

Catalysis with soluble complexes in gas–liquid–liquid systems

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Abstract

Catalysis with soluble complexes in biphasic media has made a major impact in applications of homogeneous catalysts due to easy separation of catalysts from products. In this paper an overview of important developments in gas–liquid–liquid catalytic reactions has been presented. The types of biphasic catalysts, their distinguishing features, industrial applications and reaction engineering aspects have been discussed.

1. Introduction

Catalytic reactions involving gas, liquid and solid reactants are commonly encountered in a variety of chemical transformations. These reactions are generally classified as homogeneous and heterogeneous catalysis depending on the nature of the catalyst. It is well known that homogeneous catalysts consisting of soluble metal complexes have high activity and selectivity compared to the heterogeneous catalysts. In recent years, major developments have taken place, on novel metal complex catalysts with unique properties such as regioselectivity and high activity. In spite of the several attractive features of the homogeneous catalysts, their applications in industry were limited due to difficulties in separation of catalysts and products and their economic utilization. To overcome the difficulties in recovery/recycle of homogeneous catalysts, several attempts to heterogenize these catalysts were made and some examples of these are: (a) anchoring of metal complex catalysts to polymeric or mineral sup-

ports, (b) supported liquid phase catalysts and (c) biphasic catalysis involving two immiscible solvents. Of these, the polymer bound and supported liquid phase catalysts have yet to be proven on a commercial scale due to problems such as leaching of the expensive metal, deactivation of catalysts and low activity. The development of biphasic catalysis involving two immiscible liquid phases has been a major advancement in this context [1] and has already indicated its potential for wide ranging applications.

Catalysis in two phase (liquid–liquid) systems is generally referred as biphasic catalysis, however, many variations of such systems are practised depending on the objectives in specific reactions/processes. This concept involves selection of two liquid phases, such that the catalyst is soluble only in one phase, while the product exists in the other phase. It is essential that the solubility of catalyst in another phase is almost negligible. The substrate should have finite solubility in the catalyst phase, so as to obtain reasonable reaction rate, while being immiscible with the catalyst phase. The recent development of water soluble metal complexes has made it feasi-

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Table 1
Examples of gas–liquid–liquid catalytic reactions

| Reaction | Catalyst | Category | Reference |
|---|--|-------------------------------|-----------|
| Hydroformylation of propylene to n-butyraldehyde | Rh-TPPTS or Rh-BISBIS in aq. phase | G–L–L/water soluble catalysis | [4,5] |
| Hydroformylation of 1-hexene to heptaldehydes | Rh-BISBIS | G–L–L/water soluble catalysis | [5] |
| Hydroformylation of allyl alcohol | HRh(CO)(PPh ₃) ₃ n-heptanol–water | G–L–L/organic phase catalysis | [6] |
| Selective hydrogenation of α – β unsaturated aldehyde | Rh-TPPTS or Ru-TPPTS | G–L–L/water soluble catalysis | [7] |
| Oligomerization of ethylene to α -olefins (SHOP process) | Ni-(C ₆ H ₅) ₂ PCH ₂ COOH in butanediol | G–L–L/organic phase catalysis | [8,9] |
| Carbonylation of isobutyl phenyl ethyl alcohol to ibuprofen (Boots–Hoechst process) | Pd(PPh ₃) ₂ Cl ₂ – aq. HCl | G–L–L/organic phase catalysis | [10] |
| Oligomerization of terminal alkynes | Rh/water soluble phosphines | G–L–L/water soluble catalysis | [11] |
| Carbonylation of benzyl chloride to phenyl acetic acid | NaCo(CO) ₄ /Bu ₄ NBr; aq. NaOH | G–L–L/organo metallic PTC | [12] |
| Carbonylation of allyl chloride to vinyl acetic acid/crotonic acid | Pd/PPh ₃ /aq. NaOH | G–L–L–S | [13] |

G–L–L: gas–liquid–liquid; G–L–L–S: gas–liquid–liquid–solid.

ble to conduct gas–liquid–liquid catalytic reactions in the biphasic mode to achieve easy separation of the catalyst and products. Another important area of application involving two phase reactions is the phase transfer catalyzed reactions. In this category, the catalytic cycle operates through both the liquid phases, but finally the catalyst and products are obtained in different phases.

