Development of filters based in nanostructured carbon materials for gas separation and purification

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OBJECTIVES AND NOVELTY

The aim of the Ph.D. was to develop carbon materials and apply them in processes related to the control of volatile organic compounds (VOCs) emissions from automotive vehicles and the refining and upgrading of biofuels and biogas through selective adsorption. Herein, the use of traditional activated carbons obtained from agricultural wastes (olive stones and pine wood) is complemented by the synthesis of more advanced carbon materials, such as carbon gels obtained from resorcinol-formaldehyde polymerization and the subsequent drying and carbonization. Carbon xerogels and aerogels are known as nanostructured materials, since their porosity can be controlled at the nanometric scale. Therefore, carbon materials synthesis, characterization and application are the key points of this work.

In this Ph.D. both traditional and nanostructured carbon materials, being their textural and chemical properties tailored through activation, oxidation and selective decomposition in order to achieve an excellent adsorption or separation performance. In conjunction with the choice of proper characterization techniques, these synthetic procedures allowed to study the relationship between changes in physicochemical properties of materials and their behavior as specific adsorbent of different molecules. Our studies helped other researchers to find suitable protocols for developing other adsorbents, being the exposed results of a great importance to the Carbon research community.

RESULTS

Along the first three chapters, it was studied the ethanol and *n*-octane adsorption onto activated carbons obtained by chemical activation of olive stones whose surface chemistry was modified by oxidation and selective thermal decomposition of the oxygen surface groups (OSGs). The raw material was chemically activated with a high proportion of potassium hydroxide to generate a well-developed porous texture. Part of this activated carbon was treated with an oxidizing agent (ammonium peroxydisulfate) to increase the oxygen percentage of the carbon surface, creating a rich and diverse surface chemistry with a lot of different OSGs. Then, the oxidized activated carbon was split into several portions which were treated at different temperatures, to sequentially eliminate specific OSGs from carbon surface according to their thermal stability. Both the porous texture and the surface chemistry of the materials were deeply analyzed by several techniques.

Once characterized, materials were employed as *n*-octane or ethanol adsorbent under different conditions and, in such a way, physicochemical properties of the adsorbents could be related to their adsorptive properties for each VOC. For instance, when the adsorption was tested in static regime and at high concentrations, the total porosity of the sample was the important parameter, no matter which of the pollutants was adsorbed; however, in dynamic regime and at low concentrations, while for the *n*-octane adsorption is closely related to the adsorbent microporosity, the OSGs present on carbon surface (mainly the carboxylic acid groups) are the key factor to explain the ethanol one. Moreover, the influence of the humidity was also analyzed as well as the competitive adsorption of both VOCs. Finally, the adsorptive bed composition was fitted by physical mixture of the original activated carbon and the oxidized one, looking for an improvement in the simultaneous adsorption of ethanol and *n*-octane.

In the following chapter, the application of a carbon aerogel and a series of physically activated carbon xerogel in the separation of linear and branched hydrocarbon isomers was reported. Concretely the separation of *n*-octane and 2,2',4-trimethylpentane (TMP) through dynamic adsorption was studied. Linear and branched isomers separation is a topic of industrial relevance since the octane index is higher for the formers, so fuels with a greater content on them will present a better performance in gasoline engines. The sol-gel method allows to fit the carbon gel porosity and, therefore, to fabricate carbon molecular sieves with tailored pore size. So that, in order to study the influence of the drying process, an aerogel (supercritical drying) and a xerogel (dried in vacuum furnace) were synthesized and the xerogel porosity was adjusted through carbon dioxide physical activation. After characterizing their porosity, the pelletized materials were introduced inside fixed bed reactors and exposed to contaminated air flows containing one of the hydrocarbons, stablishing relationship between carbon materials microporosity and their adsorptive behavior.

The most important result was that the narrow micropores found in the aerogel hindered the TMP molecules adsorption, and it was because of it that this sample was able to completely separate both hydrocarbon for a long period of time when competitive dynamic experiments were performed (Figure 1).

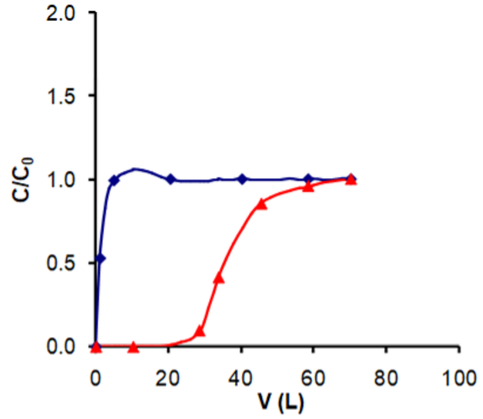

Figure 1. Breakthrough curves for competitive dynamic adsorption of TMP (♦) and n-octane (▲).

