

The methods of preparation and modification of surface properties of synthetic carbon adsorbents

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Our concern in this paper is to review the methods of preparation and modification the surface properties of synthetic carbon adsorbents, obtained by carbonization different porous organic polymers. The first section are devoted to the methods of carbonization polymers, application catalysts and the influence of some important factors such as carbonization temperature, heating rate and soak time of salt solutions on the resulting char properties. In our paper we pay special attention to application this carbon adsorbents to trace analysis of organic pollutants in environmental samples. The physico-chemical properties of synthetic carbon adsorbents are superior compared to those of the “traditional” active carbon materials.

1. INTRODUCTION

Among the numerous materials applied in adsorption, synthetic carbon adsorbents are of the most interest for their unique characteristics such as high thermal stability and chemical inertness as well as regulated porosity and surface chemistry [1,2]. Synthetic carbon adsorbents are characterized by a high degree of purity, high thermal stability under inert atmosphere conditions and good electrical conductivity, hardness and resistance to corrosion. Because of these properties they find many applications. For its applications in adsorption or in chromatography, adsorbent materials should have suitable sorption properties, and this concerns not only the sorption capacity, but also the texture of the carbonized material. Unique properties of carbons obtained by carbonization of polymers permit utilize these materials for special purposes,

for which they are practically indispensable. For example the authors of paper [3] have described the method of carbonization of organic polymers and utilization of so obtained synthetic spherical carbon adsorbents to blood hemoperfusion i.e. sorption of toxins directly from patient's blood.

Usually active carbon prepared from natural raw materials have a higher ash content in compare to the carbons prepared from artificial raw materials which are almost without ash and possess higher mechanical resistance to crushing and abrasion. Active carbon adsorption properties are affected by the chemical structure of its surface. The surface character is determined by the kind, amount and way of incorporation of various heteroatoms such as: oxygen, hydrogen, nitrogen, sulfur, chlorine and others bonded with it. Synthetic active carbon has a non-specific or poorly specific adsorption properties (depending on purity) with a well developed porous structure formed mainly by micro- and mesopores of various diameters. Well-developed specific surface area (up to 1000 m²/g or even higher) contributes to their high adsorption capacity.

2. CHOOSE THE POLYMER FOR CARBONIZATION

To obtain the synthetic carbon adsorbent different kind polymers have been applied as well as pyrolysis of proper selected of synthetically resins, sometimes prepared specially for carbonization [3-12]. Many polymers and copolymers have been described as initial materials for carbonization e.g. polyacrylonitrile, poly(vinyl chloride), poly(vinylidene chloride), styrene-divinylbenzene, polyethylene polypropylene, polystyrene, poly(ethylene terephthalate), polyamide, cellulose, viscose. Also polymer derivatives have been carbonized, as e.g. polymeric ion exchangers, polyethylenesulphone etc. An active carbon have been prepared also by carbonization and activation of nitrogen- [13] and phosphorus-containing [14] polymer. Macroporous copolymer of methylvinyl-pyridine with N-methyl-1-methyl-3-vinyl-pyridinium and divinylbenzene and phosphorylated styrene-divinylbenzene were used as a starting materials for active carbon preparation. Carbonization of nitrogen and phosphorus-containing polymer precursor yield residue with N, P, and O containing functional groups. In particular a relatively a few numbers of oxygen-containing groups give rise to hydrophilic centers and confer a capability to exchange cations in water solutions [15,16]. Nitrogen-containing active carbons show increased anion-exchange capacity [17] and catalytic activity in redox reactions [18]. Sulfur-containing carbons show high affinity to ion Hg(II) [19].

It has shown [20] that carbonization of highly cross-linked polymeric materials leads to formation of synthetic spherical carbon adsorbents. Synthetic carbon contains usually small-volume pores, which causes low total surface area and low adsorption capacity. The porous structure of polymeric carbon can

be controlled during synthesis of polymers or subsequently developed by activation carbonizate, for example with steam or carbon dioxide. Activation of the pyrolysed resin with steam at 700-900°C give an adsorbent with a surface area of 1100 m²/g [4]. Additionally, this activation process can be controlled by using a catalyst (Ca ion for example). Such a catalyst permits control of porous microstructure of adsorbents, because applicability of the final product depends not only on the nature of its pore surface, but also on the values of the pore structure parameters.

One of the first work over carbonization of polymers concerned the obtaining process of special porous carbons (for instance, the kind of molecular sieve) obtained by carbonization of polyvinylidene [21, 22]. That kind of pure carbon adsorbents possesses, like graphite carbons, homogeneous non-polar surface therefore the more polar substance (for instance water) during the chromatographic process eluted before non-polar hydrocarbon (for instance methane). If the carbonization process of polychlorvinyle materials is held in proper conditions, it is possible to obtain carbon molecular sieve. The process of making mono-sized pores in adsorbents is connected probably with diffusion on the surface of hydrochloride particles (HCl), the decomposition product of PVDC, from half-liquid polymer bloc warmed up to the temperature of 180-290°C.



