TEMPLATE SYNTHESIS METHODS OF MESOPOROUS CARBONS WITH ZEOLITES

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Introduction

Mesoporous carbons have recently attracted much attention because of their applications as adsorbents for large hydrophobic molecules and biomolecules, catalyst supports, components of electrochemical double-layer capacitors, fuel cells and Lithium batteries, chromatographic packings and templates for the synthesis of inorganic nanostructures. Template synthesis is a promising technology to prepare these mesoporous carbon materials with large surface area and uniform pores. These carbons are obtained by the pyrolysis of a carbonaceous precursor in the inner of a porous template, as zeolites.

In the present study, we report the details of the synthesis methods for preparing mesoporous carbons by different impregnation conditions of different zeolites with Petroleum Pitch, and discuss what synthesis conditions are the key to control the mesoporous/microporous structure of the resultant carbons. The resulting carbon structure can be controlled via the selection of the template, the impregnation method, the templating mixture and the pyrolysis conditions such as carbonization temperature, heating rate and reaction time.

Experimental

Petroleum Pitch (PP) was diluted in toluene at room temperature and, subsequently, the zeolites were infiltrated with these solutions. Four types of zeolites; zeolite Y, zeolite β, ZSM-5, and Mordenite, supplied by *Zeolyst International Company* (PA, USA), were used as inorganic templates. The infiltrated samples were further carbonized inside a tubular furnace at different temperatures.

In order to fill carbon into the zeolite channels as much as possible, different impregnation methods were studied for comparison; i) impregnation of PP with the zeolite template at 150 ºC for 1 h, and ii) impregnation-CVD, that is, carbonization of PP/zeolite composite followed by propylene-CVD. The carbon/zeolite composites prepared trough these impregnation methods were washed with hydrofluoric acid solution to remove the zeolite template.

The effect of the zeolite template type, PP/zeolite mixture (25, 50 and 75% wt PP), the carbonization temperature (500, 700 and 900ºC) and the impregnation method on the carbon structure was studied. The template carbons (TCs) were denoted by PP, followed by the pitch mass percentage, and by a number corresponding to the carbonization temperature in degrees Celsius and by the notation of the zeolite template used

Results and Discussion

Carbons with different porous structures, microporous and essentially mesoporous, have been obtained by the liquid infiltration of different zeolites molds with Petroleum Pitch. The resulting carbons show some structural regularity which suggests a roughly infiltration of the zeolite template.

The carbon yields of the TCs are higher than those observed for carbon materials prepared outside the inorganic matrixes (100 % PP, Table 1), due to the fact that the zeolites used as inorganic templates are well known catalysts of the hydrocarbon cracking reaction and can impose kinetic and steric constraints on the polymerization [1] and graphitization [2] reactions of the PP, increasing the yield in carbon. The carbon yields are higher for TCs prepared from zeolite Y > zeolite β > Mordenite > ZSM-5. This suggests that zeolite Y produced higher carbon infiltration at these conditions. It is also supported by the fact that zeolite Y presents the largest channel size, 7.4 Å, which implies that carbon deposition into the channels of zeolite Y is easier than into the other zeolites.

The characteristic parameters of the porous structure of the char and some TCs, obtained from the N_2 and CO_2 isotherms, are also summarized in Table 1. It is noteworthy the higher porous structure development of the carbons obtained when compared with that of the char that show a negligible specific surface area. With 50% of PP mass percentage and 700-900 ºC of carbonization temperature, depending on the zeolite used, the TCs achieved the most significant development of micro and mesoporosity compared to that of the others TCs obtained at different conditions. As a reference, template carbon sample, 50-900-Y, present A_{BET} about 1000 m^2/g.

Table 1. Structural characteristics of the char and some TCs obtained at 900 ºC and 50 wt% of PP.

Sample	carbon yields	A_{BET} (m^2/g)	A_t (m^2/g)	V_t (cm^3/g)	V_{mes} (cm^3/g)	A_{DR} (m^2/g)	V_{DR} (cm^3/g)
100PP-900	36.75	2	-	-	-	22	0.009
50PP-900-Y	60.42	1086	119	0.420	0.120	383	0.153
50PP-900-β	54.48	470	325	0.062	0.799	280	0.106
50PP-900-β-(CVD)-co	---	19	14	0.003	0.027	18	0.007
50PP-900-ZSM5	40.85	232	67	0.074	0.120	296	0.112
50PP-900-M	45.47	111	42	0.031	0.072	209	0.079

The porous structure of the TCs is highly dependent on the carbonization temperature and on the PP mass percentages. The TCs present an increase of the N_2 adsorbed with the carbonization temperature. At low carbonization temperatures an incomplete devolatilization of the carbon precursor leads to a lower porous development. Fig. 2 shows the N_2 isotherms of the zeolite β and of the TCs obtained from it using PP mass

percentages of 25, 50, and 75% wt and a carbonization temperature of 900 ºC. The highest porous development is obtained with a PP mass percentage of 50 wt%. These carbons have several interesting features, such as two distinguished hysteresis loop in the nitrogen isotherm, corresponding to different pore sizes and the largest mesopore volume, 0.8 $cm^3 \cdot g^{-1}$, among all the resultant carbons.

