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Mini Review

Progress on Synthesis and Applications of Porous Carbon Materials

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Porous carbon materials have been applied in a tremendous amount of fields recently for their various pore structures and larger specific surface area compared to other materials. They can be synthesized with low pollution and well controlled in pore size and channel. Particularly, they have high use period in cycle, chemical inertness in interface, strong mechanical strength in structure and good performance in electrical conductivity. This review summarizes several synthesis methods of porous carbon materials and applications in electrochemistry, hydrogen storage, catalyst support and gas adsorption and separation of porous carbon materials. Porous carbon materials have been further explored on using eco-friendly methods to synthesize porous carbons and directions for future research on porous carbons. The tip of the iceberg with respect to the application potential of them is just emerged. A base help was provided for further investigations into applications of porous carbons.

Keywords: porous carbon, synthesis, application, supercapacitor, hydrogen storage

1. INTRODUCTION

Carbon is the 5th and the 3rd most abundant element in the universe and in human body, respectively, which is vital constituent of the universe and all organisms[1]. In recent decades, porous carbon materials have attracted a great deal of attention on chemistry, physical, material science, etc. Carbon materials have excellent properties such as high chemical stability, good electrical conductivity and low cost [2]. Meanwhile, their rich pore structure distinguishes porous carbons from traditional carbon materials in their large specific surface area [3] and adjustable channels and pore size [4]. According to recommendation of the International Union of Pure and Applied Chemistry (IUPAC), porous carbon materials can be classified into three types based on their pore sizes: micropores < 2 nm, 2 nm < mesopores< 50 nm, and macropores > 50nm. Since Ryoo et al. [5] created the first example to synthesize highly ordered carbon molecular sieves using MCM-48 and sucrose as templates and carbon source in 1999, scientific researchers devoted themselves to the porous carbon materials and opened a door to the application of porous carbons in various fields. In nature, plenty of materials like biomass (starch [6] and wild rice stem [7]) can be artificially converted into porous carbon. Porous carbons have diverse morphology in microstructure for different demands such as nanofiber films [8,9], nanospheres [10], activated carbon tubes [11] and so on. They can be made into hierarchical porous carbons via tunable structure including pore size, channel and pore distribution, or by doping modification and loading catalyst to improve performance. Thus, porous carbons have a promising application in electrochemistry, hydrogen storage, catalyst support and gas adsorption and separation. This review sum up synthesis methods and the applications mentioned above and based on the literature report in the recent ten years. At the very end, an outlook about further development and research tendency of porous carbons is demonstrated.

2. METHODS FOR PREPARING POROUS CARBON MATERIALS

2.1. Activation methods

Activation methods are the classic method to fabricate porous carbons and they mainly divided into physical activation and chemical activation. Physical activation method mainly includes carbonization and activation two steps. First of all, carbonizing the carbon source material at the suitable temperature. Then introducing the activator such as steam [12], carbon dioxide (CO_2) [13,14] or the air [15]. And there are different types of biomass precursors including corn straws [16], banana peels [17], coconut shell [18], water hyacinth [19], soya [20] to synthesize aim carbon. Zhou et al. [12] investigated that the activated carbon prepared from wasted tea by physical activation using steam, where the research found that the maximum specific surface area reached 995 $m^2 \cdot g^{-1}$. Relatively, Javier et al. [21] produced activated carbon from barley straw by physical activation with carbon dioxide and steam. They got the conclusion that the maximum Brunauer-Emmett-Teller (BET) surface area and micropore volume were 789 $m^2 \cdot g^{-1}$ and 0.3268 $cm^3 \cdot g^{-1}$ when CO_2 as the activator, while for steam activation were 552 $m^2 \cdot g^{-1}$ and 0.2304 $cm^3 \cdot g^{-1}$, respectively. Simultaneously, coconut shell as the raw material and CO_2 as the activator were reported by Tsai et al. [22].

