

Hypercrosslinked aromatic polymers from low-value coal tar products

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Introducción

Hypercrosslinked polymers (HCPs) have attracted much attention in the last years in the search for advanced porous materials. These are a class of entangled polymers based on aromatic monomers with a very high level of crosslinking, thus resulting in materials with a stable rigid framework, and frequently possessing a porous character. HCPs have already been obtained from a large variety of precursors, which are usually single-component aromatic compounds, but generally not from multi-component substances.

In the present work, a suite of coal tar-derived products (CTPs), listed in Table 1, obtained by distillation of coal tar at different temperatures and made up of complex mixtures of polycyclic aromatic hydrocarbons with different proportions, were explored as precursors of HCPs and they were tested as adsorbents of organic pollutants.

Experimental

The HCPs were obtained following the “knitting” strategy based on the Friedel-Crafts chemistry [1] using the CTPs as precursors (ca. 20 g), formaldehyde dimethyl acetal as crosslinking agent and FeCl₃ as catalyst (precursor/catalyst/crosslinker molar ratio = 1/2/2) in 1,2-dichloroethane (200 ml). The polymerization reaction was carried out at 80 °C for at least 1 h.

The polymers were characterized by N₂ and CO₂ physical adsorption at -196 °C and 0 °C, respectively; and the morphology of the HCPs was observed by FE-SEM.

The HCPs were also tested as adsorbents to remove organic compounds from wastewaters using phenol as model pollutant. The total adsorption capacity (q_{ads}) of the materials was obtained by shaking the samples in a concentrated phenol aqueous solution (initial concentration: 2 g/l) for 24 h at 25 °C. The final concentration of the pollutant was measured by UV-vis spectroscopy.

Resultados y discusión

The N₂ adsorption/desorption isotherms at -196 °C showed similar profiles for all of the samples (see Figure 1a). For the sake of clarity, only representative samples were plotted in this figure). The shape of the isotherms was a combination of type Ib and type II according to the IUPAC classification, with different contributions of each type depending on the particular precursor. However, low-pressure “open-jaw” hysteresis loop was a common trait of all the recorded isotherms. This effect has been attributed to diffusional problems of the adsorbate within the narrow porosity and also to a certain flexibility of the polymeric structure, so the pores undergo a swelling during the adsorption. The specific surface area (S_{BET}) of the samples was in the range between 153 and 502 m²/g, with DNO being the precursor providing the HCP with the highest surface areas (see Table 1). As for the morphology of the HCPs, they showed in general a mixture of loose aggregates of micrometer-sized ribbons and round shaped-particles with different proportions of both depending on the precursor used (see Figure 1b).

Tabla 1. Porous textural parameters derived from N₂ and CO₂ adsorption isotherms and amount of adsorbed phenol

CTP	S_{BET} (m ² /g)	V_{CO_2} (cm ³ /g)	q_{ads} (mg phenol/g HCP)
Distilled coal tar pitch (DCTP)	277	0.13	57
Wash oil (WO)	321	0.15	64
Chrysene oil (CO)	153	0.12	96
Phenolic oil (PO)	379	0.14	172
Creosote B (CreoB)	371	0.16	81
Naphthalene oil (NO)	484	0.19	122
Depleted naphthalene oil (DNO)	502	0.17	92
Distilled coal tar (DCT)	420	0.16	40
Anthracene oil (AO)	320	0.16	99

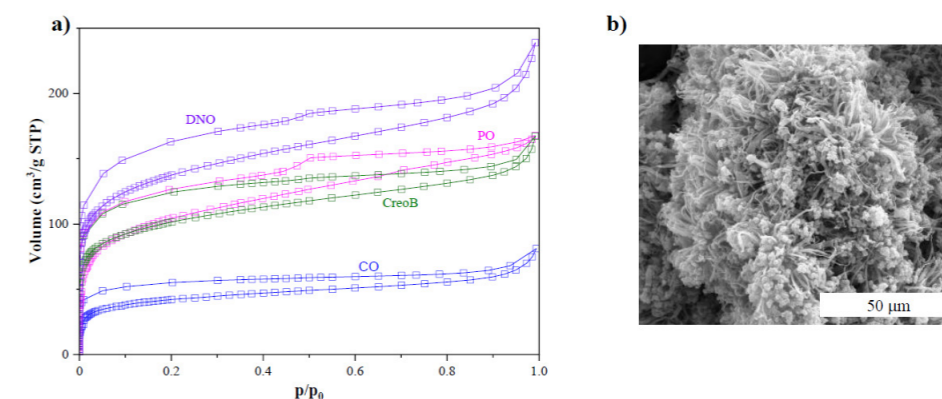


Figura 1. N₂ adsorption/desorption isotherms of the HCPs (a) and FE-SEM micrograph of the HCP obtained using creosote B as precursor.

The HCPs capacity of phenol adsorption was, in general, proportional to the narrow micropores volume obtained from the CO₂ adsorption (V_{CO_2}), with the exception of the HCP obtained from PO which showed a remarkably higher capacity (see Table 1). This polymer had a much higher amount of hydroxyl groups than the other HCPs (observed by infrared spectroscopy, results not shown here). The adsorption was therefore favored by the formation of hydrogen bonds between phenol molecules and the OH groups [2].

Conclusiones

HCPs were successfully prepared from multi-component low-value CTPs with a wide variety of porous textures and morphologies. The HCPs showed relatively low phenol adsorption capacities accordingly to their porous textures but with a high room for improvement by tailoring the surface chemistry.

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