Some of the important applications of gas–liquid–liquid catalytic reactions are summarised in Table 1. The most important examples are: hydroformylation of propylene to n-butyraldehyde using water soluble Rh catalyst (300 000 tpa production in a Ruhrchemie/Rhone Poulenc process); oligomerization of ethylene to α -olefins using Ni complex catalysts and carbonylation of benzyl chloride to phenyl acetic acid using Co complex and a phase transfer catalytic system. The common feature in these processes is the involvement of gas–liquid–liquid contacting. These examples have indicated the potential importance of biphasic catalysis, which will not only widen the use of homogeneous metal complex catalysts but will also provide easy and economic separation of the expensive catalytic systems. The overall performance of such reactions would depend on both the catalysis and reaction engineering aspects. The nature of new catalytic complexes and ligands will certainly decide the intrinsic

activity and selectivity of such catalysts. However, more important factors will be the effectiveness of contacting the reactants in such complex multiphase systems with the catalyst present in one phase. This will depend on the hydrodynamics of gas–liquid–liquid dispersion, interphase mass transfer, solubility and phase equilibria properties and intrinsic kinetics of the reactions. Certain features related to interfacial phenomena leading to enhancement of rate of such reactions also play very important role.

The synthesis of water soluble metal complexes and their use as biphasic catalysts in a variety of reactions has already been demonstrated, a detailed account of which is available in recent reviews [2,3]. However, the reaction engineering aspects of biphasic catalytic reactions have not been addressed before. The aim of this paper is to present an overview of the new developments in this area with specific reference to gas–liquid–liquid catalytic reactions.

2. Types of catalysts in two phase reactions

A variety of catalyst systems have been developed for use in biphasic liquid media to take advantage of easy catalyst and product separation. An important requirement in these is the appro-

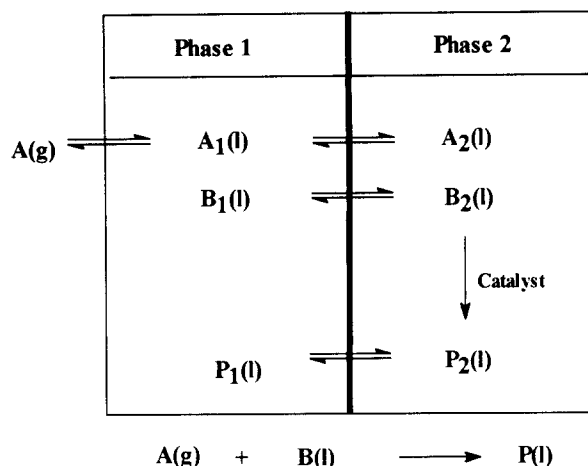


Fig. 1. Schematic of gas-liquid-liquid catalytic reactions.

appropriate choice of catalyst, ligands, and solvent systems depending on the nature of substrate and products. The type of catalyst systems used for gas-liquid-liquid reactions are: (a) water soluble metal complex catalysts, (b) biphasic catalysts with reaction in organic phase, (c) organometallic phase transfer catalysts and (d) catalysis by colloidal metal particles. A common feature in all these cases is the use of two immiscible liquid phases and a schematic of a gas-liquid-liquid reaction system is shown in Fig. 1. Some distinguishing features of these catalysts are summarized below.

2.1. Advantages of biphasic catalysts

- The most important advantage of the catalysts usable in biphasic media is the easy separation of catalysts and products by simple phase separation. This has direct impact on recycle/recovery of catalysts and their economic usage.
- Contamination of catalysts with products is minimized and helps in preventing deactivation in some cases.
- For substrate inhibited kinetics, higher activity is achievable for water soluble catalysts as the concentration of reactants in the cat-

alyst phase can be controlled taking advantage of the solubility limitations. In certain cases, a desired selectivity can be obtained.