The same is true, activated carbons were fabricate through chemical activation which is by mixing with carbon precursors under the protection of insert gas. Activator has a great impact on porosity and it acts as pore forming agent to obtain large specific surface as well as good adsorption properties. Common activators include KOH [23,24,25], NaOH [26,27], $ZnCl_2$ [28], H_3PO_4 [29], K_2CO_3 [30] and $FeCl_2$ [31]. Porous carbons is not only a candidate for green and lightweight but also an efficient microwave absorbent. Whereas, activators can adjust the pore structure and optimize the adsorption performance. Recently, Wang et al. explored the effect of $ZnCl_2$ activator on microwave performance with the walnut shell derived nano-porous carbon [32], achieved rich pore structure, high pore performance and large specific surface area via controlling the temperature and the ratio of raw materials to activators. Lately, Chen et al. [33] attempt to mix several different bases to obtain porous carbon materials with excellent adsorption. Unexpectedly, mixing KOH and NaOH as activator in a ratio of 1:1, the BET surface area and the Langmuir surface area reached 1993 and 3467 $m^2 \cdot g^{-1}$, respectively.

2.2. Template methods

With the increasing of product requirements, making use of templates to prepare orderly porous carbon gradually become a hot research direction. There are hard-template and soft-template method, the principle of hard template method is to fill carbon precursor into the pore structure of the template. Then after carbonization and removing the template, the porous carbon materials were obtained. Some preformed materials such as mesoporous silica and carbon, or aggregates of nanoparticles as hard templates usually [34]. Liang and co-workers [35] demonstrated that high specific surface area possessed when the nitrogen and oxygen co-doped ordered mesoporous carbon, which fabricated via template method using KIT-6 as template, $Fe(NO_3)_3 \cdot 9H_2O$ as catalyst and PVP as carbon and nitrogen precursor and KOH activated finally. Wan et al. [36] found that while the carbon precursor (pyrrole) was impregnated into SBA-15, the specific surface area of the template free carbon is 257 $m^2 \cdot g^{-1}$, which increase to 731 $m^2 \cdot g^{-1}$ when the SBA-15 synthesized at 130℃. Luo et al. [37] explored mesoporous carbon materials via the hard template method with attapulgite. And Zhang et al. [38] developed a versatile hard template assistant strategy to prepare ultrafine non-noble heterogeneous catalyst, ultra dispersed Co anchored on nitrogen-riched porous carbon (CoN@PCN). Nevertheless, soft templating method is a self-assembly through carbon precursor and guiding agent and then carbonization at high temperatures to obtain mesoporous structures. Du et al. [39] served ionic liquids as soft-template to prepare mesoporous sphere, and the research found that the mesoporous sphere perform a large specific surface area and superior electrochemical performance as electrode material in supercapacitor. Libbrecht et al. [40] achieved mesoporous carbons via the organic self-assembly of resorcinol or formaldehyde with the triblock copolymer F127. And researchers got the conclusion that the specific surface area and pore volume is 663 $m^2 \cdot g^{-1}$ and 1.29 $cm^3 \cdot g^{-1}$, respectively. Xiong et al. [41] operated the polymerization of dopamine with F127 as soft template in alkaline aqueous solution and then obtained hierarchical porous carbon nanospheres with the specific surface area as high as 1725 $m^2 \cdot g^{-1}$.

2.3. Direct carbonized method

Synthesis porous carbon via one-step direct carbonization with carbon based materials attracts sharply rise attention because of their easy operation and low cost. For the sake of increasing industrial demands, research workers pay close attention to metal organic frameworks (MOFs) nearly years. MOFs are crystalline porous materials consisting of metal ions (or clusters) and organic ligands via coordination bonds [42]. In the structure of MOFs, the arrangement of organic ligands and metal ions or clusters has obvious directionality and different framework pore structures can be formed, where exhibiting different adsorption properties [43,44]. An increasing number of researchers pay attention to this topic because of their potential applications and the excellent properties of large specific surface area or adjustable pore structures. For example, Liu et al. [45] prepared a porous carbon directly carbonizing a metal organic framework (MOF-5), where the research found that the MOF-5-C retained the original porous structures of MOF-5, and showed a high BET surface area (1808 $m^2 \cdot g^{-1}$) and large pore volume (3.05 $cm^3 \cdot g^{-1}$). In recent years, several researchers adopt one-step carbonization method to achieve aim materials. Chang et al. [46] got porous carbon nanofiber webs by electrospining and one-step carbonization with modified carbon black as carbon source without template removal and activation treatment. The nanoporous carbons produced from one-step carbonization of zeolitic imidazolate framework-8 (ZIF-8) investigated by Li et al. [47]. Bing et al. [48] received hierarchical porous carbon through a template-free method by direct carbonization. Unexpectedly, Niu and his team [49] directed carbonization of cattle bones without any additional activators and templates to obtain porous carbon which the specific surface area and mesopore volume is 2096 $m^2 \cdot g^{-1}$ and 1.829 $cm^3 \cdot g^{-1}$, respectively.

