

Carbon-Supported Pd Nano-Particles as Green Catalysts for the Production of Fuels from Biomass

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Abstract : The production of transportation fuels from biomass has gained a growing attention due to diminishing fossil fuel reserves, rising petroleum prices and increasing concern about global warming. In recent years, renewable hydrocarbons that are completely fungible with fossil fuels have been suggested to be efficiently produced by catalytic deoxygenation of fatty acids and their derivatives via decarboxylation / decarbonylation. Several triglycerides (tall oil fatty acids) and saturated/unsaturated fatty acids and their corresponding esters were used as feedstocks. Their impact together with the influence of the reaction conditions and the catalyst composition on the nature of the reaction pathways of the deoxygenation of vegetable oils and their derivatives were recently reviewed. Following this state of the art the aim of the present study was the investigation of Pd NPs deposited onto mesoporous carbon supports as active and stable catalysts for the deoxygenation of oleic acid. The catalysts were prepared by the deposition of Pd NPs synthesised following an organometallic route on mesoporous carbons with different characteristics. Experiments were carried out under both batch and flow conditions. They demonstrated that under batch conditions (200 atm; 573K), the extent of the reaction depended, firstly, on the Pd loading and then on the metal dispersion and the oxidation state of palladium, both influenced by the way the support has been treated before the NPs deposition and by the preparation/stabilization methodology of Pd NPs. No aromatic compounds were detected in the reaction products but octadecanol and octadecane were observed in large extents. Under flow conditions (4 atm; 573 K), the conversion of stearic acid was superior to that observed in batch conditions. The product mixture contained over 20% heptadecane. No octadecanol, octadecane, and aromatic compounds were detected. The maxima in performances are obtained after only 0.5 h. After that, the yields in heptadecane suffer from a severe decrease until 3h reaction time. However, at that time, stopping feeding the reactor with oleic acid and flushing the catalyst only with mesitylene recovered the activity and the selectivity of the catalysts. With the complete removal of H₂, the analysis revealed the presence of heptadecene in high excess compared to heptadecane (almost 7 to 1), thus suggesting decarbonylation as the main route. ICP-OES measurements indicated no leaching of palladium and simple washing of catalysts with mesitylene allowed recycling without any change in conversion or product distribution. Noteworthy, mesitylene as solvent exhibited no effect in this reaction. In conclusion, this study demonstrates the feasibility of such catalysts for the green production of fuels from biomass.

Keywords : fuels from biomass, green catalyst, Pd nano-particles , recycle catalyst

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