At the next stage, obtained adsorbent was warmed up to the temperature of 800-1200°C for obtaining inflexible skeleton of carbon adsorbents. Adsorbents of that kind are used for division the mixture of permanent gases (for instance CO, CO₂, N₂, CH₄), components of unstable gases (light aliphatic hydrocarbon) and trace analysis of different organic substance presented in the water [5,21-23].

Molecular sieves carbon (MSC) prepared according to Walker [24], were introduced in GC for the first time by Kaiser [21,25-27]. Vinylidene polychloride of high purity is used as a material for MSC production. Due to the thermal decomposition of polymer, hydrogen chloride is evolved and an homogeneous skeleton of pure carbon adsorbent with narrow pores is formed. The obtained product was microporous carbon of a specific surface area 1000-1200 m²/g and molecular sieve structure. Deng Li-ru in his experiments [22] pays special attention to the purity of vinylidene polychloride which is a raw material for MSC preparation and in its paper discusses polymer pyrolysis in detail.

Carbonization of other polymers, particularly derivative phenol-formaldehyde, styrene, vinyl and similar leads to obtaining adsorbents of glassy carbon structure [6-8,23]. The carbons of such kind possess perfect mechanic

properties, hardness, possibilities regulation of crystallographic structure and possess similar to graphitic soot surface-unspecialized properties; nonspecific interaction with polar organic compounds. Besides that, if the process is held in appropriate controlled conditions, it is possible to obtain such adsorbents in state of spherule grains [21,22], which is very useful, particularly for optimal packing the chromatographic columns or adsorption tubes with such adsorbent.

Another way for preparation synthetic carbon adsorbent were present by other authors. For the preparation of synthetic carbon adsorbents of appointed porous structure the authors of works [28] used the replication technique. It consists in allusion the polymers on adsorbents surface, for instance silica gels, of appropriate porosity then the thermal carbonization of polymers and at the end the removal of the silica gel matrix by etching of alkali or hydro fluoride.

In 1982 year Gilbert, Knox and others [6-8] applied the same method preparation of carbon materials called by them the glassy porous carbons. That methods is based on that the first thing on impregnation the high porous silica gel surface with the mixture of phenols, and then that mixture is polymerized inside the gel pores. Prepared in that way adsorbent is pyrolyzed in high temperature(600–900°C), the silica gel matrix is removed in alkali or in acid and adsorbent is warmed to temperature higher than 2000°C in the inert atmosphere. In this way there are obtained the carbon adsorbents of glassy structure of developed porous structure. These carbons have specific surface area and chromatographic properties similar to those of graphitized carbon blacks but superior them in respect of mechanical properties. They were used as the packing of GC and HPLC chromatographic columns used for separation of phenols, benzene methyl derivatives, polar monofunctional derivatives of benzene, amines and other compounds [7,8].

The template method has also been used in the preparation of highly ordered mesoporous carbons [29-31]. However, micropores cannot be totally eliminated because of the properties and nature of the precursors used such as sucrose, phenolic resin and furfuryl alcohol. In the paper [16] the preparation of mesoporous carbons using procedures known from the carbon fiber fabrication literature, which lead to fibers with surface areas less than 10 m²/g has been reported. A combination of this technique and Knox's templating method [8] allows the preparation of purely mesoporous carbon, which could be suitable for adsorption and chromatographic separations. This technique can also be extended to prepare non-microporous thin films or carbonaceous replicas of highly ordered mesoporous materials [31]. It should be noted that petroleum pitch and polyacrylonitrile (PAN), which are typical carbon fiber precursor, were also used as precursors to prepare mesoporous carbons via catalytic activation with transition metal compounds, but the latter were not removed after carbonization [32,33]. In addition to carbonization, these resulting materials

were activated [34]. Even without activation step the aforementioned procedure afforded carbons with a mesopore ratio about 60-80 % only [32].

The synthesis of mesoporous carbons reported in the work [35] was performed by using the Lichrospher Si 100 silica gel as template and a synthetic mesophase pitch (s.p. 273 °C) or acrylonitrile as carbon sources. The mesophase pitch was first treated with quinoline and only soluble components were used. Additionally silica was treated at 650 °C in air for 10 h to reduce its surface hydrophilicity. Then the silica gel was impregnated with quinoline solution of the mesophase by refluxing at 100-250 °C for 10 h. Later the quinoline solvent was evaporated slowly (<0,1 °C/min.). In the case of the mesoporous carbon obtained from acrylonitrile, the high temperature treated silica was impregnated with dimethyl sulfoxide (DMSO) solution of acrylonitrile. Then, a small amount (1 wt %) of radical initiator (2,2'-azobisisobutyronitrile) was introduced. The polymerization was performed at 60 °C for 5 h under protection of nitrogen gas. The removal of DMSO was achieved by slow evaporation. The stabilization process for both kinds of impregnated silicas was the same. Both samples were heated in a flowing dry air with a rate of 5 °C/min. Until 180 °C, stabilized in the range from 180 to 330 °C at a heating rate of 0.2 °C/min. and kept at the final temperature for 10 h. The stabilized samples were then carbonized at 1000 °C under nitrogen protection for 2 h. The silica template was removed by using a hot sodium hydroxide solution. Then, the resulting carbons were thoroughly washed with distilled water and dried. The completeness of the template was monitored by thermogravimetry. The resulting carbon exhibited a well-developed mesoporosity was obtained, with specific surface area of 600 up to 1200 m²/g.