2.4. Element doping method

In order to explore more accessible specific surface area and enriched porousness, element doping method has turned into a research hotspot. Such as N-doped [50-53], B-doped [54-56], P-doped [57], Zn-doped MOFs [58] and so on. Naturally, several elements doped together also can achieve the same effect. For instance, Maryam et al. [59] synthesized N, P-doped porous carbon and Gao et al. [60] prepared porous carbon nanofibers via co-doped with nitrogen and sulfur (N, S-doped). Typically, unexpected results achieved by utilizing several methods together. Wang et al. [61] obtained nitrogen-doped porous carbon nanowires by KOH activation. Xu et al. [62] manufactured O-doped carbon tubed with hierarchical pore structure via the direct pyrolysis. Recently, Liu et al. [63] fabricated N-doped carbon material through the direct ink writing, a conventional 3D printing technology. Apart from the different preparation methods of porous carbon to enhance the surface area, capacity and adsorption, the morphology of the carbon materials and some assists also play a vital role. For example, Tan et al. [64] made use of hydrothermal method to improve the specific surface area and adsorption performance when they synthesized porous carbon materials. With the permission of experimental conditions and the needs of industrial society development, the realization of high efficiency, low cost, easy operation, environmentally friendly and other aspects of porous active materials have become production.

3. POROUS CARBONS IN ELECTROCHEMISTRY AS ELECTRODE MATERIALS

3.1 Supercapacitors

Energy shortage and environmental deterioration are two of the most acute problems facing mankind with the continuous development of economy and the massive consumption of non-renewable fossil energy. The exploration of new energy sources has become topical and popular issue in the near future. Electrochemical capacitors are also called supercapacitors. As a unique electrical energy storage facility, supercapacitors are widely applied because of their high energy-density, fast charge and discharge, good electric conductivity and long-cycling stability [65], which includes computers, hybrid vehicles, mobile communications and national defense. Becker proposed the concept of electrochemical capacitor for the first time in 1957. And Panasonic realized its commercialization successfully in 1978 [66]. The supercapacitor is a new and outstanding type of green energy with hardly contamination to the environment.

According to the mechanism of charge storage, supercapacitors are divided into two categories, that is, pseudocapacitors and electrical double-layer capacitors (EDLCs) [65]. The electrode materials of the former can be conducted polymer electrode materials [67] or metal oxide materials (MnO_2 [68], NiO [69] etc.) and the latter includes active carbons [70], carbon fibers, carbon aerogels and carbon nanotubes. Porous carbon electrode materials have attracted considerable interest in many energy-related applications due to abundant capacitance, chemical stability, processability and tunable physical structure [71]. The followings are the research of porous carbon materials in supercapacitors mainly focusing on carbon microspheres and carbon nanotubes.

3.2 Application of porous carbons nanospheres in supercapacitors

The superior cycle performance is directly associated with the property of carbon materials. In the paper of Fan and his coworkers [72], the morphology, porosity and surface chemical property of porous carbons for electrode materials were proved to relate to capacitive performance. Their carbons derived from chemical activation by KOH after hydrothermal carbonization of alginic acid. The porous hollow carbon spheres had excellent specific surface area of 2421 $m^2 \cdot g^{-1}$ and exhibited outstanding specific capacitance of 314 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$. Zhu and coworkers [73] developed a exceptional Fe-catalyzed method for fabrication of porous carbons spheres with high graphitization degree using glucose as carbon source, which had a diameter of 2 μm and long cycle stability over 10,000 times with almost no decay at 5 $A \cdot g^{-1}$.

Hierarchically porous carbon materials with advantages of hierarchical pore structure and specially high specific surface areas, which can shorten the path of ion diffusion and increase the efficiency greatly, because ions can transport merely from macropores to the adjacent mesopores or micropores in the process of charge-discharge. Xu et al. [74] synthesized novel hierarchically microporous carbon spheres decorated three-dimensional graphene frameworks with glucose as carbon source. They found that hierarchical porous structure created large surface area and low charge transfer resistance. When the current density was 0.5 $A \cdot g^{-1}$, the highest specific capacitance of their spheres was 288.77 $F \cdot g^{-1}$. The macroporous structures formed through spheres piling up, the free slipping between the carbon balls, and the good conductivity of the carbon microspheres make porous carbon electrode materials own plenty of double layer structures and showing outstanding electrochemical performance while served as supercapacitors electrode materials.

