Multiphase catalysis using water-soluble metal complexes in supercritical carbon dioxide

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Hydrogenation of cinnamaldehyde was performed in a supercritical carbon dioxide–water biphasic catalyst system, which eliminates gas–liquid–liquid mass transfer and gives better activity and selectivity.

Supercritical carbon dioxide ($scCO_2$) is considered as an ecologically benign and economically feasible reaction medium for metal catalyzed reaction.[1] It has several advantages such as nonflammability, lack of toxicity, absence of a gas–liquid phase boundary and possible simplifications in work up. This makes $scCO_2$ an alternative to conventional solvents. The physicochemical properties of $scCO_2$ can be tuned within a certain range by adjusting the pressure and temperature. Use of organometallic catalysts in $scCO_2$ is interesting, as demonstrated in some previous works.[2] Water-soluble organometallic catalysis has widened the scope of homogeneous catalysis in practice as it gives easy separation of catalyst and reactants/products, which is an important step towards the development of environmentally friendly processes.[3] Hoechst AG is operating a 300,000 tonnes per annum plant for hydroformylation of propylene using Rh and a water-soluble phosphine complex in a biphasic mode of operation. Several new concepts such as use of co-solvents[4] and surface active ligands,[5] interfacial catalysis using catalyst binding ligands,[6] supported aqueous phase catalysis,[7] and supported ethylene glycol phase catalysis[8] have emerged to improve poor reaction rates, which are due to limitations in liquid–liquid mass transfer and/or solubility of reactants. Considering the advantages of $scCO_2$ as a reaction medium and water-soluble metal complexes, there is a need to combine these two approaches to develop a truly environmentally friendly process (see Table 1). This eliminates the use of organic solvents and also gives easy catalyst/product separation and catalyst recycling. Here we demonstrate integration of biphasic catalysis and supercritical carbon dioxide using hydrogenation of an α,β-unsaturated aldehyde, cinnamaldehyde. This gives significant enhancement in the reaction rate and selectivity to cinnamyl alcohol and easy separation of the catalyst and reactants/products.

Hydrogenation of α, β-unsaturated aldehydes to give unsaturated alcohols with high selectivity is a challenging task due to several possible side reactions using heterogeneous metal supported catalysts.[9,10] However, good selectivity and activity were reported with Ru–PPh_3 based catalysts using homogenous and biphasic catalyst systems.[11] Table 2 summarizes the present results for hydrogenation of cinnamaldehyde using several catalyst systems.† Under the conditions used, unsaturated alcohol (UOL) and saturated aldehyde (SAL) were the main products with other very minor products. All the catalysts were reduced with H_2 for 1 h at 40 °C in order to form the active catalytic species. The catalytic chemistry for hydrogenation of α,β-unsaturated aldehydes using Ru–TPPTS [TPPTS = $P(C_6H_4SO_3Na)_3$] has already been explored well by earlier investigators.[11] In homogeneous reaction systems gas–liquid mass transfer is a key rate determining parameter. In the case of toluene solvent, 29% conversion was obtained with 92% selectivity to UOL. Homogeneous catalysis in general suffers from the major drawback of catalyst and product separation and, hence, the concept of biphasic catalysis has emerged. When this system is converted to a biphasic mode of operation keeping all parameters constant, the conversion of cinnamaldehyde drops from 29% to 11%, retaining the selectivity performance (Table 2, run 3). The important parameters such as gas–liquid–liquid mass transfer and liquid–liquid mass transfer (*i.e.* solubility of substrate in catalyst phase) are key factors in controlling the rate of reaction. In this case the substrate, cinnamaldehyde, has finite solubility in the catalyst phase, and therefore that is not a major limitation unlike hydroformylation of higher olefins in a biphasic mode of operation.[3–6] When this reaction is subjected to $scCO_2$ as medium instead of an organic solvent like toluene, the $RuCl_3$–PPh_3 catalyst system performs very poorly (run 2). It is mainly due to the very poor solubility of the phosphine ligand in $scCO_2$. Visual observation through a sapphire window confirms that solid catalyst particles are suspended in $scCO_2$. Since there is no interaction of catalyst and reactants, a poor reaction rate is observed. Presently, many researchers are working on enhancing the solubility of phosphine ligands in

Table 1 Catalysis using metal complexes

System	Type	Advantages	Disadvantages
Homogeneous	Gas–liquid	High activity and selectivity	Catalyst/product separation; gas–liquid mass transfer; organic solvent needed
Biphasic (organic–water)	Gas–liquid–liquid	High selectivity; high activity possible with water soluble substrates; easy catalyst separation and recycling	Low reaction rates for water insoluble substrates; gas–liquid–liquid mass transfer limits rate of reaction; organic solvent needed
SAPC	Gas–liquid–liquid (on solid support)	High activity and selectivity; product separation by phase separation; easy catalyst recycling	Organic solvent needed; stability of catalyst film on solid support
Biphasic (supercritical solvent–water)	Supercritical fluid–liquid	High selectivity; high activity possible with water soluble substrates; easy catalyst separation and recycling; organic solvent not needed	Poor solvating ability of many supercritical fluids
SAPC in supercritical solvent	Supercritical fluid–liquid (on solid support)	High activity and selectivity; product separation by phase separation; easy catalyst recycling; use of organic solvent is avoided	Poor solvating ability of many supercritical fluids

