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Review

Multiphase catalytic reactions in/under dense phase CO_2

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ABSTRACT

This contribution reviews several catalytic reactions in multiphase systems including dense phase CO_2 and other counter liquid or solid phases such as organic liquids, poly(ethylene glycol), water, ionic liquids, fluorous liquids, solid acid/bases powders, and supported metal particles. The features and potentials of dense phase CO_2 for the multiphase catalytic reaction and separation will be presented.

Contents

1. Introduction

Dense phase CO_2 is an interesting component for multiphase catalytic reaction and separation systems. Compared with ordinary gaseous or liquid reaction media, *homogeneous* supercritical fluids (SCFs) including CO_2 may have several advantages, which are the absence of gas–liquid mass transfer limitations, relatively high rates of molecular diffusion and heat transfer, and the possibility of molecular interactions with the dissolved reacting species (substrates or catalysts) [1–6]. The reaction rate and the product selectivity in homogeneous SCFs media may be altered by changing pressure and temperature. The features of dense phase CO_2 will also appear in liquid phases (substrates or solvents) when a large quantity of CO_2 can be dissolved in the liquid phases under pressurized conditions. *Multiphase* systems including dense phase CO_2 would be advantageous over the *homogeneous* ones. For the multiphase reactions, there is no concern about the solubility of reacting species in CO_2 gas phase, the catalysts effective in organic or aqueous media may be used without structural modifications, and larger quantities of substrates may be processed. Solubility of a significant quantity of CO_2 in the liquid phase enhances the dissolution of coexisting reactant gases. The properties of the liquid phase, as a continuum of reaction medium, may be altered from the neat organic solvent to neat CO_2 by changing the pressure-dependent

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amount of CO_2 dissolved. Microscopic effects through molecular interactions of CO_2 may appear in the liquid phase as well as in the dense phase CO_2. This contribution reviews multiphase catalytic reactions in/under dense phase CO_2 depending on the types of counter-phases (solvents or catalysts). It focuses on the merits and the functional role CO_2 plays in multiphase reactions.

2. Multiphase catalytic reactions

Various multiphase reaction systems are possible to design and prepare with dense phase CO_2, in which a counter-phase is a solvent, a substrate, or a catalyst itself. In the following, we will review several multiphase catalytic reactions using, as a counter-phase, organic liquids, poly(ethylene glycol), water, ionic liquids, fluorous liquids, solid acid/base powders, supported metal particles, and others (Fig. 1).

