ROLE OF OXYGEN IN THE DEHYDRATION OF METHANOL AND ETHANOL ON CARBON-BASED ACID CATALYSTS

***M. J. Valero-Romero*, E. M. Calvo-Muñoz, M. Rodrigues-Gomes, M. Serrano-Pérez de Gracia, J. Rodríguez-Mirasol, T. Cordero**

Universidad de Málaga, Andalucía Tech, Departamento de Ingeniería Química, Campus de Teatinos s/n, 29071 Málaga, Spain

mjvalero@uma.es

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Activated carbons are receiving great attention in the last decades as catalysts and catalyst supports due to some advantages, such as, their very high specific surface area, high thermal and chemical stability and the presence of stable basic and acid surface sites as oxygen surface groups. We have previously reported the preparation and characterization of activated carbons by chemical activation of different lignocelullosic waste and by-products with phosphoric acid [1,2]. The carbons obtained showed a particular surface chemistry due to acid surface phosphorus groups of high thermal stability that remain over the carbon surface, providing the carbons a high oxidation resistance and surface acidity.

In this work, we study the catalytic conversion of ethanol and methanol over an acid carbon-based catalyst obtained by chemical activation of olive stone with H_3PO_4. The carbon catalyst is active for both reactions, yielding mainly dehydration products, that is, dimethyl ether (S_{DME}>82% at 350ºC) and ethylene ($S_{ethylene}$>91% at 325ºC), with lower amounts of diethyl ether, for methanol and ethanol decomposition, respectively.

The activated carbon catalytic activity and stability, under inert and oxidant atmospheres, as well as, different regeneration procedures were analyzed. Results evidence that catalytic performance strongly depends on the type of atmosphere in which the reaction proceeds and suggest that oxygen would play a key role on theses catalytic processes. In the absence of oxygen, catalyst suffers a progressive deactivation by coke deposition on the active acid sites, being faster and more pronounced for methanol decomposition (Fig. 1). However, in the presence of air, the carbon surface chemistry is modified, probably through oxygen spillover on the catalyst surface, where the availability of labile oxygen would inhibit catalyst deactivation and allow steady state conditions to be reached. Furthermore, the presence of oxygen leads to significant enhancements of both alcohol conversions and could even partially regenerate the catalyst.

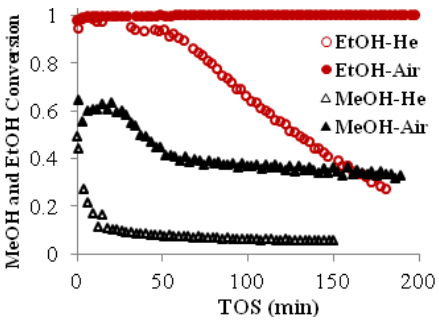

Fig. 1. Methanol and ethanol conversion as a function of TOS in the absence and presence of oxygen. (350 ºC, $P_{MeOH/EtOH}$=0.02 atm, $W/F_{MeOH/EtOH}$=100000 g·s/mol)

References

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