- For processes with nonvolatile products, conventional separation methods are uneconomical but biphasic catalysts can be effectively used in practice. For example, hydroformylation of higher α -olefins (C_6 – C_{13}) to aldehydes using water soluble Rh complex catalysts in the manufacture of oxo alcohols.
- New catalyst systems with improved activity and selectivity at milder operating conditions can be evolved like carbonylation of organic halides using Co complex-PTC combined catalyst in a two phase system. This combination is practical only in biphasic media.

In recent years, the biphasic catalysts have been extensively studied to develop new routes and efficient processes for a variety of products. Some important developments are discussed in the following sections.

3. Water soluble catalysis

Many useful reactants and products in industrial processes consist of water immiscible organic compounds and hence, the concept of water soluble catalysis provides an important tool for separation of homogeneous catalysts and products. This approach involves synthesis of catalytic complexes such that they are highly soluble in water and insoluble in the organic phase. Several ligands and catalytic complexes have been synthesized and their applications as water soluble catalysts investigated. These are generally based on modification of conventional ligands by introducing hydrophilic functional groups (e.g. $-\text{OH}$, $-\text{SO}_3\text{H}$, $-\text{NH}_4^+\text{X}^-$) so that the catalysts prepared from these have high solubility in water.

In the first attempt to prepare a water soluble derivative of PPh_3 [14], monosulfonate triphenyl phosphine was prepared by direct sulfonation of PPh_3 at 25°C using 20% oleum. But, it was the

work of Kuntz and colleagues [4,15,16] on the synthesis of triphenylphosphine trisulfonate (TPPTS) ligand, which led to a commercially useful water soluble catalyst. TPPTS is a versatile ligand due to its high solubility in water and stability. Several catalysts consisting of Rh, Ru and Pd complexes of TPPTS have been reported for hydroformylation, hydrogenation and telomerisation reactions [2,3]. The application to hydroformylation of olefins has made a major impact on the oxo alcohols technology as evidenced by the commercial success of the Ruhrchemie–Rhone Poulenc process for hydroformylation of propylene to n-butyraldehyde using water soluble Rh-TPPTS catalyst [16]. However, Rh-TPPTS catalyst system is suitable only for the substrates (e.g. propylene) having appreciable solubility in water. For higher olefins, which have very low solubility (in ppm range) in water, this catalyst gives very poor rates. The research activities in this area were therefore directed towards increase in the rates by the use of co-solvents, surfactants or new type of surface active ligands. Also, synthesis of new water soluble ligands has attracted considerable attention.

Hydroformylation of propylene and 1-hexene using Rh-diphosphane 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl-sodium salt (BIS-BIS) water soluble catalyst has been studied [5] at 125°C and 4.9 MPa pressure in a continuous stirred tank reactor. It is shown that Rh-BISBIS catalyst gives higher hydroformylation activity as well as n/iso ratio than Rh-TPPTS catalyst. The use of surfactants in the biphasic system forms micelles, which lead to increase in liquid–liquid interfacial area and cause increase in the rate of reaction [17]. Similarly, water soluble phosphines have been modified by introducing long alkyl chains, having surfactant properties [18,19].

The kinetics of hydroformylation of 1-octene using Rh-TPPTS catalyst has been investigated by Chaudhari et al. [20], wherein it is observed that the liquid–liquid mass transfer of 1-octene from organic to aqueous phase is a rate controlling step. These authors have also shown that in the presence

of a co-solvent, the rate of reaction increases as a result of increase in 1-octene concentration in the aqueous catalyst phase (see Fig. 2). An interesting feature of promoting an interfacial catalytic reaction induced by a ligand present in the catalyst immiscible (organic) phase is also reported by Chaudhari et al. [20]. It is shown that in the presence of a small amount of PPh_3 in the organic phase, the rate of biphasic hydroformylation of 1-octene increases by 10–50 fold (see Fig. 3). These studies indicate several novel features as well as the complexities of water soluble catalytic reactions.