3.3 Application of porous carbons nanotubes in supercapacitors

The carbon nanotubes (CNTs) was first synthesized via an arc-discharge evaporation method in 1991 by Sumio lijima [75]. CNTs have the advantages of unique hollow structures, suitable pores and inter-winding and nanoscale network structures for electrolyte ion migration, which have also been favored in supercapacitors recently. Singu et al. [76] reported a novel ternary electrode prepared by insitu chemical polymerization of aniline in the presence of multi-walled carbon nanotubes and titanium oxide. The ternary electrodes for supercapacitors shown maximum specific capacitance of 525 $F \cdot g^{-1}$ at a scan rate of 1 $mV \cdot s^{-1}$ when used as electrode material for supercapacitors.

Liu et al. [77] reported the introduction of functional groups to the surface of CNTs through surface modification, which could modify their intrinsic chemical and physical properties, such as providing pseudo capacitance through redox reactions and enhance the wettability of CNTs. And their report indicated that the porous and hierarchical structure offered adequate ion paths for efficient electrolytes transportation.

Sun and coworkers [78] used chemical vapor deposition (CVD) method to grow highly conductive CNT networks on flexible Ni mesh. Then MnO_2 nanoflake layers were deposited on the CNT based on the spontaneous redox reaction through a simple solution method. Ultimately, a MnO_2 nanoflake@CNT hierarchical core-shell structure on Ni mesh was formed. This unique structure acted as electrode exhibited a high specific capacitance of 1072 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$ in three-electrode configuration. Moreover, it had a wide working voltage while made for symmetric supercapacitor and an impressive energy density and power density.

3.4 Application of element doping in supercapacitors

Doping heteroatom in carbon materials can enhance the hydrophilicity of the carbon material and improve the infiltration performance of the electrode material, in order to adsorb electrolyte ions and accelerate the transmission of the electrolyte ion in the carbon channels. Meanwhile, functional groups endow surfaces with acidic or alkaline active site, and the Faraday redox reaction occurs between the active sites and the electrolyte ions, which plays an important role in enhancing the specific capacitance. Hou and his coworkers [79] fabricated a hierarchical porous nitrogen-doped carbon nanosheet applied on a two-electrode-based supercapacitor. The research revealed a high cycling life stability that only loses 9% of capacitance after 10,000 cycles with a N-doping of 4.7 wt %. They used silk as carbon source and carbons were activated and graphitized simultaneously, which shown a high specific surface area of 2494 $m^2 \cdot g^{-1}$. This also had been in the case of a functional porous carbon prepared from tannic acid as phenolic carbon precursors and urea as nitrogen precursors by Tiruye et al. [80], with a maximum nitrogen content of 8.83 wt %. It exhibited a coulombic efficiency higher than 95%, and revealed that the urea changed the condensation mechanism and morphology of porous carbons, which meant higher contents of nitrogen optimized surface chemistry, morphology and even conductivity of the carbon materials. Xin and coworkers reported a porous carbon electrode for supercapacitor of 13.5 wt % N [65], which was higher than most current reports. They carbonized Zn-metal-organic frameworks (ZIF-8), and with controlling appropriate temperature and reaching a superior energy density of 18.0 $Wh \cdot kg^{-1}$ at a power density of 475 $W \cdot kg^{-1}$.

4. HYDROGEN STORAGE OF POROUS CARBON

Hydrogen (H_2) is an ideal, clean and pollution-free energy source and it is a promising alternative to fossil fuel in the future. This is because, on the one hand, the energy H_2 content is higher than fossil fuels. On the other hand, the extensive existence of hydrogen element provides an abundant source for the preparation of H_2. Nevertheless, one of the major bottlenecks on the application of H_2 energy is storage. Porous carbons, with high specific surface area and pore volume, tunable and highly developed pore structures and low density and cost [1], are used for H_2 storage materials recently.

4.1 Physical method for hydrogen storage

Physical method [81] for hydrogen storage requires the material to have a large adsorption surface and high hydrogen adsorption enthalpy. That is, high pressure encapsulates H_2 in porous carbon materials of high specific surface area and large pore volume.

