Hydrogenolysis of lignine in supercritical ethanol. The influence of nature of catalyst active sites and reducing agent

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Lignin depolymerization into lignin monomers has fascinated researchers for decades as a pathway to valorize lignin biopolymer. However, there are a number of obstacles that need to be overcome before lignin processing becomes economically viable. Here, we report the study of the catalytic hydrogenolysis of birch wood ethanol-lignin in the supercritical ethanol over solid catalysts.

The hydrogenolysis was conducted at 260 °C and 60-80 bar during 6 hours. The products of reaction were studied using GC-MS and GC.

The influence of catalyst support nature was studied using three different acid-basic materials namely: sepiolite, zeolite ZSM-5 supported on Al₂O₃ and Sibunit graphite-like carbon promoted via oxidation. The Sibunit material was found to produce highest yield of liquid products due to the highest amount of surface acid sites.

The bifunctional Ni- and Ru-containing catalysts based on oxidized Sibunit support were prepared and characterized. Metal-containing Sibunit catalyst in lignin depolymerization process allows us to decrease the coke formation and to increase the amount of aromatic monomers and the total yield of liquid products up to 84 % (58 % is monomeric components). According to GC-MS Ru-contained catalysts leads to formation of deoxygenation products. Ni-contained catalysts provides cracking process of alkyl fragments of lignin. Reducing agents significantly affect on process: using of H_2 / i-PrOH / HCOOH leads to increasing of liquid phase content up to 89 % and decrease coke formation (less than 4 %). Moreover, of reducing agent leads to changing of main product components: in case of H_2 and i-PrOH it is 4-propilsyringol, when HCOOH used it is 4-allylsyringol.