Czechoslovak research used of turn polytetrafluoroethylene (PTFE) as starting material to preparation of carbon adsorbents [9-11]. Obtained product was produced by reduction of PTFE with lithium amalgamate at room temperature. Because of very high microporosity and high content of polar functional groups of oxygen origin (13% w/w of oxygen) this adsorbent was subject thermal treatment in order to reduce of strong adsorption centers and heterogeneity of carbon surface.

The authors of [10,36,37] obtained another kind of active carbon (JADO) by the original method of polytetrafluoroethylene (PTFE) electrochemical reduction with lithium amalgam at low temperature. The obtained product had a very large specific surface area (about 2600 m²g⁻¹).

Recently, a new method for MSC preparation based on pyrolysis of polysulfonated polymers for chromatographic purposes has been described [38]. The firm Supelco (USA) offers this carbon (commercial name Carboxen) for capturing and concentrating volatile organic impurities in air before their further analysis [39].

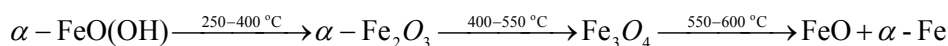
Analogous method of carbonization of polymers was used by Zwier and Burke [12]. These authors have also used the electrochemical reduction of Teflon (PTFE) with lithium amalgamate. Using this method they obtained also the carbon adsorbents of very strong adsorption properties and large specific surface area ($1400\text{m}^2/\text{g}$). These adsorbents were subjected chemical modifications including surface reactions with chlorosilanes or Grignard compounds after previous chlorination of the surface of the obtained carbons. This permitted to reduced significantly adsorption properties of these carbon adsorbents and utilize them as the packing of HPLC columns for separation of aromatic compounds.

In another paper [4] there are demonstrated the possibilities of preparation of spherical carbon adsorbents from consumed ion-exchange resins. Cation-exchange resins such as Dowex, Wofatite, or Zeolite (containing surface sulfate groups) were subject of pyrolysis. The obtained in this way carbon adsorbents of relatively low specific surface area before further use were activated with steam at temperature of $800\text{-}900^\circ\text{C}$. In some cases this process was performed in the presence of catalyst for controlling gasification process. The used procedure have permitted to obtain the adsorbents of specific surface area nearing to $1000\text{ m}^2/\text{g}$ and pore volume to $0,75\text{ cm}^3/\text{g}$. These adsorbents were used to enrichment of different organic compounds contained in water and air by solid phase extraction (SPE) or thermodesorption (TD) [4,40,41] methods.

In another paper phenol-formaldehyde resins were used as the starting material for the preparation of porous carbon. The resins were synthesized under an atmosphere of nitrogen at 95°C , using an initial formaldehyde-to-phenol ratio of 1.33 by mole. A base-catalyzed method was used in the synthesis with ammonium hydroxide as the base. After synthesis, the resins were cured by heating in vacuum for 2h at 60°C , followed by 12h at 120°C [42,43].

In the work [44] have been studied catalytic carbonization of three kind of polymers: polyethylene, polyvinyl alcohol, and polystyrene. The experiments shown that PVA gives the maximum yield of amorphous carbon PVA and was used as a starting carbon material in subsequent syntheses. A new method producing of amorphous carbon with catalyst particles uniformly distributed throughout the matrix bulk have been developed. Iron hydroxide used as the catalyst precursor was prepared from Fe nitrate by precipitation with NaOH, next washed with distilled water, and dried at 150°C up to constant weight. Next iron hydroxide was mixed with aqueous polymer solution in the weight ratio of 1:20 relative to the dry polymer. The suspension of the catalyst precursor in aqueous polymer solution was sonicated, and the residual solvent was evaporated at 60°C until constant weight. The resulting $\sim\mu\text{m}$ thick solid polymer films with incorporated Fe hydroxide particles were crushed, and the samples were loaded into the quartz reactor of a flow setup. The setup allowed

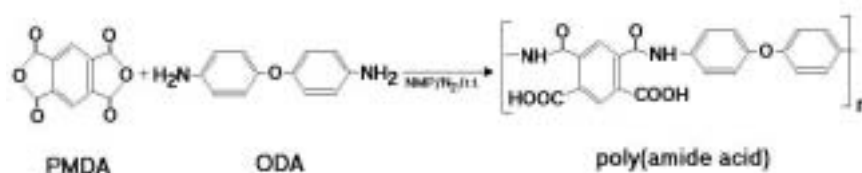
regulation of the reactor heating mode and control of the temperature of the sample bed. The samples were heated at a rate of 125°C/h and kept for 2h sequentially at 250°C and 400°C for removal of volatile and liquid products of PVA decomposition. Subsequent carbonization of the samples was carried out at 600°C for 2h. The phase transitions that occur during the heating and interaction of the catalyst precursor particles with gaseous, liquid, and solid products of the polymer decomposition are shown in the scheme below [45].