Recently, Li et al. [82] reported a simple method to obtain porous carbon spheres with biomass starch as carbon precursor and CO_2 as activator. They had excellent surface area (3350 $m^2 \cdot g^{-1}$) and high uptakes for H_2 (6.4 wt %, 77 K), which surpassed the performance most of other materials characterized to date. In addition, Wang and his coworkers [83] focused on N-doped porous carbons for hydrogen storage. They applied chitosan as carbon source via hydrothermally carbonization and chemical activation to synthesize porous carbon, which had different nitrogen contents (0.56-6.53 wt %) and large surface areas (1362-3009 $m^2 \cdot g^{-1}$). And the porous carbon exhibited an excellent performance of hydrogen storage of 6.77 wt % at 20 bar, 77 K.

4.2 Chemical hydrides or complex hydrides for hydrogen storage

Hydrogen also can be stored in the porous carbons in the form of nanoscale chemical hydrides or complex hydrides like $NaAlH_4$ [84], $NH_3 \cdot BH_3$ [85] and MgH_2 [86]. This method optimizes hydrogen storage from kinetics and thermodynamics through the increase of surface energy and decrease of nucleation activation energy [80]. More recently, an effective route based on space-confined chemical reaction to synthesize uniform $Li_2Mg(NH)_2$ nanoparticles was reported, which stored H_2 inside porous carbon nanofibers [87]. They used the hierarchical pores inside the one-dimensional carbon nanofibers as intelligent nanoreactors for the reaction of Li_3N with Mg-containing precursors to prepare uniformly discrete $Li_2Mg(NH)_2$ nanoparticles. As shown in Fig.1, the hydrogenation could be done around 80 mins at 2.9-3.0 MPa as low as 105℃. At the temperature of 135 ℃, it reached a plateau in less than 40 minutes with a H_2 capacity of 5.5 wt %; As for the charged, H_2 could be completely discharged when the dehydrogenation time was only about 80 minutes. Furthermore, there was only a minor loss in hydrogen capacity even after a total of 50 cycles, indicating an excellent reversibility.

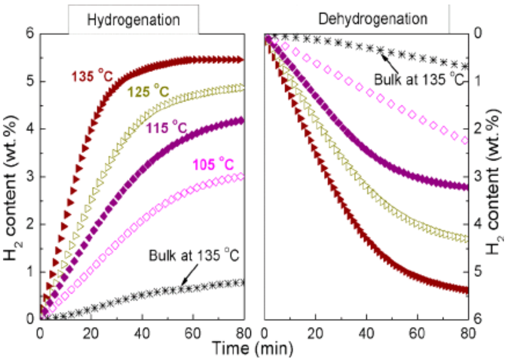

Figure 1. Hydrogenation and dehydrogenation of $Li_2Mg(NH)_2$@ CNFs at different temperatures. Reprinted with permission from Ref. [87]. Copyright (2017) American Chemical Society.

5. POROUS CARBON FOR OXYGEN REDUCTION REACTION(ORR) AS CATALYST SUPPORT

Fuel cell is a new energy technology that converts chemical energy into electric energy directly, with the virtue of exceptional energy conversion efficiency and environmental protection, which attracted much interest of researchers in recent years [88]. Conventional cathode catalysts for ORR were often noble metals such as Pt, Pd in the past [89]. But their large-scale commercial application had been precluded by the high cost and susceptibility to time dependent drift and CO deactivation of Pt-based electrodes [90]. Nevertheless, Non-noble metal catalysts supported on porous carbon materials opened a new avenue for it.

5.1 Non-noble metal catalysts supported on porous carbon for ORR

Non-noble metal oxygen reduction catalysts were often loaded on porous carbons by the compounds of transition metals (Fe, Co, Ni, Mn) [91]. Iron carbide and iron nitride [92,93] supported on porous carbons as catalyst for ORR have received widely attention and research in recent years. Yang and his coworkers had a significant research on Fe_3C, in which they obtained the new one-dimensional bamboo-like carbon nanotube/Fe_3C nanoparticle hybrid nanoelectrocatalysts [94]. They annealed a mixture of PEG-PPG-PEG Pluronic P123, melamine, and $Fe(NO_3)_3$ at 800°C directly to synthesize the electrocatalysts. The hybrid shown a half-wave potential 49 mV more positive than that of 20 wt % Pt/C catalyst. Due to the property of carbon materials, the electrocatalysts had a better ORR activity in acidic media, higher stability and better methanol tolerance. Another work undertaken by Jiang et al. [95], which reported a Fe-N-C ORR catalyst and revealed the origin of its activity, that is, Fe/Fe_3C nanocrystals boosted the activity of Fe-N_x when Fe/Fe_3C nanocrystals coexisted with Fe-N_x in catalysing oxygen reduction reaction, because iron compound was reduced by carbon to metallic iron at high temperature. Then the excessive Fe, after reacting with nitrogen atoms to generate the Fe-N_x species, would aggregate to form Fe nanocrystals and subsequently form Fe_3C with carbon atom.