A new concept of supported aqueous phase catalysis (SAPC) has been proposed by Arhancet et al. [21] in which an aqueous phase $\text{HRh}(\text{CO})(\text{TPPTS})_3$ complex is supported on silica. In SAPC, a thin layer of water soluble catalyst exists as adhered to silica surface and such a catalyst shows significantly higher activity for hydroformylation. However, when SAPC is used for hydrogenation of α – β unsaturated aldehydes [22], in which polar solvents or products are involved, deactivation of the catalyst is observed. Hence, industrial applications of SAPC for such systems is viewed with scepticism [3].

Hydrogenation of olefins, α – β unsaturated aldehydes and ketonic functions using water soluble Rh and Ru complexes has also been studied and a detailed review of literature is available elsewhere [2]. The studies on asymmetric hydrogenation using water soluble chiral ligands reveal some interesting features on the role of water on enantio selectivity. Since, most of the products of asymmetric hydrogenation are complex molecules and non-volatile in nature, their separation from the conventional homogeneous catalysts often poses difficulties. The biphasic catalysts have tremendous potential for applications in this area.

4. Biphasic catalysis with reaction in organic phase

For reactions involving water soluble reactants or products and those where water adversely

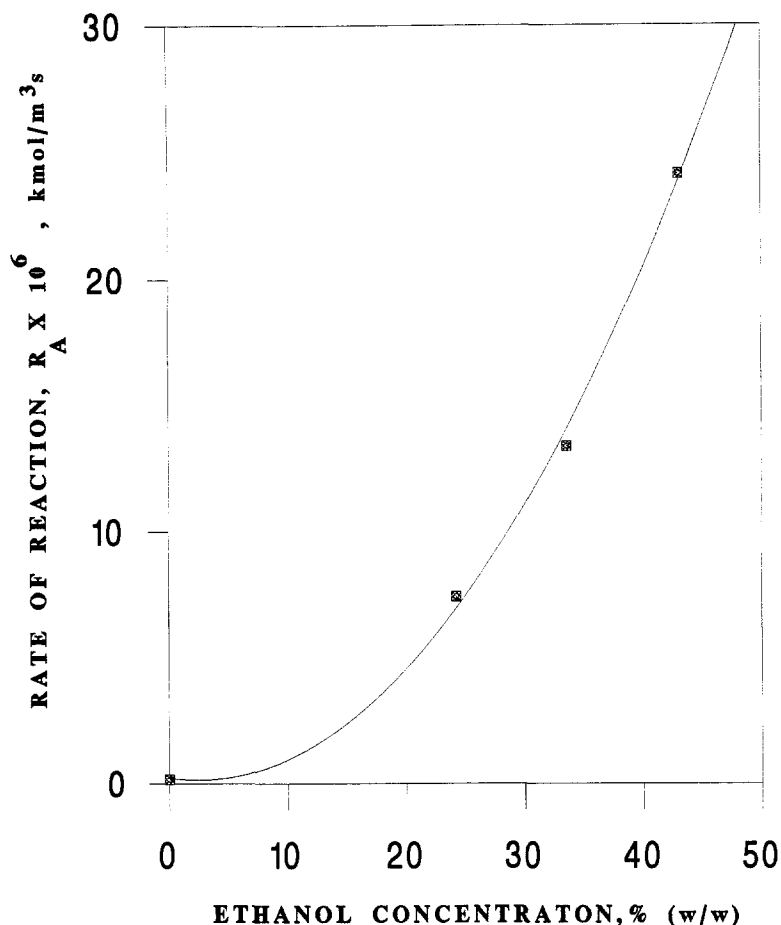


Fig. 2. Effect of co-solvent in biphasic hydroformylation of 1-octene [20]. Reaction conditions: $(\text{Rh}(\text{COD})\text{Cl})_2$: $1 \cdot 10^{-4}$ kg; 1-octene: $0.89 \cdot 10^{-5}$ kmol; temperature: 60°C; agitation speed: 23.3 rpm; pressure: 2.01 MPa ($\text{CO}/\text{H}_2 = 1:1$); Rh:TPPTS: 1:8; solvent system: octane–water–ethanol; total volume of liquids: $2.5 \cdot 10^{-4}$ m³.

