Multiphase reaction media involving water and carbon dioxide for selective hydrogenation

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ARTICLE INFO

ABSTRACT

The features of multiphase reaction media using water (bulk water, supported thin aqueous phase) and dense phase carbon dioxide are reviewed for selective hydrogenation of carbonyl, nitro, and cyano compounds. The interface of aqueous and organic phases is important in determining the rate of hydrogenation and the product selectivity. For supported aqueous phase catalysts, the interface between the thin aqueous film and a support material (for example, porous silica gel) has also an influential impact. The pressurization of a liquid reaction mixture (organic and/or aqueous phases) with carbon dioxide shows interesting positive effects on the reaction rate, the product selectivity, and the deactivation of a conventional supported metal catalyst. In some cases the use of both water and dense phase carbon dioxide serves as an effective reaction medium. In other words, these green solvents may act as reaction promoters. Possible roles of their actions are discussed.

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1. Introduction

Multiphase reaction systems have several merits in industrial chemical processes, which include the easy separation of products and catalysts and the easy recycling of catalysts and solvents. An excellent first example is the biphasic hydroformylation process in which an organic layer contains the olefin and aldehyde products and an aqueous phase a water-soluble Rh complex with sulfonated triphenylphosphine ligands, commercialized by Ruhrchemie AG in 1984. Then, similar biphasic systems were investigated for other organic synthetic reactions and water-soluble organometallic catalysts were designed and developed [1]. In addition to bulk water, the organometallic complex catalysts can be contained in a very small quantity of water that is supported in the form of thin film or islands on the surface of a solid material; that is, supported aqueous phase catalysts [2–4]. The supported aqueous phase catalysts provide a larger interfacial area between the aqueous and organic phases, which should be an important factor determining the contact of the catalysts with organic substrates and consequently the overall reaction rate. These catalysts may be handled similar to conventional solid catalysts.

In addition to water, other components may contribute to the development of effective green multiphase reaction systems and one of those is supercritical CO_2 [5]. The physical and solvent properties of supercritical CO_2 in organic synthesis were demonstrated for several reactions [6–8]. Homogeneous reactions using supercritical CO_2 as a solvent are interesting but may not be widely applicable because of the limitation of solubility of organic substrates and molecular catalysts in the solvent. The solubility of metal complex catalysts can be increased by fluorination of ligands used [7]. The fluorination may also improve the solubility of organic substrates in supercritical CO_2. Even at lower pressures below its critical pressure, however, CO_2 shows interesting functions as a reaction promoter in liquid-phase organic reactions [9]; CO_2 is dissolved in a liquid phase (substrate, solvent) and significantly changes the solvent properties of the liquid phase. This facilitates the dissolution of gaseous reactants such as O_2, H_2, and CO and so accelerates the reactions involving these gases. It is noteworthy that some reactions with no gaseous reactants like Heck coupling and Diels–Alder reactions are also promoted by the presence of CO_2 [10,11]. The CO_2 molecules dissolved in the liquid phases have interactions with certain functional groups of initial substrates and/or intermediates, as proved by *in situ* high pressure FTIR measurements [12], and then alter their reactivity. As a result, the presence of CO_2 may have a desirable/positive impact on the reaction rate and the product selectivity of the liquid phase organic reactions.

It is therefore interesting to use water and CO_2 together for multiphase catalytic reaction media. This short article will review their features in selective hydrogenation reactions using supported

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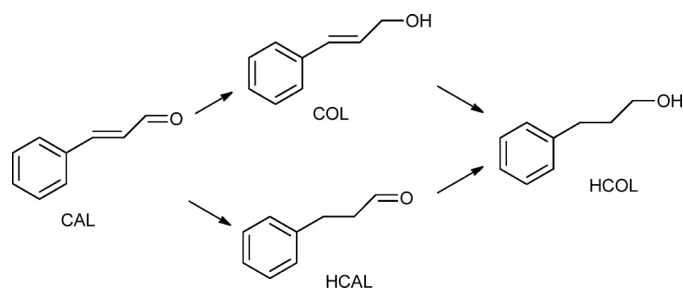
Scheme 1. Hydrogenation of cinnamaldehyde.

aqueous phase catalysts and conventional supported metal catalysts, mainly making reference to the authors' works. The interface of aqueous and organic liquid phases is important for determining the overall rate of reaction and the product selectivity. The importance of the aqueous–organic interface is pointed out for several synthetic reactions using molecular catalysts and no gaseous reactants [13,14]. The CO_2 may also improve the reaction results and affect the life of supported metal catalysts. The roles of water and CO_2 in the heterogeneous selective hydrogenation may change depending on the kind of initial substrates used. Because of their environment benign nature, the use of water and CO_2 serves the current demand of Green Chemistry principle in industry.

