

Reseña Tesis. Carbon-based catalysts for oxidation and alcohol dehydration reactions

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OBJETCTIVES AND NOVELTY

Carbon materials have been used for a long time in heterogeneous catalysis since they can act as direct catalysts and they can satisfy most of the desirable properties required for a suitable support. 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. Nevertheless, 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. This activation procedure leads to phosphorus surface complexes which remain very stable on the carbon surface, at relatively high temperatures, and confer to the carbon high oxidation resistance and high acidity, increasing the catalytic applications in which these catalysts can be used. Therefore, there is a growing interest on these materials in catalysis involving oxidizing conditions.

The main purpose of the thesis work was to provide some insights into the role of the different phosphorus species on the oxidation resistance of activated carbons, prepared by activation of biomass with phosphoric acid. Oxygen plays a key role not only in all catalytic processes involving oxidizing conditions, but also in the catalyst performance, since the carbon

surface chemistry is being modified. Therefore, the study of the chemical surface modification under oxidative conditions was also investigated. It was studied some of their potential applications in catalytic processes, as catalytic supports or as catalysts by themselves, for reactions that take place at relatively high temperatures and under oxidizing conditions; i) the catalytic decomposition (dehydration/dehydrogenation) of (bio)alcohols and ii) the selective oxidation of light hydrocarbons.

This report also include examples of activated carbons with a high number of strong basic active sites on the carbon surface and some discussion on zeolite/carbon composites as supports of Co species for syngas conversion, also part of the thesis work.

RESULTS

Chemical activation of olive stone with phosphoric acid produces activated carbons with relatively high content of P surface groups that remain very stable on the carbon surface at relatively high temperatures, Figure 1a [1]. TPD and XPS results pointed out that P surface groups preferentially reacts with molecular oxygen, prior to carbon gasification, through the oxidation of C-P bond to form C-O-P ones, which are thermally stable at temperatures lower than $700\text{ }^\circ\text{C}$ (Figure 1b). At higher temperatures, these C-O-P type surface groups decompose to less

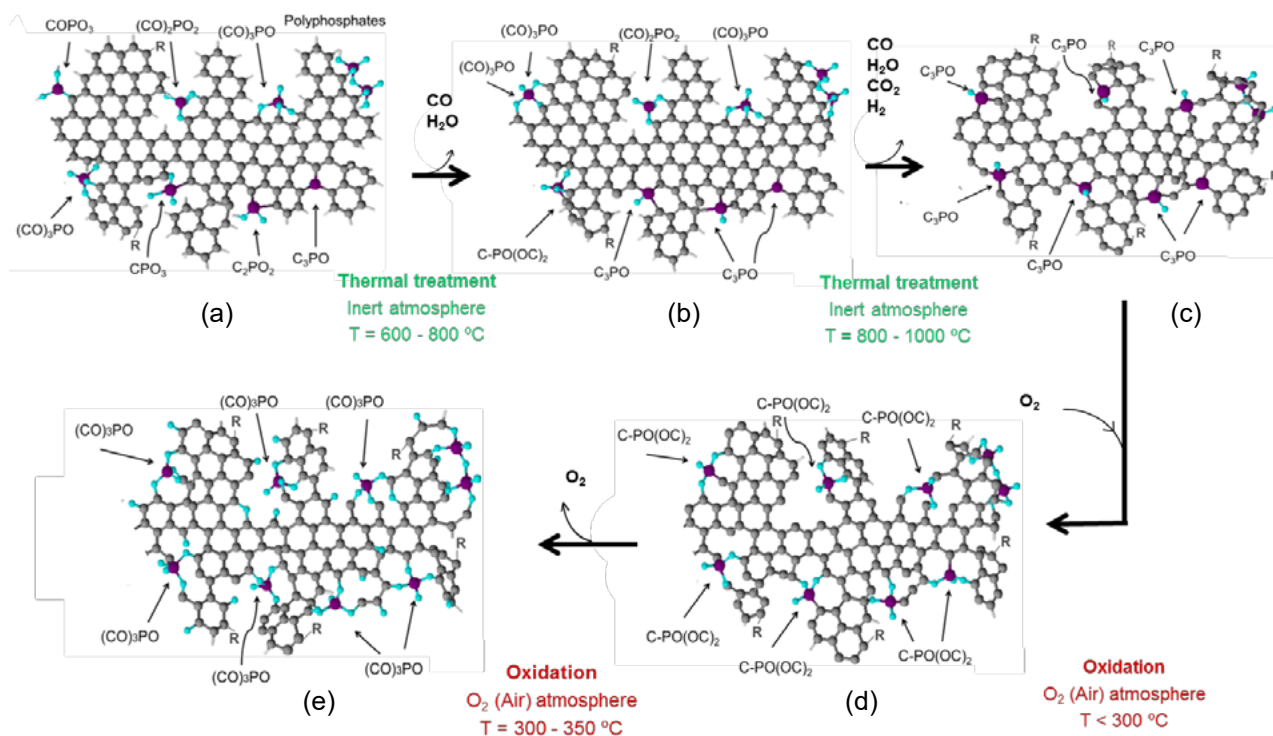


Figure 1. Possible P surface groups formed during phosphoric acid activated carbons surface oxidation and reduction reactions. (Greys: C, purple: P, blue: O, silver: H; R represents other similar carbonaceous matrix structures).