Scheme 1.

Porous carbon films were prepared by the pyrolysis of poly(urethane-imide). First the films of polymers were prepared by a reaction between phenol-terminated polyurethane polymer and poly(amide acid) obtained from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA). Upon thermal treatment of the poly(urethane-imide) films at 300 to 400°C, the thermal less stable urethane domains decomposed, leaving porous polyimide films. The porous polyimide films were further pyrolyzed at 900°C for 1 h to give porous carbon films [46].

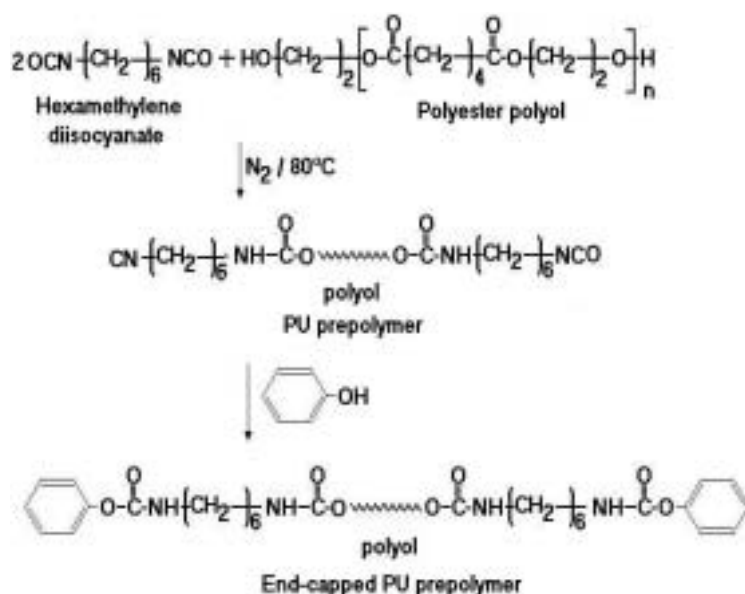
Preparation of prepolymer from ODA under nitrogen atmosphere, is shown in the scheme, following to the procedure described previously [46,47].



Scheme 2. Preparation of PMDA / ODA poly(amide acid) [46]

PU prepolymer was prepared, as shown in upper scheme, by adding HDI and catalyst: dibutyltin dilaurate polyethylene adipate under nitrogen atmosphere and stirred at 80°C. Next the polymer was conducted after adding 2% excess of phenol [48]. This gave a white viscous material.

The product was diluted with NMP to 50 wt.% solution. The poly(urethane-imide) films were peeled off from the glass plate, and then were sandwiched between glass plates followed by thermal treatment at 300, 350 or 400°C for 1h each under ambient pressure to give porous polyimide films [47]. Next, porous polyimide films were pyrolyzed by heating up to 900°C at a heating rate of 1K/min and maintaining at 900°C for 1h in a nitrogen flow [47].



Scheme 3. Preparation of polyurethane prepolymer [46]

In the paper [49] macroporous carbon supports were prepared by blending fine particles of graphite with a phenolic resin. This blend was pressed at 1200 bar in a static press resulting in disk-shaped supports of 35mm in diameter and 2.5mm in thickness. The supports were cured in air at 100°C and subsequently carbonized under nitrogen flow at a temperature of 800°C in a refractory steel tube. During both steps the macroporous carbons were subjected to static pressure to prevent their deformation.

The precursor polymeric membrane was prepared by depositing a small amount of a 13% solution of polyamic acid in N-methyl-pyrrolidone (NMP) over the support and spun at 1600 rev/min [49]. Uniform film of polymeric solution was formed on the macroporous carbon support. The support coated with the polymeric solution was heated following the sequence: (a) drying at 150°C during 1h in air (heating rate: 3°C/min); (b) imidization under vacuum at 380°C (heating rate: 1°C/min); (c) carbonization under vacuum at temperatures ranging between 550°C and 700°C (heating rate: 0.5°C/min) [49].

3. MODIFICATION OF POROUS STRUCTURE OF SYNTHETIC CARBONS

In the work [4] presents the methods of preparation of synthetic spherical carbon adsorbents and next its modification in order to obtain active carbon adsorbents. To modify the carbonized resin various methods are used, i.e. activation with the steam at 700-900 °C, with and without a catalyst, as well as heating in inert or hydrogen atmosphere at 800 °C. The carbonization process was performed in a quartz fluid home made reactor [50,51]. The spherical adsorbents was obtained by carbonization of a polysulfonated cation-exchange resin containing different amounts of the sulfonic group on its surface. The activation process with the steam was performed in a vertical thermo-balance at 700-900 °C.

