HIGHLY POROUS ACTIVATED CARBONS DERIVED FROM POLY(STYRENE SULFONIC ACID) BASED ORGANIC SALTS

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Introduction

The objective of this paper is to study the effect of transition metals used in organic salts on the structural properties of carbonaceous materials. To accomplish our objectives, we carbonized commercially available poly(styrene sulfonic acid-co-maleic acid), sodium salt. To study the effect of metals, sodium was exchanged with either cobalt, nickel, or iron. Park and Jung [1], and Putyera et al. [2] reported using polystyrene-based material as precursors for the preparation of activated carbon. We assume the microstructure of the precursor to be essentially the polystyrene carbon framework with interspersed chelated metal ions. The maleic moiety provides additional opportunity for chelation with metal ions. The nature of the substrate, enriched with numerous opportunities for bonding and chelating, strongly suggests that metals can be highly dispersed within the carbonaceous matrix. Moreover, the functional groups present along with nitrates from the introduced salts should act as pore formers during their thermal decomposition. Since reduced metal can migrate to the surface during carbonization the structure is expected to gradually expand leading to foam/ nanofoam formation. The pillaring effect of metals during carbonization of polystyrene-divinylbenzene based resin with sulfonic acid groups was observed by Nakagawa et al. [3]. They found their precursors useful for production of carbon molecular sieves (CMS).

Experimental

Poly(styrene sulfonic acid-co-maleic acid) salts containing sodium, iron, cobalt or nickel were used as organic precursors. First the cation exchange was done (using $Fe(NO_3)_3$, $Co(NO_3)_2$, and $Ni(NO_3)_2$) and the samples were heated at 200 ^{o}C for 4 hours. We refer to the initial polymers as PSS-MA-Na, PSSA-MA-Fe, PSS-MA-Co, and PSSA-MA-Ni. Then the carbonization was carried out in a horizontal furnace with nitrogen as an inert gas (flow rate: 300 mL/min). The samples were heated with a rate of 50 ^{o}C/min and hold at 800 ^{o}C (final carbonization temperature) for 40 min. As a next step a Soxhlet washing with distilled water was performed to remove an excess of water-soluble inorganic salts (sodium and excess of transition metal salts). The carbon samples are designated as C-Fe, C-Co and C-Ni where the last two letters refer to the transition metal ion used in a precursor. The initial sample is referred to as C.

To remove metals the carbonized materials were washed with 18 % HCL for 24 hours. Then the Soxhlet washing was done with distilled water to remove the excess of water-

soluble chlorides and hydrochloric acid. After this treatment letter "A" is added to the names of the samples.

On the materials obtained sorption of nitrogen at its boiling point was carried out using ASAP 2010 (Micromeritics). Before the experiments, the samples were outgassed at 120 ^{o}C to constant vacuum (10^{-4} torr). From the isotherms, the surface areas (BET method), total pore volumes, V_t, (from the last point of isotherm at relative pressure equal to 0.99), total surface area S_{DFT} ,volumes of micropores, V_{mic}, mesopore volume V_{mes} along with pore size distributions were calculated. The last four quantities were calculated using density functional theory, DFT [4, 5].

The pH of a carbon sample suspension provide information about the acidity and basicity of the carbon surface. A sample of 0.4 g of dry carbon powder was added to 20 mL of distilled water and the suspension was stirred overnight to reach equilibrium. Then the pH of suspension was measured.

Thermal analysis was carried out using TA Instrument Thermal Analyzer. The instrument settings were: heating rate 10 ^{o}C/min and a nitrogen atmosphere with 100 mL/min flow rate. For each measurement about 25 mg of a ground carbon sample were used.

Scanning electron microscopy images were obtained at Zeiss-LEO using LEO 1550 FESEM. SEM images with EDX were obtained on LEO 1455 VP SEM with Tungsten source with EDAX Phoenix-Po EDX analyzer in Lamont Doherty Earth Observatory of Columbia University. The as-received samples were mounted using silver support.