We have investigated the possibility to control these two types of pores independently since they seem to be generated by two different mechanisms [3]. That is, it should be possible to tune the pore system of this template carbon, 50-700-β, by varying the synthesis conditions, such as the PP concentration and the impregnation method. The N_2 isotherms of the TCs corresponding to different impregnation methods are also shown in Fig. 1.

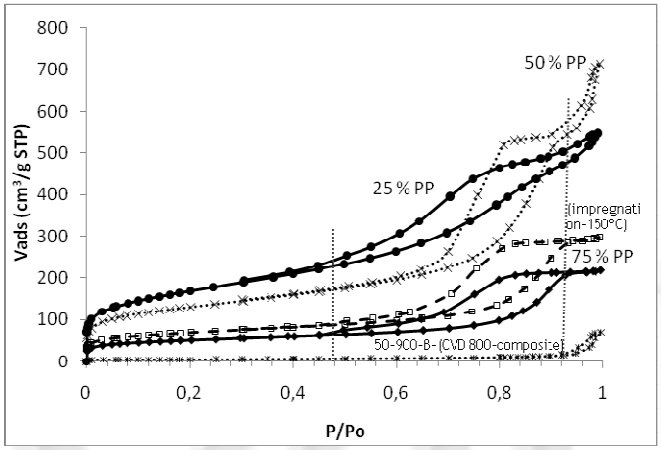

Fig. 1 N_2 isotherms of the TCs obtained from zeolite β at 900 ºC and different PP mass percentages. The TC generated by other infiltration methods (impregnation at 150ºC or impregnation-CVD-composite) is also observed.

The isotherm for the sample that was impregnated with 75% wt of PP differs from those of the other samples synthesized at low pitch concentrations, because it shows only one hysteresis loop in the relative pressure range of 0.5–0.9. This was also observed for the TC obtained by impregnation at 150ºC. In contrast, all other samples clearly show two hysteresis loops with closing points around $p/p_0 = 0.9$. This could correspond to a complete blockage of the mesopore space of the zeolite β by the PP at these conditions.

The BET surface area of the composite from the impregnation-CVD method was 19 m^2/g (Table 1), indicating that the zeolite channels were fully filled by the pyrolytic carbon or blocked by the pyrolytic carbon deposition on the outer surface. The isotherm of the composite (Fig. 1) shows only N_2 adsorption at relative pressures > 0.9, corresponding to pores of large size. This suggests this pore is originated by the incomplete filling of the zeolite channels.

Transmission electron micrographs of sample 50PP-900-Y (Fig. 2) reveal that the structure this TC is quite similar to that of the zeolite Y (not shown). Two structures can be clearly differentiated in the carbon particles, a dense and compact structure forming the external boundary and a less dense constituting the interior [4].

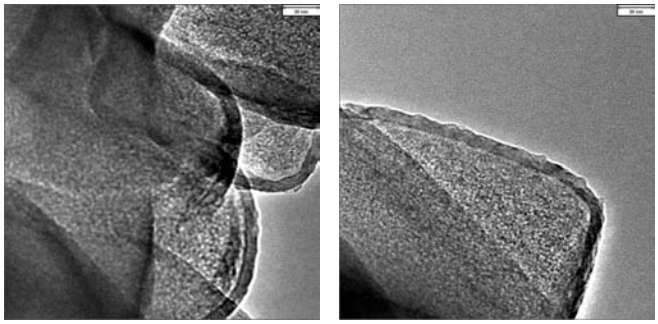

Fig. 2 Transmission electron micrographs for 50PP-900-Y template carbon.

Conclusions

We have prepared microporous and essentially mesoporous carbon materials by liquid infiltration of different zeolite templates using Petroleum Pitch solutions as carbon precursor, a low-cost by-product derived from the heavy gas oil fraction of crude oil.

The pore system of these carbons can be tailored by selecting the proper conditions such as the PP concentration and the impregnation method.

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