More recently, Aijaz and his coworkers, via a MOF-templated assembly method, prepared a non-noble metal Fe_3C ORR catalysts encapsulated carbon nanotubes (CNTs) [96]. It was proved that CNTs playing a vital role on preserving the high activity of the catalysts in both alkaline and acidic media for their perfect encapsulation of the Fe_3C nanoparticles. And their pore size distribution mainly centered at 3.7 nm, in which the porous nature are extremely favorable for rapid diffusion.

5.2 Non-noble metal co-doped catalysts supported on porous carbon for ORR

Fe/Co/Ni (N) co-doped porous carbons [97] were also used as non-noble metal ORR catalysts, which was reduced to metal nanoparticles from metal compounds then impregnated on surfaces or channels of carbon-based support. Zhao and coworkers using Fe (N) co-doped catalysts for ORR [98]. They found that Zn-air battery assembled from hierarchical porous Fe-N carbon nanofibers outperforms 30 wt % Pt/C in power density and long-term stability, displaying strong practical applicability. More recently, Tong et al. [99] utilized eggshell membrane as both carbon and nitrogen source. The precursor was directly pyrolyzed at 700-900℃ after mixing nitrates to obtain a Fe/Co (N) co-doped porous carbons electrocatalyst for ORR. It had better methanol tolerance and long-term stability than commercial Pt/C (20%).

5.3 Metal-free catalysts supported on porous carbon for ORR

Metal-free catalysts are more significant and promising in fuel cell applications for their economical efficiency [90]. As mentioned in the literature review by Liu and coworkers [100], different carbon-based heteroatom-doped (N, B, S, P, Si, Cl, Br, I) electrocatalysts could polarize adjacent carbon atoms to facilitate the ORR process. They also found that there was a synergetic effect between the co-doped N and B due to their the contrary electronic properties. Especially, their group first reported F-doped ORR catalysts [101], which used carbon blacks and NH_4F as precursors. In their views, The catalysts possessing a excellent performance for ORR was attributed to C-F bond and the improving of both defect sites and the degree of graphitic induced by F-doping.

Recently, biomass materials catch much attention for sustainable development. Lu et al. [102] utilized one-step and low-cost method to obtain heteroatoms-doped (S, P, B) porous carbon catalysts for ORR with eggs as carbon and elements source and $g\text{-}C_3N_4$ as both template and nitrogen source. For more elements contained, their carbons had outstanding electrocatalytic activity towards ORR compared to the commercial Pt/C catalyst in neutral media. Biomass-based catalysts may accelerate the commercialization of fuel cells in the future because the raw material is inexpensive and abundant.

6. ADSORPTIVITY OF POROUS CARBON IN GASES

Adsorption is defined as the phenomenon of enriching molecules, atoms or ions in the vicinity of an interface [103], and the adsorbed solid material becomes an adsorbent. Adsorption method [104] turn into the main hot-spots of current research. Li and coworkers [82] still raised these parameters as mentioned above with sustainable and cheap starch as raw material to prepare porous carbons, which shown a great specific surface area of 3350 $m^2 \cdot g^{-1}$ and high pore volume of 1.75 $cm^3 \cdot g^{-1}$. And the excellent adsorption for CO_2 and CH_4 were 21.2 mmol/g and 10.7 mmol/g at 20 bar, respectively.

6.1 Modified porous carbon for adsorption

Studies of Gao et al. [105] turned the research to enhance the mechanical strength of porous carbon which could be up to 1951 $m^2 \cdot g^{-1}$ of S_{BET}. They utilized the adequate waste material cyanobacteria as the raw material and KOH as the pore agent. In addition to highly developed porosity discussed above, surfactivity played an important role for porous carbon adsorption. Choi and coworkers [104] reviewed carbonaceous porous materials for CH_4 adsorption including activated carbons, ordered porous carbons, and activated carbon fibers in detail. The carbonaceous adsorbent materials for CH_4 storage with low energy consumption were not sensitive to wet conditions and could be applied under atmospheric pressure. Namely, these porous carbon materials with strong mechanical strength and high specific surface area are of great potential for the gas adsorption.

