Catalytic Hydropyrolysis of Biomass using Molybdenum Sulfide Based Catalyst. Effect of Promoters

Catalytic hydropyrolysis of beech wood was conducted in a fluid bed reactor at 450°C and a total pressure of 26 bar. The differences in hydrodeoxygenation activity, selectivity and the resulting product composition between sulfided Mo/MgAl₂O₄, CoMo/MgAl₂O₄ or NiMo/MgAl₂O₄ catalysts have been investigated. The acidity and molybdate species in the oxide catalyst precursors were characterized with ammonia temperature programmed desorption and Raman spectroscopy. The spent sulfided catalysts were also extensively characterized by scanning electron microscopy (SEM) and by scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS). The catalytic hydropyrolysis of beech wood produced four kinds of products: Liquid organic and aqueous phases, solid char and gases. The solid char and aqueous phase yields were not affected by the type of catalyst. The sum of condensed organics and C₄+ gas yield varied between 24.3 and 26.4 wt.% on dry, ash free basis (daf) and was highest for the Mo catalyst and lowest for the NiMo catalyst. The NiMo catalyst had the highest hydrogenation, cracking, and de-carbonylation activity. The oxygen content in the condensed organic phase was between 9.0 and 12 wt.% on dry basis (db) and was lowest for the CoMo catalyst and highest for the Mo catalyst. The carbon recovery in the condensable organics was 39 % for both the CoMo and the Mo, and 37 % for the NiMo catalyst. These results indicate that the CoMo, due to its high deoxygenation activity and high carbon recovery, is the most suitable catalyst for catalytic hydropyrolysis. The carbon content on the spent CoMo was between 1.5 and 3.3 wt.% and between 0.9 and 3.1 on the spent NiMo catalyst, but between 5.0 and 5.5 wt.% on the spent Mo catalyst. The higher carbon content on the spent Mo catalyst was probably due to its lower deoxygenation and hydrogenation activity. Calcium particles and small amounts of potassium (≤1.5 wt.%) were detected on all spent catalysts using STEM-EDS, showing that alkali metals are transferred from the biomass to the catalyst, which potentially could lead to catalyst deactivation.