



INFLUENCE OF PHASE BEHAVIOR ON THE SELECTIVITY OF HYDROGENATIONS IN scCO₂

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Supercritical carbon dioxide (scCO₂) is playing an important role in the development of green chemical industrial processes for its environmentally benign nature, nontoxicity, abundance, low cost and wide tuning ability of solvent parameters. It has become of interest that complete miscibility between hydrogen and scCO₂ is particularly beneficial for hydrogenation reactions since the reactions in conventional solvents depend on the concentration of dissolved hydrogen and have often been limited by the rate of diffusion of hydrogen from the gaseous to the liquid phase. However, the lower solubility of organometallic complexes in scCO₂ prevents scCO₂ utilization in homogeneous catalytic synthesis. While, poly ethylene glycol (PEG) can dissolve most metal complexes, as well as, it can also dissolve large amount of CO₂ forming an expanded-liquid at high pressure. Such expansion is accompanied by the changes in the physical properties of the liquid solution, including lowered viscosity, increased gas/liquid diffusion and the solubility of the gases. In addition, PEG has a very limited solubility in scCO₂, thus the immobilization and separation of homogenous catalysts is possible in scCO₂/PEG system. This paper reviews our recent progresses in the selective hydrogenations of unsaturated aldehydes, nitrocompounds, and aromatic rings in multiphase. The influence of phase behavior on the product selectivity has been discussed in detail.

REFERENCES

- [1] C. Xi, H. Cheng, J. Hao, S. Cai, F. Zhao "Hydrogenation of chloronitrobenzene to chloroaniline over Pd/C in supercritical carbon dioxide" *Journal of Molecular Catalysis A: Chemical* 2008, 282, 80-84.
- [2] H. Wang F. Zhao S. Fujita, M. Ariai, "Hydrogenation of phenol in scCO₂ over carbon nanofiber supported Rh catalyst *Catalysis Communications*, in press.



- [3] R. Liu, F. Zhao, S. Fujita , M. Arai, “Selective hydrogenation of citral with transition metal complexes in supercritical carbon dioxide”, *Applied Catalysis A: General*, 2007, 316, 127–133.
- [4] F. Zhao, S. Fujita, M. Arai , Developments and Applications of Supported Liquid Phase Catalysts. *Current Organic Chemistry*, 2006, 10, 1681-1695.
- [5] F. Zhao, S. Fujita, Y. Ikushima, M. Arai, Hydrogenation of benzaldehyde and cinnamaldehyde in compressed CO₂ medium with a Pt/C catalyst: A study on molecular interactions and pressure effects, *Journal of physical Chemistry A* 2005, 109, 4419-4424.
- [6] F. Zhao, S. Fujita, J.Sun,Y. Ikushima, M. Arai , Carbon dioxide-expanded liquid substrate phase: an effective medium for selective hydrogenation of cinnamaldehyde to cinnamyl alcohol, *Chemical Communication*, 2004, 2326-2327.