2. Hydrogenation with supported aqueous phase catalysts

Homogeneous metal complex catalysts possess greater activity and selectivity as compared with conventional heterogeneous catalysts; however, the homogeneous catalysts have a drawback in their separation and recycling. Davis and co-workers showed supported aqueous phase catalysts (SAPC) to be one of the methods overcoming the drawback of the homogeneous catalysts [15–21]. In SAPC, a very small amount of water containing a water-soluble metal complex is supported on such a hydrophilic high surface area solid as silica gel or porous glass. Triphenylphosphine trisulfornated sodium salt (TPPTS) is frequently used as the ligand for water-soluble metal complexes. SAPC is used in an organic solvent immiscible with water and can be separated by simple filtration. Another advantage of SAPC is that there can be large interfacial area between the supported water and the organic solvent, giving faster overall reaction rates than in conventional water–organic solvent biphasic systems. The good performance of SAPC was proven for several organic reactions such as hydroformylation, hydrogenation, Heck reaction, and alkylation [4]. Over SAPC, reactions would proceed at the interface between the supported water and the organic solvent. So, the overall reaction rates and/or the reaction selectivity should depend on the mode of dispersion of the supported water. Thus, the reaction systems using SAPC are more complicated compared with homogeneous ones. This section is to describe how the water loading affects the performance of SAPC in the case of cinnamaldehyde (CAL) hydrogenation.

Sometimes, ethylene glycol (EG) is used as the supported liquid instead of water. Those catalysts are called supported-liquid phase catalysts (SLPC). SLPC can also be a heterogeneous catalyst when it is used in a non-polar solvent like toluene. In the latter part of this section, the SAPC and SLPC using EG will be compared from the viewpoint of the dispersion mode of the supported liquid.

Selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols is an industrially important reaction in the fields of fragrance and flavor chemistry. In the case of cinnamaldehyde (CAL) hydrogenation, cinnamyl alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamyl alcohol (HCOL) are produced (Scheme 1). Among the products, the most desired one is the unsaturated alcohol of COL. For this reaction, therefore, not only the

Table 1
Comparison of SAPC, biphasic, organic homogeneous and aqueous homogeneous systems for CAL hydrogenation.

Entry	System and conditions[a]	TOF (h^{-1})	COL selectivity[b] (%)
1	Organic homogeneous $RuCl_3$ 0.15 mmol; TPP/Ru = 4; DMF 60 cm^3	415.2	48
2	Aqueous homogeneous[c] $RuHCl(TPPTS)_3$ 0.022 mmol; water 2 cm^3	45.1	67
3	Biphasic $RuCl_3$ 0.3 mmol; TPPTS/Ru = 4; water 1 cm^3; toluene 60 cm^3	0.8	100
4	SAPC $RuCl_3$ 0.3 mmol; TPPTS/Ru = 4; water 1 cm^3; silica 2 g; toluene 60 cm^3	19.2	89

[a] CAL 3 cm^3; temperature 60 °C; H_2 pressure 4 MPa.
[b] At conversions around 80%.
[c] CAL 0.095 mmol.

overall reaction rate but the reaction selectivity is also an important issue. Our group carried out this reaction using Ru complexes in SAPC, biphasic, organic homogeneous and aqueous homogeneous systems [22,23]. Table 1 compares the overall reaction rate and the COL selectivity among those systems. The organic homogeneous system gives the fastest reaction rate because of better contact between the catalyst and the reactant; however, the selectivity to COL is smaller than 50% (entry 1). A very small quantity of CAL can be dissolved in water. So, the reaction was also conducted in the aqueous homogeneous system (entry 2). In this system, the COL selectivity was slightly improved, but not so high. Compared with these homogeneous systems, the COL selectivity is much larger in the biphasic and the SAPC systems (entries 3 and 4). Thus, the presence of water–CAL interface is significant for the selective formation of COL. The high selectivity to COL in the biphasic system can be ascribed to more hydrophilic nature of aldehyde group of CAL compared with C=C bond, as pointed out by Sánchez-Delgado et al. [24]. The C=O bond should be pointing toward the water phase in which active Ru complexes exist, resulting in the selective hydrogenation of C=O bond producing COL. The overall reaction rate in the SAPC system is significantly larger than that in the biphasic system. A reason for this is larger water–toluene interfacial area in the former system. The selectivity in the SAPC system will be discussed later.

Considering the superiority of SAPC over homogeneous and biphasic systems, we further examined the influence of catalyst preparation conditions on the performance of SAPC containing Ru-TPPTS complexes (Ru-SAPC) for the CAL hydrogenation in toluene [22]. Fig. 1 shows how the catalyst concentration in the supported
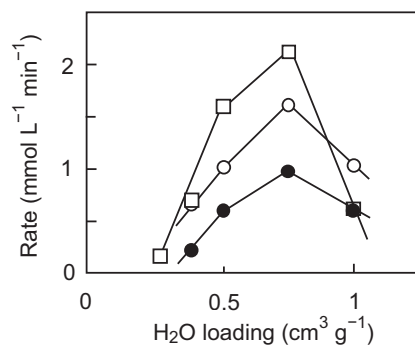

Fig. 1. Influence of the water loading onto SiO_2 and Ru catalyst concentration in the loaded water on the reaction rate of CAL hydrogenation using SAPC in toluene. Ru concentration in H_2O (□) 0.30 mmol/cm^3, (○) 0.20 mmol/cm^3, (●) 0.15 mmol/cm^3. Other reaction conditions: TPPTS/Ru = 4, SiO_2 2 g, H_2 4 MPa, toluene 60 cm^3, 60 °C.