Table 2 Hydrogenation of cinnamaldehyde using various catalyst systems[a]

					Pressure/MPa			Selectivity (%)	
Run	Reaction type	Catalyst precursor	Ligand	Solvent system	$scCO_2$	H_2	Conversion (%)	UOL	SAL
1	Homogeneous	$RuCl_3$	PPh_3	toluene	—	40	29	92	8
2	Homogeneous	$RuCl_3$	PPh_3	$scCO_2$	140	40	1.5	89	11
3	Biphasic	$RuCl_3$	TPPTS	toluene–water	—	40	11	92	8
4	Biphasic	$RuCl_3$	TPPTS	$scCO_2$–water	140	40	38	99	0.5
5	Biphasic	$RhCl_3$	TPPTS	$scCO_2$–water	140	40	35	—	100
6	Biphasic	$Pd(OAc)_2$	TPPTS	$scCO_2$–water	140	40	22	—	100
7	SAPC	$RuCl_3$	TPPTS	toluene–water	—	40	13	93	7
8	SAPC	$RuCl_3$	TPPTS	$scCO_2$–water	140	40	44	96	4

[a] Reaction conditions: Catalyst precursor: 0.012 mmol; ligand/Ru: 8; $T = 40$ °C; cinnamaldehyde: 7.8 mmol; toluene (for 1,3,7): 25 cm^3; time: 2 h; water: 0.5 cm^3; silica (for 7,8): 1.5 g.

$scCO_2$ by using flourous substituents.[12] Biphasic catalytic systems such as $scCO_2$–water (runs 4–6) give much better conversion than conventional biphasic reactions (11 to 38%) and normal homogenous modes of operation (29 to 38%). This catalyst system differs from conventional gas–liquid and gas–liquid–liquid catalytic hydrogenation, since gas–liquid and gas–liquid–liquid mass transfer are completely eliminated in the case of $scCO_2$ as solvent. The concentration of hydrogen in a supercritical mixture of H_2 (85 bar) and CO_2 (120 bar) at 50 °C is 3.2 M, while the concentration of H_2 in THF under the same pressure is only 0.4 M.[13] This property of $scCO_2$ allows a reduction in viscosity and an increase in diffusion rate as compared with the liquid phase, so that transport to and from the catalyst phase is no longer a limiting factor. This causes significant rate enhancement as observed in Table 2 and might be advantageous in improving selectivity performance. $RuCl_3$ as metal precursor gives 99% selectivity towards UOL (run 4), while $RhCl_3$ and $Pd(OAc)_2$ give 100% selectivity towards SAL. Earlier investigators have already examined this feature. Supported aqueous phase catalysis (SAPC) in which the metal complex is supported on a solid surface like silica has been successfully used for biphasic reactions which have substrate solubility limitations. SAPC can also be used in $scCO_2$ as solvent and better activity and selectivity were observed when compared with toluene as solvent (12.4 to 44%). Although the application of SAPC is not particularly attractive in the case of hydrogenation of cinnamaldehyde (since it has finite solubility in the catalyst phase), it may be more attractive in the case of water insoluble substrates.

In conclusion, $scCO_2$–water was shown to be a good alternative solvent system for conventional biphasic catalytic systems. This eliminates gas–liquid–liquid mass transfer limitations due to the very high solubility of reactant gases in $scCO_2$.

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Notes and references

† Typical experimental procedure for an experiment involving the $scCO_2$–water biphasic catalytic system is as follows: $RuCl_3$ (0.012 mmol) and TPPTS (0.096 mmol) dissolved in water (0.5 cm^3) were charged to a 50 cm^3 reactor maintained at 40 °C. Hydrogen (10 bar) was introduced into the reactor and left for 1 h. Cinnamaldehyde (7.8 mmol) was introduced into the reactor after depressurizing the hydrogen. Hydrogen (40 bar) and liquid carbon dioxide were subsequently introduced into the reactor using a JASCO Model 880-PU syringe pump and compressed to the desired pressure (180 bar). The pump delivered the CO_2 at a flow rate of 3.5 ml min^{-1}. Pressure control was achieved using a JASCO Model 880-81 back pressure regulator. The reaction was started by stirring the mixture with a magnetic stirrer and continued for 2 h. After reaction, the pressure was released and the reaction mixture was analyzed *via* GC (Shimadzu GC-8A, Ucon Oil 8HB 2000 Uniport B, 6 m). Details of the experimental apparatus and procedures are described elsewhere (ref. 14).

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