The content of metals in the samples was determined using ICP in Shiva laboratories, Syracuse, NY. Content of carbon, hydrogen, oxygen and sulfur was determined in Huffman labs, Boulder, CO.

Results and Discussion

Table 1.
pH, metal content in transition metal modified samples and yield of materials.

Sample	pH after water washing	pH after HCl treat.	Initial metal content [%]	Metal content after HCl treat. [%]	Yield after carbonization* [%]	Yield after Water washing [%]	Final yield (after HCl treat. [%]
C	7.21	5.50	---	---	37.5	10.9	10.8
C-Co	7.99	4.95	9.0	0.05	41.6	17.6	13.8
C-Ni	7.78	5.22	10.7	0.27	40.6	16.8	7.5
C-Fe	6.08	5.70	8.3	1.00	43.0	16.4	13.9

The DTG curves for samples after carbonization and washing with water are presented in Figure 1A. As expected, they reveal the differences in the species present on the materials surfaces. A common feature for all samples (from the point of view of the position and intensity) are the peaks between 200 and 550 $^{\circ}$C. Based on the strong exothermic effect upon exposure to air and the acidic pH of carbons after HCl washing (Table 1) we assign those peaks to decomposition of oxygen containing functional groups. An intense peak at 350 $^{\circ}$C for the iron modified sample is a result of overlapping of the decomposition of those groups with decomposition of iron oxides (F_2O_3 x H_2O) or hydroxides present on the surface after reexposure of the iron clusters to oxygen from air [26]. The peaks over 600 $^{\circ}$C, since they are not revealed on the curve for the C sample, represent reduction of nickel and cobalt sulfates.
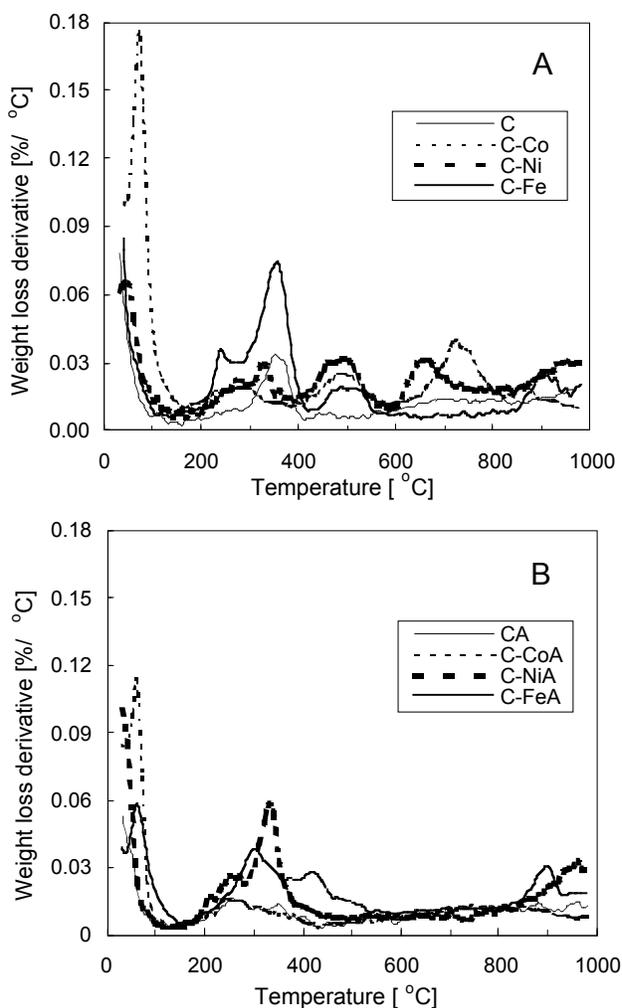

Figure 1.
DTG curves in nitrogen for water washed (A) and acid washed (B) samples.