In the work [52] were described the results of a catalytic graphitization of amorphous carbon matrix at relatively low temperatures (600-800 °C) in nitrogen flow. Carbonized of polyvinyl alcohol (PVA) with Fe-containing catalyst at temperature of 600 °C in nitrogen flow was used as the carbon matrix containing catalyst particles uniformly distributed in its bulk.

Carbonization of methylene-bridged aromatic oligomers prepared from naphthalene (N), methylnaphthalene (MN), ethylnaphthalene (EN), tetralin (TET), methylated tetralin (MTET), biphenyl (BP), methylated biphenyl (MBP), and ethylated biphenyl (EBP) by condensation with methyral as follows below has been presented in paper [53]. Aromatic compound and methyral were dissolved with chloroform, into which sulfuric acid (95%) was added slowly at 0°C, and stirred for 6 hours at room temperature [53]. After removing sulfuric acid by repeatedly washing with water, the oligomer was extracted with chloroform. Thus, prepared oligomers (the chloroform - soluble fractions) were abbreviated as NC, MNC, ENC, TETC, MTETC, BPC, MBPC, and EBPC, respectively [53]. Carbonization reactions of the above oligomers were carried out under an atmospheric pressure by the following procedures. Pyrex tube containing the oligomer was immersed in a molten salt bath kept at 300 °C, and then heated up to 420 °C at a rate of 5 °C/min under an atmospheric nitrogen stream, which was introduced into the tube throughout the reaction [53]. The optical textures of the carbonized sample were observed by polarized light microscopy after conventional polishing.

Carbonization of other polymers, particularly derivative poly(terephthalate)ethylene (PET), furfuryl alcohol and thermal stability of active carbon obtained from nitrogen-containing polymers [54, 55] was performed in resistance pipe furnace in inert gas (nitrogen). For carbonization process there were subjected either pure PET or PET especially prepared with addition of $\text{FeCl}_3 \cdot 7 \text{H}_2\text{O}$ and $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot n \text{H}_2\text{O}$. Evaluation of solid carbonization products obtained from the mixture of poly(terephthalate) ethylene (PET) and

polyacrylonitrile (PAN) used as a raw material for production of active carbon. 200 g of finely grinded PET granulate dispersed in FeCl_3 solution (1,64 % w/w used as chemical activator) were boiled for about 5 h. After the drying the PET was mixed with PAN in proportion of 1:1 and so prepared mixture was pressed into pellets by means of hydraulic press. The pellets were placed in „boat” sample container. The samples were calcinated in pipe furnace with gradual increase of heating temperature (50 deg/h) [55]. The sample was maintained at final carbonization temperature for 2 hours.

Puzij et al. [56] have carbonized obtained earlier copolymer of 4,4' – bis (maleinimidiphenyl) methane and styrene (BM – ST) in inert or in methane atmosphere. As a result of carbonization process they have obtained three following samples [56]:

- Sample C 1 obtained owing to polymerization of starting BM – ST copolymer to temperature of 600 °C in nitrogen atmosphere; heating rate was 10 °C/min.
- Sample C2 obtained during thermal treatment of C 1 sample for 1 hour at temperature of 900 °C in methane atmosphere
- Sample C 3 obtained during two-steps carbonization process including:
a) oxygen stabilization in air for 1 hour at 300 °C, b) carbonization in methane atmosphere until the temperature of 900 °C.

Carbonization in inert atmosphere influences the formation of micro- and mesoporous carbons, while during the thermal treatment performed in methane atmosphere there decrease the porosity, which is due to precipitation of pyrolytic carbons of small pore dimensions ($R < 2\text{-}3$ nm).

4. PREPARATION OF CARBON MOLECULAR SIEVES

Molecular sieving carbon (MSC) is a special form of activated carbon, which has almost uniform micropores of several angstroms in diameter. The unique pore structure of MSC has enabled us to separate molecules by their dimensions. MSC has some advantages over molecular sieving type zeolite (MSZ) such as high heat-resistance, high corrosion-resistance and hydrophobicity [57]. MSC has been used extensively for gas separation processes [58,59] including N_2 production from air by the pressure swing adsorption (PSA) process. The possibility of using MSC as a shape selective catalyst and/or catalyst support has also been examined [60]. Several methods have been proposed for producing molecular sieving carbon (MSC) since Emmet [61] reported the molecular sieving property of a carbonized Saran in 1948. The majority of methods are intended to slightly modify the pores created by carbonization of carbonaceous materials. Since the pore structure of carbonized materials is highly dependent on the starting materials, selection of a proper starting material is a key factor in the production of a MSC having the

desired pore structure. Various carbonaceous materials such as synthetic polymers, coconut shell, wood, coal, and cellulose have been used as starting materials to produce MSC [62-65].