affects the catalysts or reaction rate, a biphasic system involving conventional homogeneous catalysts (organic soluble) with water as a second phase can be used. In this case, the reactant may be present in the aqueous or organic (catalyst) phase, but the product is soluble in the aqueous phase, thus allowing easy separation after the reaction. For substrate or product inhibited reactions, such biphasic systems are useful in enhancing the reaction rates, selectivity and in some cases preventing catalyst deactivation. An important application of this case is the hydrogenation and hydroformylation of water soluble substrates (e.g. allyl alcohol, 1,4-butanediol). Hydroformylation

of allyl alcohol using $\text{HRhCO}(\text{PPh}_3)_3$ catalyst in organic phase [6] in the presence of water is reported to prevent deactivation of the catalyst and improve recycle efficiency. Here, allyl alcohol and the product aldehydes are water soluble but the catalyst is present in the organic medium.

A well known example of two phase catalysis with reaction in the organic phase is the oligomerisation of ethylene to α -olefins (SHOP process) [8,9]. This reaction is carried out using $\text{Ni}-(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{COOH}$ catalyst in a polar 1,4-butanediol phase at 80–120°C and 7–14 MPa pressure and the products separate as a second immiscible phase. This process is commercially

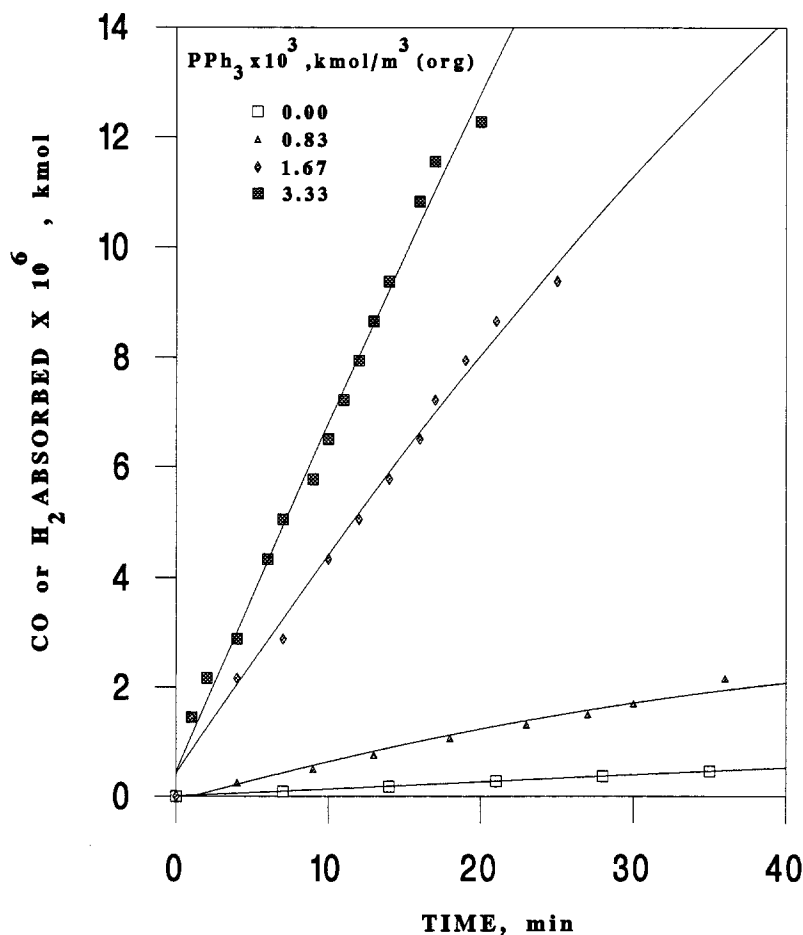


Fig. 3. Effect of PPh_3 in biphasic hydroformylation of 1-octene: promotion of interfacial catalytic reaction [20]. Reaction conditions: $(\text{Rh}(\text{COD})\text{Cl})_2$: 0.01 kmol/m^3 ; 1-octene: 0.85 kmol/m^3 ; temperature: 100°C ; agitation speed: 15 rps; pressure: 4.14 MPa ($\text{CO}/\text{H}_2 = 1:1$); Rh:TPPTS: 1:6; solvent system: toluene–water; total volume of liquids: $2.5 \cdot 10^{-5} \text{ m}^3$.

practised for the production of α -olefins (C_4 – C_{20} range). In this case, two immiscible organic phases are used and this approach is particularly useful for reactions which require water free conditions.