oxygenated P groups on the carbon surface (of C-P type) generating CO (and CO₂) in the gas phase (Figure 1c). These C-P type surface groups seem to be very reactive and are (re)oxidized upon contact with air, even at room temperature, forming again C-O-P type groups (Figure d). Thus, the presence of these oxygen-containing P surface groups with an interesting redox functionality of high chemical and thermal stability seems to be responsible of the high oxidation resistance and high oxygen content (once exposed to ambient air) of this type of porous carbons.

The catalytic conversion of methanol and ethanol over an acid carbon-based catalyst obtained by chemical activation of olive stone with H₃PO₄ was analysed [2]. The catalytic decomposition of methanol and ethanol over the activated carbon yields mainly dehydration products, that is, dimethyl ether ($S_{\text{DME}} > 82\%$ at 350 °C) and ethylene ($S_{\text{E}} > 90\%$ at 325 °C), with lower amounts of diethyl ether, for methanol and ethanol decomposition, respectively. It was showed that the presence of oxygen in the reaction gas plays a key role on the alcohols catalytic decomposition. Figure 2 displays the methanol conversion, X_{MeOH} , as a function of time on stream (TOS) at 350 °C, using in an initial step methanol in air, later methanol in N₂ and, finally, once the catalyst is deactivated, methanol in air again. In the first part of the experiment, using air in the reaction gas, a stationary state is reached very quickly and the methanol conversion remains constant with TOS ($X_{\text{MeOH}} \approx 40\%$). In the second part of the experiment, in N₂ flow, the methanol conversion decreases progressively to 10% after 100 minutes of TOS, indicating deactivation of the catalyst by C-O-P reduction and coke deposition (deduced by TPD and XPS analyses). The introduction of air, in the last step of the experiment, seems to produce a regeneration of the catalyst, increasing the methanol

conversion to a value of 30% that remains constant with TOS. Under oxidant conditions the P groups are continuously reoxidized and they ease an oxygen spillover on the catalyst surface, where the availability of labile oxygen inhibit catalyst deactivation and allow methanol and ethanol steady state conversions to be reached.

The rate expressions derived from the optimization of the kinetic parameters of the models (Eley-Rideal mechanism for methanol dehydration and Langmuir-Hinshelwood mechanism for ethanol dehydration) properly described the experimental results, being the activation energy obtained for the formation of dimethyl ether around 85 kJ/mol and for the formation of ethylene, around 165 kJ/mol.

In addition to its use as solid acid catalyst, redox functionality has been also incorporated by impregnation of these P-containing activated carbons with vanadium species, obtaining a bifunctional catalyst that is active for hydrocarbon partial oxidation reactions [3,4]. When vanadium is incorporate to these carbon materials, a VPO (Vanadium and Phosphorous mixed oxides) catalyst is obtained. These VPO materials are commercially used as catalysts for the transformation of n-butane into maleic anhydride and we have shown that they can be used for alkane partial oxidation reactions. These activated carbons can be also prepared with controlled morphology, by this manner VPO supported catalysts with spherical morphology and high surface areas have been described.

In the case of basic carbons, it was investigated new routes for the preparation of basic carbons containing Ca, Ba, or Na basic sites [5]. The best activation method resulted to be physical activation of olive stone with CO₂ followed by deposition of the Ca precursor by incipient wetness impregnation. This material (6CaO/ACG900 sample) presented a high

