Hydrogenation of levulinic acid to γ-valerolactone in supercritical CO_2-ionic liquid systems

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Efficient conversion of renewable lignocellulosic biomass into platform chemicals and biofuels is an important topic in green and sustainable chemistry.[1] Practically, biomass-related compounds have an excess of oxygen groups that must be hydrogenated before they can be used as platform chemical feedstocks. [2-3] Many catalytic approaches have been developed for hydrogenating biomass-related compounds with hydrogen gas being widely used, however, H_2 gas has low productivity due to its limited solubility in most solvents.[3] Ionic liquids (ILs) are being studied in this work with supercritical CO_2 ($scCO_2$), because ILs can dissolve biomass-related compounds[4] and $scCO_2$ can be used to enhance H_2 solubility and to separate products.[5] The objective of this work was to develop an efficient reaction system for the hydrogenation of levulinic acid and to elucidate the role of CO_2 in the hydrogenation reaction system.

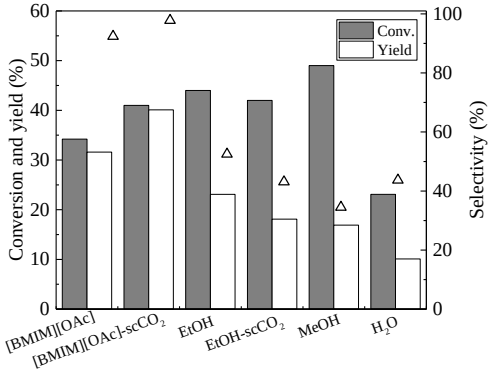

Fig. 1. Catalytic hydrogenation of LA to GVL enhanced with $scCO_2$. (1.2 g of LA, 2.28 ml of FA, 0.1 g of Ru/C (5%), 1.5 ml of solvent, 160 ºC, 3 h, 12 MPa at 160 ºC)

Therefore, the hydrogenation of levulinic acid to γ-valerolactone (GVL) in $scCO_2$-ionic liquid (IL) is being studied. GVL selectivities as high as 98 % with 40 % conversion were obtained in [BMIM][OAc]-$scCO_2$ at 3 h reaction time at 160 °C. Solvent physical chemistry and their effect on the hydrogenation reaction were investigated. The solubility of LA and GVL in CO_2 was measured and correlated with Peng-Robinson equation of state (PR-EoS). The solubility of GVL in CO_2 is 10 times higher than the solubility of LA in CO_2 phase. The role of $scCO_2$ in the reaction system is to enhance the hydrogen solubility in ionic liquid and to suppress side-reactions via GVL product removal. A mechanism is proposed for acetate anion ionic liquid-$scCO_2$, in which CO_2 interacts with the acetate anion IL to promote hydrogen gas transport and the formation of active hydrogen with the aid of a hydrogenation catalyst. The interaction of CO_2 with the acetate anion IL lowers reaction phase viscosity and allows efficient hydrogenation of LA to form product GVL.

References

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