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Deactivation of a CoMo catalyst during catalytic hydropyrolysis of biomass

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Catalytic hydropyrolysis of beech wood has been conducted in a fluid bed reactor loaded with a CoMoS catalyst at 450°C and 26 bar pressure followed by a fixed bed hydrodeoxygenation (HDO) reactor loaded with a NiMoS catalyst. The stability was investigated by converting approximately 5 kg of biomass and collecting the products for every 1 kg fed. The condensed organics and C\textsubscript{4+} yield was 22.1 ± 1 wt.%, which was within the experimental uncertainty. The oxygen content in the condensed organic phase increased during the experiment from 40 to 2832 ppm, which indicates that deactivation of the catalyst in the fluid bed and HDO reactor occurred. The spent catalysts were thoroughly characterized by Raman spectroscopy, scanning electron microscopy (SEM and STEM), and inductively coupled plasma optical emission spectroscopy. This showed that potassium and calcium were transferred from the biomass to the catalyst and the concentration increased proportionally with time on stream (TOS). Therefore the effect of doping the catalyst in the fluid bed with 1.9 wt.% potassium was investigated and compared with an experiment with a fresh catalyst, both experiments conducted without the HDO reactor. This showed that potassium decreases the catalyst’s cracking, hydrogenation, and hydrodeoxygenation activity. In addition, the char and coke yield increased from 13.3 to 14.6 wt.% daf when the catalyst was doped with potassium. SEM images of the spent potassium doped catalyst showed that the catalyst particles were encapsulated by a layer of coke and that this layer was probably continuously removed by knock-off. The encapsulating coke layer indicates that potassium can act as a catalyst for polymerization of pyrolysis vapors.