Miura and Hayashi [65] have reported the preparation of MSC by modification of pore size distribution. The idea of this method is to modify the carbonization behavior of coal and consequently to change the pore structure of the char by adding modifiers, such as pitch and phenol-formaldehyde resin to coal. Only polymers that do not undergo transformation to the thermodynamically preferred graphite phase at high temperatures can be used for MSC synthesis [66]. This non-graphitizing character, which is present in materials like poly(acrylonitrile) (PAN), polyfurfuryl alcohol (PFA) and poly(vinylidene chloride) (PVDC), has been attributed to the presence of heteroatoms of cross-links between the polymer chains when pyrolyzed [66]. Several authors have shown that for most precursors, high temperature sintering leads to a diminution in porosity, with concomitant shrinkage of pores. Eventually, depending on the polymer precursor, a collapse of the structure and creation of macroporous defect occurs above a certain temperature, leading to a loss in sieving capability [67,68].

In the work [69] molecular sieves carbon were prepared by deposition and carbonization of polyfurfuryl alcohol on activated carbon. These materials are characterized by a high selectivity towards O_2 and a large uptake of this gas when compared with nitrogen. The equilibrium isotherms are essentially the same both for N_2 and O_2 . After the first deposition of polyfurfuryl alcohol, the micropore volume increases and the pore width decreases. A second deposition decreases the pore width, which approximates the pore width of the carbonized polyfurfuryl alcohol. The material prepared by two depositions has characteristics similar to those of commercial MSC.

Recently the authors [70] have shown that an MSC can be produced by simply carbonizing a waste ion exchange resin, and found that calcium ion in the resin played an important role for the formation of uniform micropores [71]. This suggested that the cation presented in an ion exchange resin can be utilized to control the formation of micropores during the carbonization of the resin. Since ion exchange resin is a well defined material, and since the cation type and its loading can be well controlled, carbonization of ion exchange resins with different cation type and controlled cation loading is expected to be a step for producing 'tailored MSC'.

The paper [70] present a new method for controlling the micropore structure of porous carbon by used of pillar effect of metal and/or sulfur compounds. An ion exchange resin having sulfonic acid groups as ion exchangeable functional groups was used as a raw material. Resins having various cations of H^+ , K^+ , Na^+ , Ca^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} and Fe^{3+} were prepared from the ion exchange resin. They were carbonized at 500-900°C in a nitrogen stream to prepare

porous carbons. The micropore distributions of all the resins carbonized at 500°C were rather sharp and their average diameters varied in the range of 0.38 to 0.45 nm depending on the kind of cations exchanged. At the carbonization temperature of 900°C, the carbonized polymers prepared from the resins with di- or trivalent cations maintained sharp pore distributions, whereas those prepared from the resins with univalent cations lost most of the pores. The difference was brought about, because di- or trivalent cations can form ionic crosslinkings connecting two or three functional groups in the resins, but univalent cations cannot. The crosslinking functional groups and cations are converted to highly dispersed metal sulfides or elemental metals etc. during the carbonization, which would form a kind of pillar to maintain pores in the carbonized resins. The micropore distributions could be controlled by changing the kind of di- or trivalent cations.

5. CARBON COATING MEMBRANES

Another approach to provide gas separation membranes has been reported by Rao et al. [72]. These authors prepared carbon membranes by coating a thin macroporous graphite sheet with a thin, uniform layer of polyvinylidene chloride-acrylate terpolymer latex solution. The coated disk was heated at 1000°C under nitrogen. The procedure was repeated five times to produce a defect-free membrane. The resulting membrane is 2.5 μm in thickness, the average pore size being around 5-6 Å. This membrane was successfully tested for the recovery of hydrogen from hydrogen and C₁-C₄ hydrocarbon mixtures. However, there are not data about its efficiency for separation of permanent gases.

Hayashi et al. [73] obtained a carbon membrane by coating an α -alumina porous tube with a polyimide synthesized in the laboratory. The carbonization was carried out at temperatures between 500 and 900°C under nitrogen atmosphere. The procedure was repeated three times to achieve a defect-free membrane. The resulting membrane is 2 μm in thickness, approximately, and has micropores around 4 Å. This membrane is efficient for separation of permanent gases. Thus, the permselectivity CO₂/N₂ is around 40 and He/N₂ around 100. Additionally, these authors reported its efficiency for separation of propane/propylene and ethane/ethylene achieving permselectivities of 50 and 7, respectively.

6. ACTIVE CARBONS WITH THE HETEROATOMS

Active carbons containing heteroatoms (O, N, P, S, etc) can be obtained using several methods:

1. surface treatment of finished active carbon with heteroatom-containing reagent (e.g. oxidizing agents [74,75], heating with NH_3 or HCN [17,76-78], pyridine [79], H_2S , SO_2 [80], PCl_3 [81]);
2. pyrolysis of raw material in presence of heteroatom-containing substances [82,83];
3. pyrolysis of raw material containing heteroatoms in different forms (e.g. polyacrylonitrile or vinylpyridine copolymers [84], aromatic polyimide [85]).