In the case of carbon xerogel, its micropore volume was smaller and the micropores were wider so the difference between both hydrocarbon adsorption was too short. This is the reason why microporosity was fitted through physical activation and it was found that at low activation degree results for separation were better, since new microporosity was generated, while samples activated above 20 % presented wider micropores, so the adsorption of TMP started to be favored.

The last part of the Ph.D. covered the work carried out in Porto, during a temporary stay with the Emeritus Professor Alirio Rodigues at the Laboratory of Separation and Reaction Engineering (LSRE) which belong to the University of Porto Engineering School. This work consisted on the study of the carbon dioxide selective adsorption for biogas upgrading. Biogas is obtained by anaerobic digestion of different residues and it contains carbon dioxide in high concentrations (around 40 %) which needs to be removed to get the biomethane. To do that, several technologies have been developed, and adsorption-based ones compete mainly with chemical absorption through liquid amines, the most used process applied nowadays. The main problem of this technique is related to the high energy needed to regenerate the liquid amine, and this can be mitigated by employing adsorbents that can be recovered at lower temperatures. Therefore, not only a suitable adsorbent microporosity for the selective adsorption of carbon dioxide was considered but also the easiness for regenerating the adsorbent through desorption which is related to its meso and macroporosity. Two different type of materials were tested at this purpose: PINPEL and PINPEL20, activated carbons obtained by direct physical activation of pine wood pellets (employed in domestic heating) and XCs300 a base-catalyzed carbon xerogel. Both materials were characterized and their adsorptive behavior for the two gases was analyzed by obtaining the adsorption isotherms at high pressures and at several temperatures as well as their performance in fixed bed system in dynamic regime. All of them presented large selectivity values, an outstanding behavior for the separation of the two gases and they were totally regenerated by just switching the inlet gas to pure Helium, without the needing of increasing the reactor temperature. Therefore, they can be considered as suitable candidates for biogas upgrading through carbon dioxide selective adsorption.

CONCLUSIONS

Carbon materials prepared in this Ph.D. thesis presented an outstanding behavior for the adsorption of VOCs present in biofuels, the separation of linear and branched hydrocarbon isomers and biogas upgrading through CO_2 selective adsorption.

Therefore, the use of carbon materials in adsorption processes was the main research field of this work. In such a way, both activated carbons obtained from agricultural waste, as well as resorcinol-formaldehyde carbon gels were employed in these specific applications. In the first case, it was shown the versatility of activated carbons obtained from olive stones and how their textural properties and surface chemistry can be tailored to increase the adsorption capacity of molecules with different chemical nature (ethanol – polar; n-octane – non polar); furthermore it was demonstrated that activated carbons prepared by physical activation of pine wood pellets are suitable candidates to proceed to the separation of CO_2 from biogas by adsorption, obtaining very large selectivity values. The results for this application were also very promising when a carbon xerogel was used, and carbon gels were also employed in the separation of linear and branched hydrocarbon isomers with excellent results.

This Ph.D. was awarded with a **Second place in the Carbon Journal Prize 2018** given for **"an outstanding Ph.D. thesis in carbon material science and technology"**.

RELATED PUBLICATIONS

[1] Vivo-Vilches JF, Bailón-García E, Pérez-Cadenas AF, Carrasco-Marín F, Maldonado-Hódar FJ. Tailoring activated carbons for the development of specific adsorbents of gasoline vapors. J Hazard Mater 2013; 263 Part 2: 533-540.

[2] Vivo-Vilches JF, Bailón-García E, Pérez-Cadenas AF, Carrasco-Marín F, Maldonado-Hódar FJ. Tailoring the surface chemistry and porosity of activated carbons: Evidence of reorganization and mobility of oxygenated surface groups. Carbon 2014; 68: 520-530.

[3] Vivo-Vilches JF, Pérez-Cadenas AF, Carrasco-Marín F, Maldonado-Hódar FJ. About the control of VOC's emissions from blended fuels by developing specific adsorbents using agricultural residues. J Environ Chem Eng 2015; 3: 2662-2669.

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