DTG curves done on the samples after acid washing support our hypothesis about the species present on the surface (Figure 1B). After that treatment the peaks over 600 °C disappear for C-CoA and C-NiA due to dissolution of sulfates. Peaks representing decomposition of oxygen groups are smaller. This is likely the result of "cleaning" of the carbon surface and the removal of water soluble small molecule organic compounds containing oxygen. It is interesting that for the nickel modified sample a new peak at about 350 °C is revealed. That peak might represent decomposition of nickel hydroxide [6] formed during contact with air and not totally removed by washing. It overlaps with the peak from decomposition of oxygen containing groups. On the surface of the C-FeA sample iron oxides seems to be still present and a new peak appears between 300 and 500 °C. This peak might be related to iron hydroxides and chlorides [7] formed when the sample was exposed to HCl and hydrolysis of chlorides occurred.

Supporting for the results described above are changes in the content of transition metals present in samples before and after acid washing. They are summarized in Table 1. For all carbonized samples without acid treatment the content of metals is similar and ranges between 8 and 11 %. Washing with HCl significantly decreases cobalt and nickel content while the content of iron is still about 1 %. The yield of materials after various steps of carbonization also indicates the "history" of formation and removal of various inorganic species (Table 1). Around 40% yield for materials after carbonization decreased to about 17% (11% for sodium form) after water washing which suggests that more than 23 % of mass consists of water soluble salts containing sodium (sufides, sulfates, carbonates) and sulfates (nickel, cobalt or iron). Acid washing further decreased the yield for the transition metal modified samples removing few percent of weight in sulfides and oxides.

Table 2.
Structural parameters calculated from nitrogen adsorption isotherms.

Sample	S_{BET} $[m^2/g]$	S_{DFT} $[m^2/g]$	V_t $[cm^3/g]$	V_{mic} $[cm^3/g]$	V_{mes} $[cm^3/g]$	V_{mic}/V_t
C	1378	1117	0.93	0.46	0.14	0.49
C-Fe	658	668	0.57	0.23	0.12	0.40
C-Co	861	734	0.79	0.25	0.29	0.32
C-Ni	798	629	0.67	0.23	0.11	0.34
CA	1348	1125	0.89	0.47	0.14	0.53
C-FeA	709	576	0.58	0.2	0.09	0.34
C-CoA	996	818	0.89	0.28	0.24	0.31
C-NiA	913	800	0.74	0.30	0.13	0.41

The structural parameters of carbons calculated from nitrogen adsorption isotherms are collected in Table 2. Analysis of the data indicates differences in the porosity of materials, which are likely governed by the effect of metal cation. It is noteworthy that adsorbents obtained from nickel and cobalt salts have larger surface areas and higher volumes of micropores than the C-FeA sample. The degree of microporosity (ratio of V_{mic}/V_t) is around 32 % for all transition metal containing samples. These differences are likely the results of the differences in the mechanism of carbonization. The most

microporous appears to be the sample obtained from the sodium form of material where the chelation does not require multiple covalent bonds and thus material is less " compact".