Synthetic carbon, i.e. carbons obtained from polymers offer the prospect of the third approach by carbonization of polymers containing various heteroatoms. For example the work [14] discussed the properties of carbon residue obtained from nitrogen- and phosphorus-containing polymer precursor. Carbonization of nitrogen - and phosphorous - containing synthetic polymer precursor yields carbon residue with N-, P-, and O- containing functional groups. This functionality makes the surface hydrophilic and confers cation-exchanging properties to the carbon.

7. MODIFICATION OF POROUS STRUCTURE OF CARBON ADSORBENTS

A wide range of applications of carbon has developed for analytical purposes. A need for an elaboration of the methods for synthesis and characterization of activated carbons with a defined porous structure required different methods its modification. Among other for creation controlled mesopore and micropore structures deals with steam gasification of various carbon materials, heating in inert gas atmosphere at high temperature and oxidizing by different agents (liquid or gas oxidizers). Adsorption, electrochemical, hydrophilic-hydrophobic, acid-basic and other properties of carbon adsorbents depend strongly on chemical structure of their surface. For the non-modified active carbons in the presence (or absence) of oxygen atoms on carbon surface influence strongly on its chemical properties has been observed. Oxygen atoms play a very important role especially in the processes of ion adsorption from the electrolyte solutions (e.g. water) because of the possibilities of formation of oxygen containing surface groups capable of ion exchange as well as the decisive participation of oxygen in electrochemical reactions occurring on carbon surface and causing potential drop at the carbon solution interface. Oxygen can be introduced into active carbon either during its production process or later during its modification.

The surface of unmodified active carbon is covered partly (max. 10%) with an oxide layer. Oxidation of carbon with a strong oxidizer e.g. concentrated nitric acid results in the increase of coverage degree of the surface with chemisorbed oxygen from ten to twenty or even more percent. For meso- and macropores the surface coverage degree with the oxides can attain even tens percent.

With the development of chromatography and knowledge about active carbons [86,87], the active carbon surface was modified by removing ash (removing mineral impurities) by chemical treatment, removing oxygen units on the carbon surface by heating at high temperatures in oxygen-free atmospheres and porous structure modification by catalytic activation, pyrocarbon deposition acted under suitable conditions. Active carbon modification consists in removal of chemical heterogeneity and unification of carbon porous structure. Both these methods can be combined. In the first stage of active carbon application in chromatographic separation, its modification consisted of heating the column with carbon at 150-200°C for a few hours and pumping out to reach a pressure of 0.1 mm Hg [86-88]. This was performed mainly to remove moisture without changing the adsorbents surface character. In time carbon thermal treatment was used at different temperatures from several hundred degrees to annealing at about 1000°C in a stream of pure gas or hydrogen for a few hours [89-94].

From the technical point of view, oxidation of active carbons at high temperatures is a simple way to obtain effective adsorbents of analytical purposes [94-96], such a treatment causes a change in surface chemistry and porosity of active carbon [95-97]. During the action of air on active carbons at high temperatures, organic tar substances are removed from their surface. (These substances usually remain after carbonizate activation with water vapour in active carbon production.) As a result, the scatter of pore size is smaller and physical and chemical heterogeneity of the adsorbent decreases which results in significant increase of the adsorbent efficiency. The effects of such a treatment are presented in the paper [94] by Kirsz et al. The mixtures of methane, ethylene, propane, propylene as well as air, CO₂, water and propene were separated on the prepared adsorbents. Though chromatographic separations of saturated and unsaturated hydrocarbons were not effective. It is important that such a simple treatment allows for preparation of active carbons for moisture determination in hydrocarbon gases which is not a simple analytical task [98].

Another approach to modification of the active carbon surface is to spread different substances on it. During the analysis of nitrogen oxides, good results were obtained spreading up to 10% NiSO₄ on the active carbon surface [99]. Saturation of carbon from the alkaline solution with iodine accelerated separation and made the analyses more precise [100]. Some attempts for carbon surface modification were made by spreading liquid-solid chromatography

[101]. Deposition of 10% (w/w) di-nonylphthalate significantly alters carbon adsorption properties.

As follows from the literature review, removal of chemical heterogeneity on the carbon surface can be achieved with good results by relatively simple methods. Particularly, if the modification consists in a few methods already described e.g. removal of mineral impurities by extraction with mineral acids and the removal of surface complexes by reduction in a hydrogen stream at high temperature. Modification of heterogeneity of active carbon geometrical surface proves to be much more difficult, although some progress in this field has been observed. A good example of this is microporous so-called carbon molecular sieves, which will be discussed in the next section. Homogeneity of pores is obtained during their preparation but not modification. As known in the carbonization process, a primary porous structure of active carbon forms which is developed in a given direction and cannot be changed. Moreover, the terminal porous structure is significantly affected by the initial raw material. Therefore efforts have been made to create the required structure of active carbon during its production. It is impossible to discuss all these approaches, but because of their importance, active carbon are still the object of many investigations. One of the methods used to modify the porous structure in a controlled way is high-temperature treatment of active carbon with steam. However, this physical modification mainly causes changes in the microporous system of the adsorbent and does not solve the problem of preparation of carbon adsorbents of large pore volume with a minimal content of micropores.

