

METHANOL DEHYDRATION ON CARBON-BASED ACID CATALYSTS

M.J. Valero-Romero, E.M. Calvo-Muñoz*, R. Ruiz-Rosas,
J. Rodríguez-Mirasol, T. Cordero

Dpto. de Ingeniería Química, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Tfno.: +34 951 952529; e-mail: elisacm_18@uma.es

Ingeniería Química

Methanol dehydration to produce dimethyl ether (DME) is an interesting process for the chemical industry since DME is an important intermediate and a promising clean alternative fuel for diesel engines. Pure or modified γ -aluminas (γ -Al₂O₃) and zeolites are often used as catalysts for this reaction. However, these materials usually yield non desirable hydrocarbons and undergo fast deactivation.

In this work, we study the catalytic conversion of methanol over an acid carbon catalyst obtained by chemical activation of olive stone with H₃PO₄. A significant amount of phosphorus remains over the catalyst surface after the activation process, mostly in form of C-O-PO₃ and C-PO₃ groups, which provide the carbon a relatively high surface acidity and oxidation resistance. Methanol decomposition on this catalyst yields selectivities to DME higher than 82% at 623K and methanol conversion of 34%, under the operating conditions studied.

The activated carbon catalytic activity and stability, under inert and oxidant atmospheres, as well as different regeneration procedures, were studied. In the absence of oxygen, the catalyst suffers a progressive deactivation by coke deposition on the active acid sites (Fig. 1). The presence of oxygen modifies the carbon surface chemistry, probably through oxygen spillover on the catalyst surface, where the availability of labile oxygen avoids catalyst deactivation. A reaction mechanism has been proposed where methanol dehydration seems to proceed through an Eley-Rideal

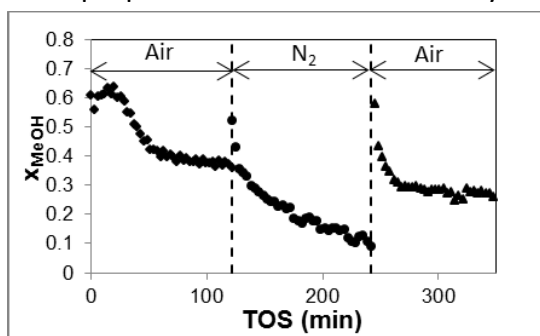


Fig. 1: Methanol conversion as a function of TOS in the presence and absence of air in the reaction gas. (T=350°C, P_{MeOH}=0.02 atm, W/F_{MeOH}=100000 g·s/mol)

mechanism, which assumes the adsorption of water and oxygen spillover on the acid active sites, avoiding coke deposition.

Acknowledgements

Spanish Ministry of Economy and Competitiveness (CTQ2012-36408) and Junta de Andalucía (P09-FQM-5156 and P10-FQM-6768).
University of Malaga. Andalucía TECH ICE