Synthesis of ordered microporous carbons via template technique

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Abstract

A new microporous carbon with uniform pore size around 1.0 nm has been successfully synthesized by template method, using Y zeolite (a commercial products) as a template and furfuryl alcohol as carbon precursor. The carbon materials are characterized by XRD, SEM and EDX. The effect of experiment conditions and process on properties of microporous carbon has been addressed. The results demonstrate that a two-step process, i.e. filling carbon into zeolite channels by impregnation of furfuryl alcohol first under vacuum and then under the pressure, is favorable for preparing carbon with highly ordered periodic structure in high yield. In addition, the removal of the Y zeolite framework using HF under the ultrasonic conditions can greatly shorten the synthesis time.

1. Introduction

The template approach for synthesis of new materials has been a research focus in materials science for many years. Since the development of M-41 materials by Mobil Oil scientists in 1992, great progresses have been made in this field. Many different porous materials have been prepared using various types of templates. Highly ordered mesoporous carbons were first synthesized using cubic mesoporous silica MCM-48 as the template in 1999[1]. Since then, ordered porous carbons with different structure have been synthesized using HMS [2], MCM-48 [3] and SBA-15 [4] as templates. Recently, the pioneering work by Kyotani and Tomita et al. showed that a novel type of microporous carbons could be obtained using Y zeolite as template [5-8], which has a three-dimentional nano-array structure and is nearly 100% microporous, of which the surface area and micropore volume could be as high as 5100 m^2/g and 2.1cc/g, respectively. Following Kyotani's work, here we report a new preparation process to make microporous carbons with high surface area and well ordered periodic structures.

2. Experimental

Details about the preparation of carbon products can be found elsewhere [9]. A commercial Y zeolite sample was dried at 120 ^oC under vacuum for 1 h before use. The carbon precursor (furfuryl alcohol, termed as FA thereafter) was introduced into the porosity of the Y zeolite template via a two-step process, in which the dried Y zeolite

samples were first soaked with FA under the vacuum and then under a pressure of *ca.* 1.3MPa at room temperature. Then, the FA-treated zeolite samples were heated at 95 ^{o}C in N_2 atmosphere to let FA being polymerized inside the zeolite channels, resulting in polymerized FA/zeolite composites. The obtained composites were then transferred into a quartz boat and the boat was put into a tube furnace. The furnace was ramped at a rate of 5 ^{o}C/min to 700 ^{o}C. When the temperature reached 700 ^{o}C, propylene gas (3.0 vol% in N_2) was introduced into the reactor that was kept at 700 ^{o}C for 3 h. Then, the furnace was further heated at 900 ^{o}C for 3 h under flowing N_2 before cooling back to room temperature. The carbonized PFA/zeolite composite was taken out from the furnace and was washed using HF acid (46% aqueous HF solution) under the ultrasonic conditions to remove the zeolite matrix, which resulted in the insoluble carbons that were further washed with abundant water, then filtered and dried. The obtained carbon materials were studied by an X-ray diffraction (Cu-Kα/40V/100mA), scanning electron microscopy (JEOL JSM-5600LV, operated at 20KV) and EDX.

3. Results and Discussion

Fig. 1 shows the typical XRD patterns of Y zeolite template and the obtained microporous carbons. In the XRD pattern of the original zeolite (a), there many sharp peaks that are due to the ordered structure in the zeolite framework. For the microporous carbons obtained via the Y zeolite template, a monodisperse sharp peak around 6º in the XRD pattern can be clearly seen, which corresponds to the spacing of the {111} plane of Y zeolite, indicating that the microporous carbons have an analogical structure with the Y zeolite template. In other words, the carbons possess an ordered structure corresponding to the negative replica of the Y zeolite with a period of about 1.429 nm, which is in agreement with the result reported by Professor Kyotani and his colleagues [6].

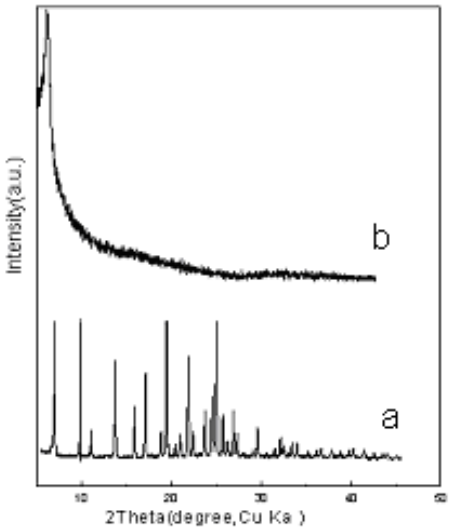

Fig. 1 The XRD patterns of Y zeolite (a) and the resultant carbon (b).

