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INSIGHT INTO THE DEVELOPMENT OF 2-4 NM MESOPORES IN KOH-ACTIVATED HIERARCHICAL POROUS CARBONS: THE ROLE OF SMALL POLYCYCLIC AROMATIC HYDROCARBONS MOLECULES

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Introduction

Porous carbons (PCs) have been widely used as adsorbents in water purification and gas separation or storage, as catalysts or catalyst supports, and as electrode materials in batteries or supercapacitors. However, most KOH-activated PCs produced commercially are micropores (pore size <2 nm) and suffer from kinetic limitations as adsorbents or electrode materials [1]. Thus, hierarchical porous carbons with narrow mesopores (2-4nm) revealed a rapid kinetic transport without sacrificing the accessible surface areas are reckoned more beneficial for high-performance applications [2]. Many efforts have been performed to produce mesopores for PCs by introducing additives or using template methods [3,4]. Prospective from both the fundamental research and the practical application points of view, it is therefore highly urgent to prepare HPCs with rich tunable 2-4 nm mesopores based on the molecular self-assembly and pyrolysis characteristics of precursor without using additives or templates. Herein, the effect of small polycyclic aromatic hydrocarbons (PAHs) and their compounds on the pore development of KOH-activated PACs has been investigated using naphthalene-derived pitch as a model precursor. The small PAHs are obtained from the pitch precursor by toluene extraction. An assessing criterion of the fundamentals, beginning with the content of small PAH molecules in precursor, would enable researchers to fabricate the PACs with goal-directed porous feature that could be used to guide future research.

Materials and Methods

Typically, naphthalene (200 g) and anhydrous $AlCl_3$ powder (10 g) was added into a certain amount of $CHCl_3$ in an autoclave. Under stirring, the reaction was allowed to proceed at 80^{o}C for 4 h. Heating was continued to 150 ℃ at 3 ℃ min^{-1} and maintained for another 4 h under an air flow of 200 mL min^{-1}. In order to remove $AlCl_3$, the product was washed using 0.025 mol L^{-1} NaOH solution and in tandem with deionized water. Finally the obtained product was dried under reduced pressure at 50^{o}C for 24 h. According to the dosage of chloroform, the NPs were denoted as NPx. Chemical activations of precursor using KOH as activator were performed by identical processes. As a typical process, slurry mixed quantitative H_2O, KOH and precursor was initially prepared, and then dried at 100^{o}C for 12 h in a vacuum oven. Subsequently, it was heated to 700^{o}C at a rate of 2^{o}C min^{-1} and held for 1 h under a stream of N_2 flowing at 400 ml min^{-1} in a horizontal cylindrical furnace. The products were washed with distilled water to get rid of the alkaline compounds and dried over night at 120^{o}C.

Results and Discussion

The detailed relationship between the content of small PAH molecules in the precursor and the specific surface area and pore volume of PACs is demonstrated in **Figure 1**. It can be seen from Figure 1a that the S_{micro} of PACs invariably decreases with the increasing of the content of small PAH molecules in the precursor. In addition, a volcano-shaped curve (first ascending and then descending) can be obtained upon examining the variation either of S_{meso} or S_{BET} with an increasing content of small PAH molecules in precursor. The optimal value near the peak of the volcano curve is located at the small PAH molecules with the range of 40-60 wt%. Interestingly, the curve of the S_{BET} is closely synchronous with that of S_{meso} but not for S_{micro}. It can be further confirmed that $V_{<2\ nm}$ had no evident variation for all PACs samples which may be associated with the same KOH activation mechanism; meanwhile, the mesopore volume especially the pore with diameters 2~4 nm is the most vulnerable to the variation of the content of small PAH molecules in the precursor, causing the changes of corresponding $V_{2\sim4\ nm}$ and V_{total}. These results indicate that the small PAH molecules in the precursor closely related with the mesoporous development and thus contributing for specific surface area.

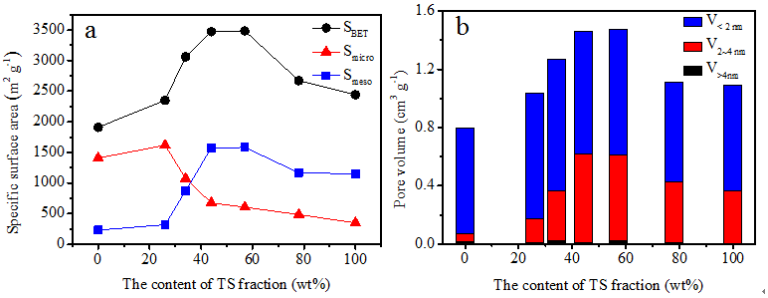

Figure 1. The relationship between the content of TS fraction in the precursor and the specific surface area (a) and pore volume (b) of PACs.

Conclusions

The specific surface area and pore volume of PCs increased with the content of small PAH molecules in precursor increased from 0% to ca. 40%, but dropped with the content of small PAH molecules increased from ca. 40% to 100%. The surface area and the proportion of mesopores to total pores in PCs improved as well when a phenolic resin mixed with small PAH molecules. An assessing criterion of the fundamentals, beginning with the content of small PAH molecules in precursor, would enable researchers to fabricate the PACs with goal-directed porous feature that could be used to guide future research.

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