Li and his coworkers [106] polymerized resorcinol and formaldehyde in the hexagonally packed mesoporous silica templates with acids including HNO_3, H_2SO_4, H_3PO_4 as catalysts to obtain N-doped, S-doped, and P-doped porous carbons. For the adsorption CO_2 properties, S-doped and N-doped samples exhibited well and were 3.60 $mmol \cdot g^{-1}$ and 3.16 $mmol \cdot g^{-1}$, respectively. which was 39.5% and 22.5% better than the samples without doping. And for CH_4, the adsorption amount of S-doped porous carbons were 3.52 $mmol \cdot g^{-1}$ and 27.1% higher than blank sample.

6.2 Selective adsorbability of porous carbons

In practical application however, the adsorption may be often in the environment of mixed gases. Thus, it is crucial to adsorb target gases selectively from complex components. The effects of N-doping on selectivities of porous carbons were investigated by Yuan et al. [107]. Their carbons derived from a mixture of algae and glucose and contained up to 3.25% nitrogen. They found that N-doping could increase the heats of adsorption of C_2H_6 and CO_2 but not including CH_4 and H_2. Following this line of research, a high N-doped (18.14%) porous carbon was prepared from carbonizing tetramethylammonium chloride, which also acted as a source of C and N, in the report of Xue et al. [108]. The selective adsorbability of CO_2 over N_2 was estimated to be about 12.1 (molar ratio). Apparently, Lewis base site (N-doped) was more active for binding acidic molecules CO_2 (1.09 $mmol \cdot g^{-1}$) than N_2.

More recently, a novel porous carbons, based on glucose and KOH as carbon source and porogenn, with BET surface area and pore volume of 3153 $m^2 \cdot g^{-1}$ and 2.056 $cm^3 \cdot g^{-1}$ respectively was designed by Wang et al. [109]. Not only could their carbons be up to as high as 22.4 $mmol \cdot g^{-1}$ at 30 bar in CO_2 adsorption, but also for the mixture of CO_2/N_2 (0.5:0.5) the IAST prediction could be up to 20 at 30 bar, and for the mixture of CO_2/CH_4 (0.5:0.5) the IAST prediction could be up to 4.5 at 30 bar.

Besides, the adsorbents had a excellent cyclic performance and CO_2 desorption efficiency reached about 97-98%. It is really worth to broaden the potential application and yield the porous carbon absorbents with outstanding physicochemical stability for their practical applications to natural gas or biogas purification and cutting down greenhouse gas emission.

7. CONCLUSION AND OUTLOOK

Several applications of various porous carbon materials were reviewed in this article so as to provide a base help for further investigations into applications of porous carbons. The porous carbons synthesized via diverse methods such as activation methods or template methods have been extensively applied on electrochemistry, hydrogen storage, catalyst support and gas adsorption and separation. By summarizing the specific surface area of porous carbons, which could even reach 4000 $m^2 \cdot g^{-1}$, which shown that there was great potential on increasing the specific surface area and applying in gas storage and separation indeed. The applications of porous carbons are far below the on-board targets at the ambient temperature. That is to say, reality breakthroughs in all applications can be nowhere near enough if only by enlarging the surface area alone. So, some feasible modification of interfacial chemical properties including heteroatom doped and metal loaded were discussed. By controlling different structure and shapes of porous carbons such as balls, sheets and tubes, it offered enough pore space for electrolyte ions and catalyst when they played the role and enhanced mechanical strength and stability.

Many aspects mentioned in this article need further investigations and explorations. The tuning of the pore size distribution or pore volume and the control of porous structures should be more precise. Preparing hierarchically porous carbons still is challenging and significant. In order to achieve green chemistry, the stability and cyclicity need to be well enhanced and the economical biomass materials should be considered to be carbon resource as wide as possible. Few studies on liquid-phase separation, namely, removal of impurities like aromatic hydrocarbons in fossil oil or hazardous materials in effluent, which really remains to be investigated and developed.

In a word, persistent research is needed in the future in order to realize inexpensive and efficient preparation of porous carbon materials for industrial and social application on a large scale. The tip of the iceberg was found with respect to the application potential of porous carbons. The cutting edge of applications still needs to be explored deeply.

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