nitrate. No metal nanoparticles can be observed in this case, which is in agreement with the conclusion of a previous study that metal ions are uniformly distributed throughout the organic aerogel [12]. When the aerogel depicted in Figure 5a is pyrolysed (Fig. 5b), then nanoparticles emerge. These are uniformly distributed in the carbon matrix and their size is in the range of 10–60 nm. Figure 5c and d depict nickel- and copper-doped carbon aerogels prepared in the same conditions as the above-mentioned Co-doped carbon aerogel. The size of metal nanoparticles in these samples is in the range of 20–150 nm for nickel containing

carbon aerogels and 3–100 nm for copper containing carbon aerogels, showing that the metal nanoparticle diameters of different metals varied. For copper containing carbon aerogels the nanoparticles had also clustered together.

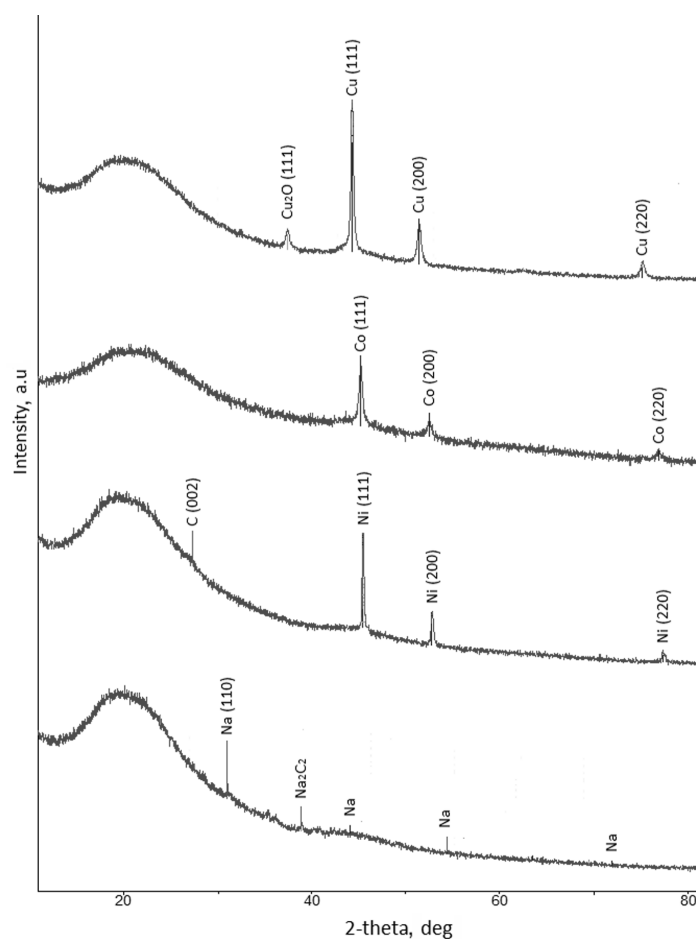


Fig. 4. Results of X-ray diffraction analysis of metal-doped carbon aerogels.

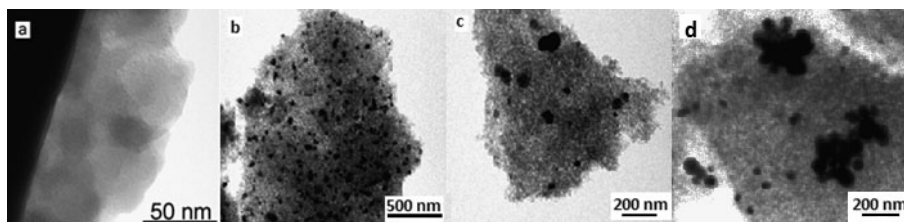


Fig. 5. TEM pictures of metal-doped aerogels. a: Co-doped organic aerogel; b: Co-doped carbon aerogel; c: Ni-doped carbon aerogel; d: Cu-doped carbon aerogel.

4. Conclusions

A method for preparing metal-doped carbon aerogels from oil shale processing by-products 5-methylresorcinol and 2,6-dihydroxy-4-methylbenzoic acid was developed. The ion-exchange process was used to introduce Ni, Co and Cu into carbon aerogels.

The specific surface area of metal-doped carbon aerogels was in the range of 380–520 m²/g and pore volume 446–610 mm³/g. It was shown that the metal content in carbon aerogels can be varied by changing the molar ratio of MR to dHMBA. In carbon aerogels the metal ions had reduced to metals during pyrolysis and formed metal nanoparticles. The size of metal nanoparticles ranged from 3 to 150 nm.

The method developed is suitable for preparing metal-doped carbon aerogels from oil shale processing by-products. The resulting materials have high surface area and porosity and it is possible to control their metal content.

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