In a recent paper Horvath and Rabai [23] reported a 'florous' biphasic catalyst for hydroformylation of olefins as an alternative to the water soluble catalyst, in which a Rh complex of a floro derivative of phosphines in a 'florous' media is used. This system is useful for reactions sensitive to water and also may improve the rates due to higher solubility of the reactants in the 'florous'

catalyst phase compared to water. Gladysz [24] suggested that miscibility of the 'florous' and non-florous phases can depend on temperature and hence the reactions can be conducted in a homogeneous phase at higher temperatures and then cooled to effect product separation.

5. Organometallic phase transfer catalysis

The use of phase transfer catalysis (PTC) has made a major impact in organic synthesis for facilitating reactions between mutually immiscible

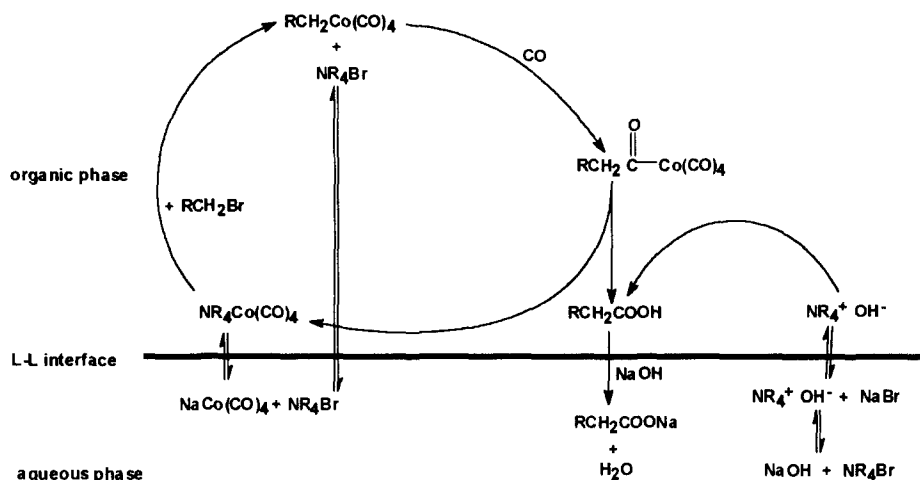
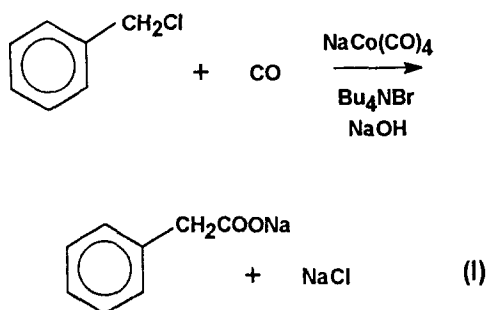


Fig. 4. Catalytic cycle in Co/PTC catalyzed carbonylation of benzyl bromide.

reactants [25]. An extension of this approach to develop organometallic PTC has proved to be highly promising in a variety of carbonylation reactions [26]. This class involves gas–liquid–liquid catalytic reactions where a combination of soluble metal complex catalyst and PTC is used. While, these reactions are also carried out in two phase systems, the catalytic cycle involves reactions in both the phases.

Carbonylation of benzyl chloride to phenyl acetic acid using $\text{NaCo(CO)}_4/\text{Bu}_4\text{NBr}/\text{aq. NaOH}$ catalyst is the most important industrial application of organometallic PTC [12].