Another methods of porous structure modification is activation in the presence of various catalysts deposited on the active carbon surface [102-105]. Gasification with steam in the presence of a suitable catalysts allows for mesoporous system development. Change of pore volume compared to the initial adsorbent can be about 300% [106].

Still another methods of modification of the active carbon porous structure is deposition of pyrocarbon on its surface [106-108]. Spreading of pyrocarbon can be achieved by various methods: passing benzene vaporous in a stream of inert gas over the heated surface of carbon, by pyrolysis of some quantity of benzene spread on the surface of carbon granules, by pyrolysis of methane etc. on the active carbon with 12% pyrocarbon spread on it [108]. There can be determined water and other polar compounds found in organic substances with the application of the gas chromatography method, which on the initial carbon give significantly broadened peaks indicating effective blocking of active centers by deposited pyrocarbon.

Active carbon modification does not increase its chromatographic application range; it is still mainly used in the separation of gases and light hydrocarbons e.g. noble gases, H₂, N₂, CO, CO₂, nitrogen oxides and light gaseous hydrocarbons up to C₄. Although this is a relatively small group, its

range of application including mainly industrial GC analyses with active carbons as analytical column packing.

Studies of polymer-based chars in carbon dioxide clearly show the influence of some important factors such as carbonization temperature, heating rate and soak time of salt solutions on the resulting char properties [109]. Under appropriate conditions, some polymers can be carbonized without melting [110]. By pretreatment of the polymer or copolymer by mild oxidation in air, the carbon yields after carbonization can be significantly increased. Chemical modification [111] of high strength PAN with hydrogen peroxide in alkaline solution causes acceleration of cyclization and oxidation reactions in the stage of thermal stabilization of the carbonized material.

During the activation phase of carbonization at intermediate temperatures (1200-1400°C) of PAN-based carbon fibers [112], a structural rearrangement of structural units that are formed at relatively low temperatures proceeds (~400°C). A significant increase in the size and orientation of these units occurs at even higher temperatures (~2500°C).

The structure of the polymer and the conditions of pyrolysis determine the structure and properties of the resulting carbonized products. Owing to the very variable crystalline ordering of graphitic structure, the carbonized products have very anisotropic, whereas glassy carbon is much less stiff and fully isotropic. Activated carbons usually exhibit polymodal distribution of pores [113], the diameters of which vary from molecular dimensions to several hundred nanometres. In contrast, it should be possible to produce carbonaceous adsorbents with the desired porosity and micropore size distribution using the appropriate starting material, as well as an adequate process of carbonization and activation.

The aim of the preheating and carbonization procedures was to raise the micropore content and thus to enhance the adsorption properties of the products. To improve the resistance to block formation in polymers during the carbonization period, solutions of some salts are soaked into the polymer. Following the literature [114], a mixture of salts (NH_4Cl , FeCl_3 and ZnCl_2), that are supposed to stabilize the porous structure, was used in the treatment of polymers at 300, 700 and 1000°C. These salts then serve as porogens, dehydration agents and oxidation catalysts at various temperatures. NaCl , NaJ , KJ , NH_4Cl , Na_2SO_4 , CoCl_2 are used as porogens, ZnCl_2 , AlCl_3 or H_2SO_4 as dehydration agents, and FeCl_3 , NaNO_3 , NaNO_2 , KNO_3 , KBrO_3 KJO_4 or their mixtures as oxidation catalysts.

8. CONCLUSIONS

Carbon adsorbents are called “fascinating material” or “old but new material” in scientific literature [115]. This is because of new possibilities in

practical chemistry and application of this type adsorbents as well as experimental and theoretical research methods used to determine their physical and chemical properties. The development of carbon adsorbents for the preconcentration of analytes utilize the result of the long-term research and development of carbonaceous stationary phases for gas and liquid chromatography (GC and HPLC). In the initial stage of the development of adsorption gas chromatography, the attitude towards carbon adsorbents was skeptical. However, in time the methods of preparation of various type synthetic carbon adsorbents have been improved and their advantages have proved to be useful in other way application in chromatography. Synthetic carbon adsorbents are expected to be useful in chromatography to the preconcentration of trace amounts of substances from air or from water and in sample pretreatment techniques in analysis, as well as in a wide variety of chemical industries. The application of synthetic carbon adsorbents have minimized the problem of contamination and artefact formation, hence they are suitable for the sampling of volatile organic compounds in quite different environments and preconcentration and isolation of semi-volatile and non-volatile organic compounds from various matrices.

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