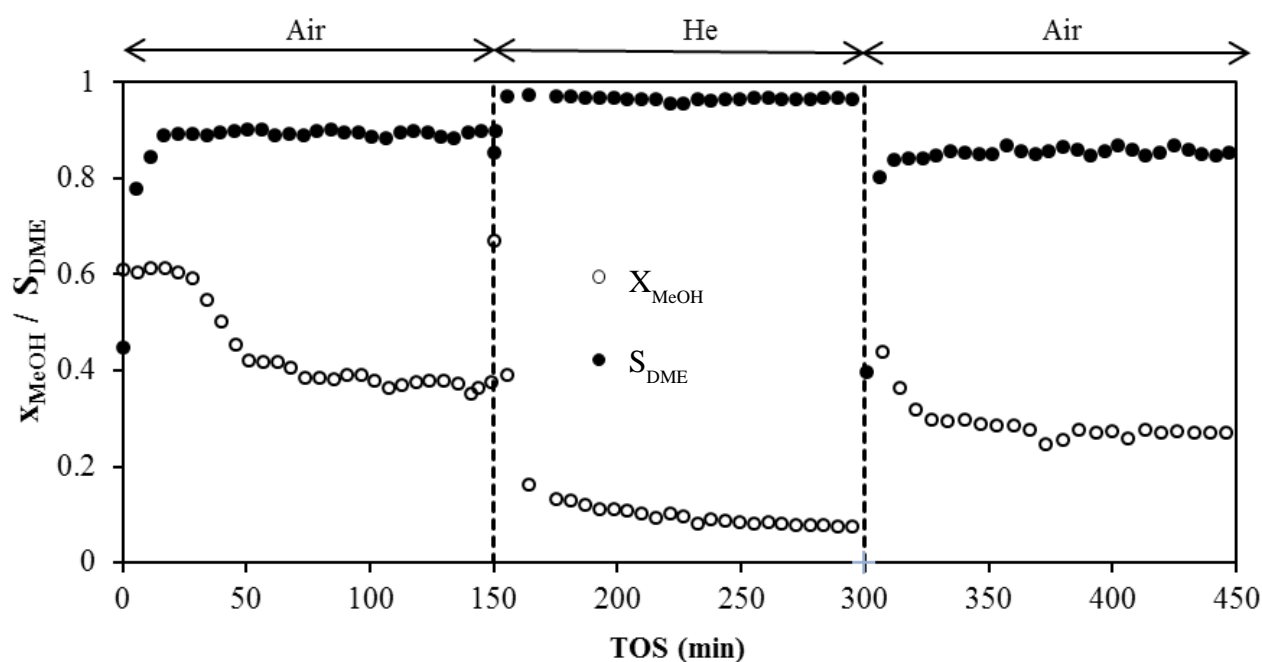


Figure 2. Methanol conversion and selectivity to DME as a function of TOS using first air, then N₂, and finally air as reaction gas. (T = 350 °C, P_{MeOH} = 0.020 atm, W/F_{MeOH} = 0.10 g·s/μmol).

amount of strong basic sites (pKb close to 9) as was detected by surface titrations. The activity results during the lactose isomerization to produce lactulose showed that this material is very promising, with a yield to lactulose close to 25 %.

Finally, carbon materials can be also used to tune the properties of conventional catalytic supports, as zeolites [6]. Mesoporous H-ZSM-5/carbon composites, were used as the support for the preparation of Co-based Fischer-Tropsch catalysts. The resulting catalysts display an improved performance during Fischer-Tropsch synthesis (FTS), with higher activity, higher selectivity towards C5-C9 (gasoline range) hydrocarbons and lower selectivity towards C1 (and C2) than Co/mesoH-ZSM5 (without pyrolytic carbon). This is due to the weaker metal-support interaction caused by the deposited carbon leading to a higher reducibility of the Co species. Further, the partial deactivation of the Brønsted acid sites by pyrolytic carbon deposition allows the modification of the zeolite acidity and therefore to tune the catalyst performance.

CONCLUSIONS

Activated carbons prepared by chemical activation of lignocellulosic materials with phosphoric acid have been evidenced experimentally to present mainly oxygen-containing P surface groups of type C-O-P with an interesting redox functionality of high chemical and thermal stability. These groups confer to the carbon high surface acidity and oxidation resistance, increasing the possibilities of these materials for applications in catalysis involving oxidizing conditions.

New routes for the preparation of carbon materials with basic properties and carbon/zeolite composites have been studied opening the door to further tune the catalytic performance of carbon-based materials.

RELATED PUBLICATIONS

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[4] Valero-Romero M.J., Cabrera-Molina A., Guerrero-Pérez M.O., Rodríguez-Mirasol J., Cordero T. Carbon materials as template for the preparation of mixed oxides with controlled morphology and porous structure. *Catalysis Today* 2014; 227, 233-241.

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[6] Valero-Romero M.J., Sartipi S., Xiaohui S., Rodríguez-Mirasol J., Cordero T., Kapteijn F., Gascon J. Carbon/H-ZSM-5 composites as supports for bi-functional Fischer-Tropsch synthesis catalysts. *Catalysis Science & Technology*, 2016; 6, 2633-2646.

Full Thesis can be downloaded from:

<http://riuma.uma.es/xmlui/handle/10630/11470>

This thesis work allowed the collaboration with two research groups of recognized international prestige in the field of catalysis, resulting in publications and communications to conferences; Catalysis Engineering group from Delft University of Technology led by Prof. Freek Kapteijn and Instituto de Tecnología Química del CSIC in collaboration with Prof. J.M. López-Nieto, Universidad de Valencia.