POS-A19, POS-D46

PD en Ingeniería Química

COMPARISON OF OXYGENATED VS. CHLORINATED COMPOUNDS IN THE PRODUCTION OF LIGHT OLEFINS FROM A COKE DEACTIVATION PERSPECTIVE

J. Valecillos-Diaz, M. Ibáñez, P. Pérez-Uriarte, M. Gamero, A.T. Aguayo, J. Bilbao, P. Castaño

Departamento de Ingeniería Química, Facultad de Ciencia y Tecnología, Universiadad del País Vasco

Light olefins are paramount intermediates in the petrochemical industry. The increase of gas reservoirs and biomass-based processes are driving attention to alternative routes for transforming methane derivatives into light olefins by acid catalysis, such as methanol-to-olefins (MTO), dimethyl ether-to-olefins (DTO) and chloromethane-to-olefins (CTO). However, these processes are limited by the rapid catalyst deactivation resulting from coke formation and deposition. Thus, we studied the effect of methyl-oxygenated or methyl-chlorinated feeds on HZSM-5 catalyst deactivation by coke. MTO, DTO and CTO reactions were performed in a catalytic fixed bed reactor at 400 ºC, 1.5 atm, feed diluted in 15 mol% He, space time of 6.5 g mol h-1 and up to 4 h time on stream. The catalyst consisted of 25 wt% HZSM-5 zeolite (SiO2/Al2O3 = 80) agglomerated with 30 wt% bentonite as a binder and 45 wt% α-Al2O3 as an inert filler. Deactivated catalysts were characterized by N2 adsorption-desorption, Raman spectroscopy and temperature-programmed oxidation (TPO) of coke followed by thermogravimetric analysis (TGA) and combined FTIR-mass spectrometry. Methyl-oxygenated feeds (MTO and DTO) showed higher conversions (95-100%) and stability than the methyl-chlorinated feed (47-67%). CTO process showed a higher selectivity to light olefins but, up to 4 h time on stream, the light olefins yield is higher for MTO (33.8%) and DTO (29.7%) than that for CTO (21.5%) as result of the higher conversion reached. TPO of coke deposited during CTO showed two distinctive peaks suggesting the presence of two types of coke. This was confirmed by Raman spectra, whereas coke from MTO and DTO was more homogeneous. The relative slower deactivation of MTO and DTO allows longer operational times, by contrast, CTO forms an additional type of coke with higher capacity to block the catalyst acid sites and its deactivating role is related to the absence of steam in the reaction medium. Acknowledgement: this work was financially supported by the Ministry of Economy and Competitiveness of the Spanish State General Administration (CTQ2013-46172-P and BES-2014-069980) and the Basque Government (UFI 11/39 UPV/EHU and BFI-2012-203).