Scanning electron microscopy (SEM) is a powerful tool for studying the various structural and surface features of carbon materials. Fig. 2 shows a typical SEM image of the obtained microporous carbons, from which the fine crystal particles can be clearly seen. The information obtained from SEM examination and RXD study reveal that the microporous carbon materials hold a regular structure even after the heat treatment at high temperature and acid washing under ultrasonic conditions. This means that acid washing under ultrasonic conditions does not destroy the ordered structure of the obtained carbons and facilitates the removal of the Y zeolite template, which will help shorten the production time of microporous carbons.

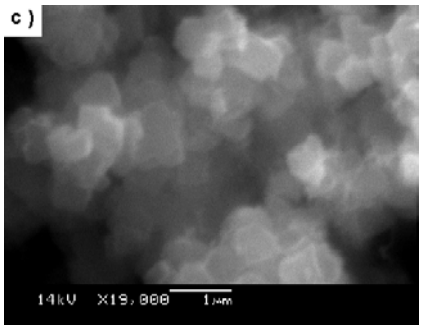

Fig. 2 A Typical SEM image of the obtained carbon

All samples obtained were analyzed by energy dispersive X-ray spectroscopy (EDX) and one typical EDX spectrum is shown in Fig. 3, showing that carbon is the dominant element in the products with a content of being nearly 100%. This indicates that no ash or mineral components are left in the carbon materials after HF treatment under ultrasonic conditions.

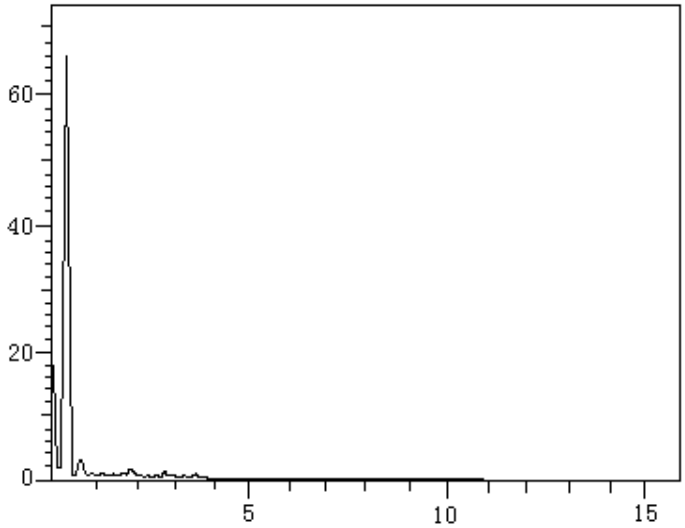

Fig. 3 Typical EDX spectrum of the obtained carbons

The yield of carbons versus the process parameters is also explored. Fig. 4 shows the relation between the yield of carbons and the holding time in soakage stage at 1.3 MPa in N_2. As can be seen from Fig. 4, the yield of carbons increases with increasing

the holding time. This means that the impregnation process parameters are very important in terms of improving the yield of carbons, thus need to be further optimized.

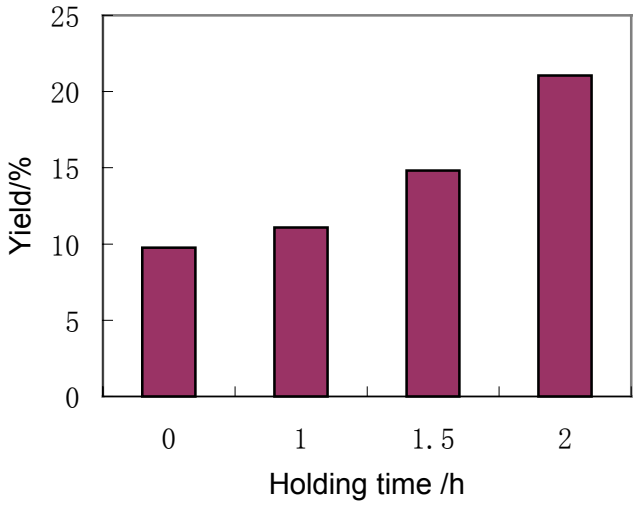

Fig. 4 The yield of carbons vs. the holding time in soakage under 1.3 MPa N_2

Moreover, the microporous carbons were also characterized by nitrogen adsorption, from which the BET surface area, pore volume and pore size distribution are obtained. It has been found that the obtained carbons have a BET surface area over 2400 m^2/g, a total pore volume of 1.3 mL/g and an average pore radius of 1.1 nm.

4. Conclusions

We have reported a new and convenient process to fabricate ordered microporous carbons with high surface area using Y zeolite as the template and FA as carbon precursor. The structure and characteristic of product carbons are related to process parameters, especially to the impregnation method and the removal method of the template. The yield of carbons increases with the holding time in soakage at the same pressure. Ultrasonic acid treatment is effective to remove the zeolite framework from carbons.

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