This reaction is carried out in a two phase system consisting of a non-polar organic solvent (e.g. diphenyl ether, toluene) and aqueous alkali at 0.1

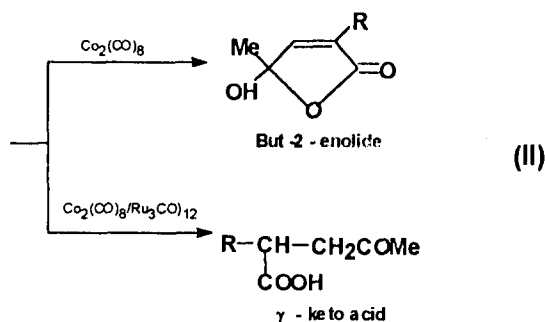
MPa and 50–60°C. The product is obtained as a Na salt of phenyl acetic acid in the aqueous phase. A catalytic cycle for this case is shown in Fig. 4. At higher pressures (> 50 MPa), phenyl pyruvic acid is formed in good yields [27]. This is an interesting example of a double carbonylation reaction using PTC. Here, the PTC plays an important role in facilitating the transport of cobalt carbonyl salt from the aqueous to organic phase. In the organic phase the cobalt anions react with benzyl chloride followed by insertion of CO to obtain a phenyl acetyl complex. Hydrolysis of phenyl acetyl complex at the organic–aqueous interface gives phenyl acetic acid (as Na salt) regenerating PTC and the Co complex catalyst. The detailed kinetics of this reaction have also been studied [28], which indicated that hydrolysis of phenyl acetyl complex is the rate determining step. Foa and Francalanci [29] reported carbonylation of *p*-isobutyl phenyl ethyl chloride to ibuprofen (*p*-isobutyl α -phenyl propionic acid) using cobalt carbonyl complex with PTC as a catalyst at 15 to 20°C and 0.1 MPa. However, improvement of selectivity for ibuprofen over *p*-isobutyl β -phenyl propionic acid is necessary for commercial viability of this route. Other examples in mono and double carbonylation and hydrogen-

Table 2
Carbonylation of allyl chloride [13]

| Catalyst | Pressure (MPa) | Temperature (°C) | Activity $\times 10^5$ (kmol/kg(Pd)/s) |
|---|----------------|------------------|--|
| PdCl ₂ (homogeneous) | 50.0 | 110 | 4.16 |
| Pd(π -allyl) Cl ₂ (homogeneous) | 8.5 | 90 | 1.67 |
| Pd(PPh ₃) ₂ Cl ₂ (biphasic) | 0.1 | 25 | 9.82 |
| Colloidal Pd metal (biphasic) | 2.0 | 35 | 26.60 |

ation reactions by metal complex/PTC systems have been described elsewhere [26].

An example of bimetallic phase transfer catalysis is reported by Alper and Petignani [30] for carbonylation of acetylenic derivatives:

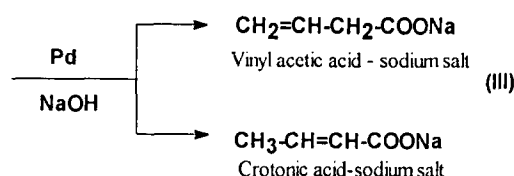


When $Co_2(CO)_8$ with dodecyl trimethyl ammonium chloride (DTAC) is used as a catalyst, but-2-enolide derivative is obtained but with $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ with DTAC as a catalyst, γ -keto acid derivative is selectively produced at 25°C and 0.1 MPa.

6. Catalysis by colloidal metal particles

Gas–liquid–liquid reactions involving colloidal metal particles as a catalyst are also reported [31]. In this case, the catalytic cycle operates through dissolution of the metal and precipitation, while the intermediate soluble complexes catalyze the reactions. In many cases, the metal particles tend to aggregate at the liquid–liquid interface due to

adhesion properties and are thus accessible to reactants in both the phases. Hydrogenation of alkenes in the presence of Rh colloids in two phase system has been recently studied [31], wherein Rh colloids stabilized by phosphine oxides are reported to be the active species. In another case, a significant increase in the activity of Pd catalyst is reported for carbonylation of allyl chloride, when used as Pd metal in a biphasic medium with aq. NaOH as a promoter [13].