The pore size distributions calculated using DFT and a slit shape pore model commonly used for activated carbons [4, 5] are presented in Figure 2. The sample obtained from the initial polymer is very microporous with the majority of pores smaller than 30 Å and high contribution of ultramicropores (< 10 Å). For C-Co and C-Ni the similarities in the PSDs exist, especially for the small pores, micropores and mesopores smaller than 100 Å. A significant difference is noticed for mesopores with sizes between 200 and 700 Å. The cobalt-containing sample has high volume of those pores (0.140 cm^3/g) while they are not formed in C-Ni. On the other hand, the nickel sample has noticeable volume of much larger pores. For C-Fe the volume of pores is much smaller, as indicated from Table 2, and the pores differ in their sizes compared to the other two counterparts. Although, micropores of small sizes (about 6 Å and 10 Å) are also present in C-Fe, there is a significant volume of pores with a mean pore width of 100 Å and 500 Å.
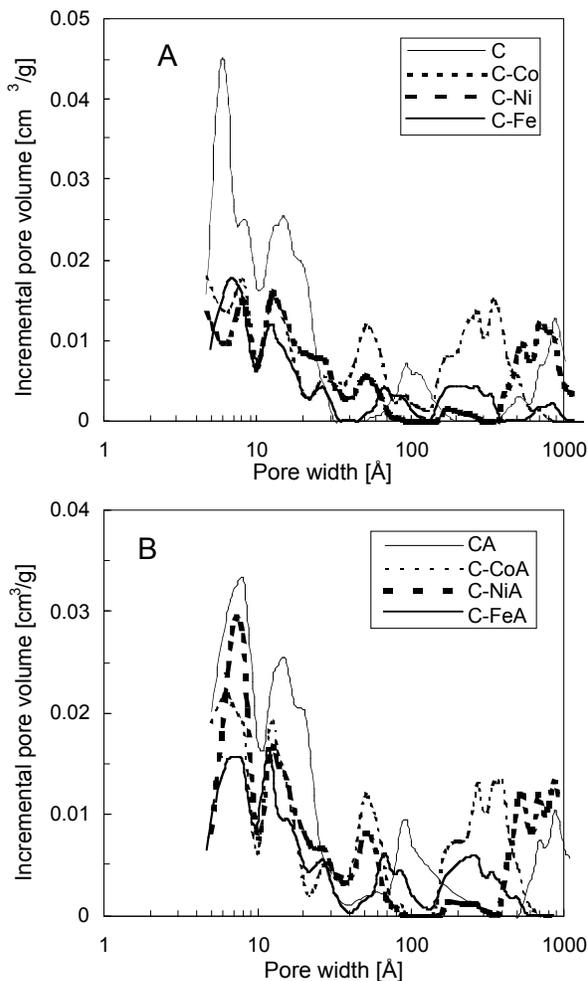

Figure 2. Pore size distributions for sample before (A) and after acid washing (B).

Acid washing changes the PSDs (Figure 2 B) especially in the range of micropores while mesopores remain almost intact. The volume of pores smaller than 10 Å for nickel-based samples becomes almost the same as for the sample obtained from the sodium form of the material. A significant increase in the volume of those pores is also noticed for the cobalt-based sample. This suggests that cobalt and nickel species are located mainly in the very small pores where high metal dispersion can be reached. On the other hand, acid washing of iron-based sample does affect the volume of micropores very slightly and the volume of large mesopores increases. This indicates that bulk crystals of iron species, likely oxides are present on the surface of the water washed material. They are formed as a result of the oxidation of reduced iron agglomerates exposed to air. The removal of large agglomerates iron compounds results in formation of new mesopores in the carbonaceous matrix.

Differences in porosity are likely related to the differences in the chelation process of ion within organic matrix. Cobalt and nickel are divalent cations whereas iron is trivalent. This, likely leads to different matrix arrangements. We would expect the iron form to be the most "compact". Indeed the similarities in the structures of C-Co and C-Ni were found. In spite of those similarities, the differences for those samples were noticed, especially in the range of larger pores. The differences in the porosity of materials related to the valency of metals were also noticed by Nakagawa and coworkers [3]. For the carbon derived from polysterene divinylbenzene sulfonic acid salts they proposed that multivalent metals and their salts create some kind of pillars during carbonization, which are responsible for development of fine microporosity. As indicated by Konno et al. [9] who studied polyamine resins complexed with Co(II) and Cu (II) ions the formation of cubic cobalt during carbonization may play a role in the development of mesoporosity. In their study, mainly 200 Å pore sizes were found in carbonaceous Co containing materials.

To further investigate the structure of materials obtained during carbonization of organic salts the SEM images were analyzed. In the case of sample obtained form the initial polymer the structure of material looks very porous with 100 nm pores seen in the micrograph (Figure 3A). Besides that highly porous phase, a layer of another carbonaceous material of less rigid nature can be observed on the surface of the particle. Acid washing caused removal of that layer. Moreover, after that treatment the surface appears "cleaner" and small round pores with the diameter of about 10 nm and smaller can be seen in that carbonaceous phase. Those pores were also detected as a peak on PSD. The structure looks "spongy' and very light resembling carbon nanofoams [9-11]. The sample was cleaned with water after carbonization so all sodium should de dissolved during that step.

