38a Hydrogenation of Unsaturated Carbonyls in Scco2 as Reaction Medium over Ni-Supported Catalysts

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Selective hydrogenation of á, â unsaturated carbonyls where molecules containing C=C and C=O double bonds has both practical importance for fine chemicals industry and theoretical significance. Various studies are reported to enhance the selective hydrogenation of C=O over group VIII such as Pt, Ir Ru, Os etc. Hydrogenation is influenced by several parameters such as the nature of the metal, particle size, the type of precursor, the method of preparation and nature of support, the promoters and the nature of solvent. Supercritical CO2 has gained significant interest in various industrial applications, particularly in extraction, separation, crystallization, polymer technologies and reaction media. In addition to the very special combination of gaslike and liquidlike properties, the properties of scCO2, such as density and solvent power, can be easily tuned near the critical point with small changes in pressure and/or temperature. CO2 is an environmentally benign solvent compared to the conventional organic solvents and offers some unique advantages. The selective hydrogenation of á â unsaturated carbonyls like cinnamaldehyde, citral, and furfural has been studied in scCO2 using Ni supported catalysts. Compare to the conventional organic solvent scCO2 medium improved considerably the activity of Ni catalyst and reaction selectivity. Ni is found to be selective in hydrogenation of conjugated double bond (C=C) in unsaturated carbonyls expect in furfural. Conversions and selectivities improved in Sc-CO2 compared to traditional liquid phase reaction conditions, where 85% yields were obtained in case of cinnamaldehyde and citral with high selectivity to (hydrocinnamaldehyde/citronelal) the result of C=C- hydrogenation. The effects of co-solvent such as acetonitrile, has been studied. Optimum conditions were identified to maximize the selective hydrogenation without affecting the C=O in supercritical CO2 medium. Effect of reaction temperature, total pressure and reaction time is elucidated. The acidic, neutral and basic supports are screened for the hydrogenation activity. SiO2 support found to be active in hydrogenation of cinnamaldehyde and citral.