OXIDATION OF ACTIVATED CARBONS CONTAINING SURFACE PHOSPHORUS FUNCTIONALITIES

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Activated carbons materials have attracted considerable attention because of their interesting application in many fields, such as catalysis, gas and liquid phase adsorption and gas and energy storage. However, the use of carbon materials in catalysis is limited since they would gasify to CO_2 (or CO) in the presence of oxygen at relatively low temperatures. On the other hand, it has been shown that it is possible to prepare carbon materials with a relatively large amount of phosphorus on the carbon surface by chemical activation of lignocellulosic materials with phosphoric acid [1]. This activation method leads, in certain operation conditions, to the generation of phosphorus surface complexes in form of C-O-PO_3, C-PO_3 and C_3PO groups, which present a very high thermal stability and confer to the carbons certain surface properties of great interest in heterogeneous catalysis applications, such as high oxidation resistance and surface acidity. The main purpose of the present work is to study the role of the phosphorus surface groups of these activated carbons on the carbon surface oxidation and reduction reactions.

An extensive study of the oxidation evolution of the activated carbon surface has been carried out by subjecting the carbon to thermal treatments in oxidizing and inert conditions, using different techniques including temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) for the characterization of the obtained carbons. It has been proved that phosphorus surface groups preferentially trap oxygen and are transformed from less to more-oxidized species prior to carbon gasification, even at low temperature. These experimental results evidence the role of phosphorus surface groups on the inhibition of carbon oxidation and gasification. The high capacity of these phosphorus species to be oxidized results in activated carbons with a high amount of oxygen surface groups of acidic character and relatively high thermal stability.

The reduction and re-oxidation of the (phosphorus) surface groups have also been proved to be reversible through successive thermal treatments in oxidizing and inert conditions. The new surface sites generated during the reduction conditions (probably of C-PO type) may react with oxygen from air and regenerate the C–O–PO system, indicating the presence of redox sites on the surface of the activated carbon. These results open new and attractive possibilities for the use of these carbon materials as catalytic supports or as catalysts by themselves for reactions that take place under oxidizing conditions and at relatively high temperatures.

References

[1] J.M. Rosas, J. Bedia, J. Rodríguez-Mirasol, T. Cordero. Ind. Eng. Chem. 2008; 47, 1288-1296.

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