Selective Conversion of Biodiesel Derived Glycerol to 1,2-Propanediol over Highly Efficient γ-Al2O3 Supported Bimetallic Cu-Ni Catalyst

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Abstract : During past two decades, considerable attention has been given to the value addition of biodiesel derived glycerol (~10wt.%) to make the biodiesel industry economically viable. Among the various glycerol value-addition methods, hydrogenolysis of glycerol to 1,2-propanediol is one of the attractive and promising routes. In this study, highly active and selective γ-Al_2O_3 supported bimetallic Cu-Ni catalyst was developed for selective hydrogenolysis of glycerol to 1,2-propanediol in the liquid phase. The catalytic performance was evaluated in a high-pressure autoclave reactor. The formation of mixed oxide indicated the strong interaction of Cu, Ni with the alumina support. Experimental results demonstrated that bimetallic copper-nickel catalyst was more active and selective to 1,2-PDO as compared to monometallic catalysts due to bifunctional behavior. To verify the effect of calcination temperature on the formation of Cu-Ni mixed oxide phase, the calcination temperature of 20wt.% Cu:Ni(1:1)/Al_2O_3 catalyst was varied from 300°C-550°C. The physicochemical properties of the catalysts were characterized by various techniques such as specific surface area (BET), X-ray diffraction study (XRD), temperature programmed reduction (TPR), and temperature programmed desorption (TPD). The BET surface area and pore volume of the catalysts were in the range of 71-78 m^2g^{-1}, and 0.12-0.15 cm^3g^{-1}, respectively. The peaks at the 2θ range of 43.3°-45.5° and 50.4°-52°, was corresponded to the copper-nickel mixed oxidephase [JCPDS: 78-1602]. The formation of mixed oxide indicated the strong interaction of Cu, Ni with the alumina support. The crystallite size decreased with increasing the calcination temperature up to 450°C. Further, the crystallite size was increased due to agglomeration. Smaller crystallite size of 16.5 nm was obtained for the catalyst calcined at 400°C. Total acidic sites of the catalysts were determined by NH_3-TPD, and the maximum total acidic of 0.609 mmol NH_3 $gcat^{-1}$ was obtained over the catalyst calcined at 400°C. TPR data suggested the maximum of 75% degree of reduction of catalyst calcined at 400°C among all others. Further, 20wt.%Cu:Ni(1:1)/γ-Al_2O_3 catalyst calcined at 400°C exhibited highest catalytic activity (> 70%) and 1,2-PDO selectivity (> 85%) at mild reaction condition due to highest acidity, highest degree of reduction, smallest crystallite size. Further, the modified Power law kinetic model was developed to understand the true kinetic behaviour of hydrogenolysis of glycerol over 20wt.%Cu:Ni(1:1)/γ-Al_2O_3 catalyst. Rate equations obtained from the model was solved by ode23 using MATLAB coupled with Genetic Algorithm. Results demonstrated that the model predicted data were very well fitted with the experimental data. The activation energy of the formation of 1,2-PDO was found to be 45 kJ mol^{-1}.

Keywords : glycerol, 1,2-PDO, calcination, kinetic