The microstructure of the cobalt derived sample looks much more interesting. On the surface of the C-Co 50-100 nm crystals of inorganic phase are seen (Figure 3B). They are in the brick wall-like agglomerates between which big macropores are formed. Those agglomerates cover carbonaceous phase almost totally. Acid washing completely removes inorganic phase and a fascinating structure of cardboard-like

carbon is revealed with regularly organized graphene sheets (Figure 3C). As in the case of the C sample, remains of less rigid porous carbonaceous phase are seen on the surface. Underneath of that phase, the cardboard-like pattern can be recognized. In the case of nickel and iron-based samples, after acid washing and removal of either sulfides or oxides, the foam-like structure, similar to that obtained for C-A sample is revealed.

In order to understand the process of carbon nanofoam formation and the existence of cardboard-like porous structure in the case of cobalt modified sample, the differences in the porosity are related to the differences in the form and crystalline structures of inorganic species deposited on the surface. Materials exposed to air showed significant exothermic effect, which we link to the formation of oxides, oxygen containing functional groups and sulfates. In the case of iron, which is the easiest to be reduced by carbon and to be oxidized by air, dense agglomerates of needle-like crystals are present with sizes in the range of the pores seen in the clean carbonaceous matrix. Based on the shape of cobalt oxide phase seen on SEM micrographs, it is likely that the small agglomerates of reduced cobalt present between graphene sheets significantly expand when sulfates and sulfides were formed at 720 ^oC and those "pillars" pushed the graphene layers apart. Their removal by HCl treatment results in cardboard like structure seen in Figure 3C. Such phenomenon does not occur in the case of nickel form whose sulfide phase appears light and flaky.
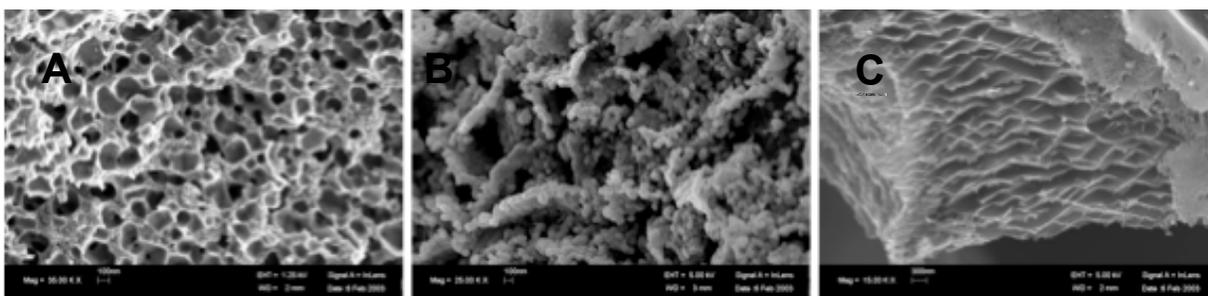

Figure 3. SEM micrographs of CA (A), C-Co (B), and C-CoA (C) samples.

Since in our materials the main structural form, common for all samples is foam-type we link its formation to removal of SO_2 and water from decomposition of sulfonic groups, C_xH_y from polycondensation, and migration of reduced metals from bulk phase to the carbon surface and formation of agglomerates. The decomposition of nitrates which occurs with a noticeable expansion in the volume of material at T< 300 ^oC may be also responsible for formation of meso- and macroporosity. Removal of metal oxides and sulfides also contributes to opening more mesopores..

CONCLUSIONS

The results of this study clearly show the foam-like nature of materials obtained by carbonization of metal salts of polysterene sulfonate co-maleic acid. The materials look very light with high volume of micropores and the presence of mesopores.. Moreover, the carbonization of polymer with cobalt resulted in the formation of new, a cardboard-

like carbonaceous structure. An important aspect of the preparation procedure is that the surface properties can be tailored using various contents of the metals and different ligands. Moreover, the exposure of the active surface formed during carbonization to various gases reacting with metals present there can result in expansion of graphene layers and formation of additional porosity. This may open the door for engineering the texture of the materials toward desired applications.

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