2.1. Organic liquids

A biphasic mixture of dense phase CO_2 and an organic liquid (solvents or substrates) will often generate a CO_2-dissolved expanded liquid (CXL) phase [7,8]. When a liquid solvent or substrate phase is pressurized by CO_2, it will expand by dissolution of a large quantity of CO_2. This will facilitate the dissolution of other coexisting gases and may accelerate the reactions involved with these gaseous reactants although CO_2 is not a reactant but rather a diluent. Subramaniam et al. studied oxidation of cyclohexene in CO_2-expanded acetonitrile using an iron porphyrin chloride complex-loaded MCM-41 catalyst [9]. For the oxidation with a gaseous oxidant O_2, the total conversion is larger by a factor of 2 in CO_2-expanded acetonitrile than that in the neat organic solvent, while the product distribution (cyclohexeneon, cyclohexeneol, and cyclohexene oxide) is not different. The rate enhancement is maximized at a CO_2 pressure that gives a CO_2 mole fraction of ∼30% in the liquid phase. Higher CO_2 pressures have a negative effect on the reaction, for which CO_2 is a diluent. When another oxidant, iodosylbenzene, is used, the CO_2 pressurization of the solvent phase has negligible effects on conversion and selectivity values. It is also suggested that the stability of the immobilized iron complex catalyst against leaching is improved in the CO_2-expanded acetonitrile than in the neat solvent. Subramaniam's group investigated hydroformylation of 1-octene with a $Rh(acac)(CO)_2$ catalyst and those modified by various phosphorous ligands [10]. For all the Rh catalysts examined, the rate of the hydroformylation can be enhanced in CO_2-expanded organic solvents. In addition, the selectivity to aldehyde products is improved from ∼70% in neat solvents to nearly 95% in CXL phases for the most active catalyst of $Rh(acac)(CO)_2$ modified by biphephos ligand. The enhancement in the reaction rate and selectivity may be attributed to increased syngas availability in the CXL phases. Eckert et al. [11] studied hydrogenation of nitrile and imine in CO_2-expanded organic solvent phases and showed the potential of CXL media for selective hydrogenation and product separation. In heterogeneous hydrogenation of benzonitrile and phenylacetonitrile with $NiCl_2/NaBH_4$ in CO_2-expanded ethanol, the yield of the primary amines is increased; this is because the primary amines are protected by CO_2 and so their further hydrogenation to the secondary amines is effectively suppressed. Those authors also used CO_2-expanded tetrahydrofuran for homogeneous hydrogenation of the same nitriles with $RhH(P\text{-}i\text{-}Ph_3)_3$ and benzophenone imine with $Rh(1,5\text{-}CsH_{12})\{p(C_6H_5)_3\}_2]PF_6$. In these reactions, the primary amines are separated in situ in the form of solid carbamic acid and/or ammonium carbamates while the catalysts remain in the solution. Zhao et al. show the effectiveness of CO_2-expaned liquid substrate phase to enhance the total conversion and the selectivity to cinnamyl alcohol in selective hydrogenation of cinnamaldehyde using a Ru–TPP complex catalyst [12] or a Pt/C catalyst [13]. High-pressure FTIR measurements indicate the presence of interactions of dense phase CO_2 with carbonyl groups and these interactions facilitate the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols [13]. The authors have recently reported a systematic FTIR study on molecular interactions of CO_2 with various carbonyl compounds of aldehydes, ketones, and amides, which depend on their structures and CO_2 pressure [14]. It should be noted that the potential of CO_2 pressurization appears for reactions including no gaseous reactants such as Heck and Diels-Alder reactions [15]. The rate of Heck coupling of methyl acrylate with modified bromobenzenes with a Pd–TPP catalyst in toluene is enhanced at a relatively low CO_2 pressure of ∼3 MPa. This positive effect is limited to a few selected bromobenzenes depending on their structures. In Diels-Alder reaction of isoprene with carbonyl compounds (dienophiles) in toluene or ethanol using a heterogeneous silica–alumina catalyst, the ratio of [3] adduct/[2] adduct is increased with CO_2 pressure up to 16 MPa although the rate of reaction is simply decreased. The CO_2 molecules dissolved in the organic solvent (non-polar or polar) could affect the approach between the diene and the dienphile on the solid catalyst.

2.2. Poly(ethylene glycol)

Recently increasing attention has been paid to poly(ethylene glycol) (PEG) as one of environmentally benign solvents for chemical reactions [16]. PEG is superior to ionic liquids and fluorous liquids because it is even less costly and its toxicities are very low [17]. PEG can dissolve common organic compounds, metal phosphine complexes, and CO_2 but it has negligible solubility into dense

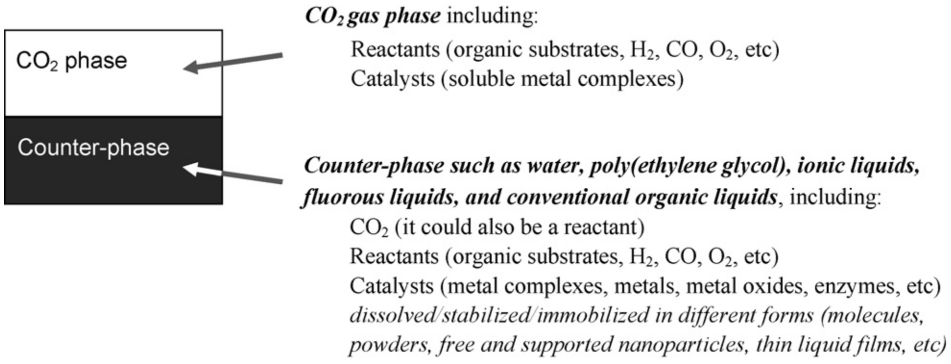

Fig. 1. Multiphase catalytic reaction systems using dense phase CO_2 and various counter-phases. These are effective for chemical transformations in the presence and absence of gaseous reactants such as H_2, CO, and O_2 owing to physical and/or chemical impacts of CO_2 under pressurized conditions.