The reaction occurs at 25°C and atmospheric pressure while with the homogeneous catalyst [32], 90°C and 8.5 MPa pressure is required. A comparison of the catalytic activity for homogeneous and biphasic catalysts is shown in Table 2. The selectivity of crotonic acid was found to increase with an increasing NaOH concentration. Here, Pd metal is observed to exist at the organic–water interface. Though, a detailed understanding of the mechanism of such reactions is not yet developed, they appear to be promising in improving activity and selectivity.

7. Reaction engineering aspects

The biphasic catalytic reactions discussed above mainly involve gas–liquid–liquid reactions,

wherein the reaction may occur in one or both the phases depending on the type of catalysts and the specific application. The reaction mechanism and the concept of catalysis may differ in each case, however, a common feature is the contacting of the gas–liquid–liquid phases. The reaction engineering aspects of gas–liquid and liquid–liquid reactions have been very well studied [33–35], but these studies need to be extended for applications to gas–liquid–liquid systems. The overall performance of such reactions would depend on hydrodynamics of the multiphase dispersion, mixing of fluid phases, interphase mass transfer steps, phase equilibria and kinetics of the reactions involved. While, research in this area has attracted considerable attention in the last few years, it has mainly addressed the issues concerning new catalysts synthesis and applications. In spite of important commercial successes in hydroformylation, oligomerization and carbonylation processes, there is limited published information on the analysis of the reaction engineering aspects of these complex multiphase reactions. The phase equilibria under conditions of hydrogenation of 1-octene using Rh-TPPTS catalyst and the kinetics have been studied recently [36]. Some important issues are highlighted here, which may form a basis for detailed analysis of gas–liquid–liquid catalytic reactions.

7.1. Mode of operation

The gas–liquid–liquid reactions can be classified in two broad categories (for analysis of the overall rate) depending on the mode of dispersed liquid phase: Case (A) for conditions, where the aqueous phase holdup is lower than the organic phase holdup, one expects that the aqueous phase droplets will be dispersed in the continuous organic phase with the gas bubbles also dispersed and Case (B) when the organic phase holdup is smaller than the aqueous phase holdup, organic droplets will be dispersed in the continuous aqueous phase with dispersed gas bubbles. These two modes will obviously give different performances for the biphasic catalytic reactions depending on

the type of catalyst and the solvent system. The droplet size of the dispersed liquid phase and its distribution would depend on the reactor type, internal details of design and properties of the liquid phases involved. The average drop size would also depend on the coalescence and breakage frequencies of droplets, which is known to be strongly dependent on system properties, particularly in the presence of electrolytes and surfactants. This will ultimately affect the liquid–liquid interfacial area and hence the mass transfer. Similarly, the gas–liquid mass transfer may also be affected by the presence of the dispersed liquid phase.

7.2. Overall rate of reaction

For analysis of the overall rate of gas–liquid–liquid catalytic reactions, it is necessary to define the mode of operation of the dispersed liquid phase, and catalyst/reaction phase. The contributions of gas–liquid and liquid–liquid mass transfer, phase equilibria and intrinsic kinetics of the reactions must be considered. For the two modes of operation discussed above the important steps involved are highlighted below assuming that reaction occurs in the aqueous phase.

Case (A), aqueous catalyst droplets dispersed in continuous organic phase:

- (i) transport of gas phase reactant A from gas to organic phase
- (ii) transport of dissolved A and liquid reactant, B from organic phase to organic–aqueous interface
- (iii) transport of A and B from organic–aqueous interface to aqueous catalyst phase with reaction in aqueous phase
- (iv) transport of water immiscible products from aqueous to organic phase.

Case (B), organic phase dispersed in continuous aqueous catalyst phase:

- (i) transport of gas phase reactant A from gas phase to aqueous catalyst phase
- (ii) transport of liquid reactant B from organic droplets to the organic–aqueous interface

- (iii) transport of B from organic–aqueous interface to the aqueous phase
- (iv) reaction of dissolved A and B in aqueous phase
- (v) transport of products from aqueous to organic phase.

For reactions using soluble catalysts, the kinetics of the overall catalytic reaction can be considered but for organic/PTC catalysed reactions, a different approach considering reactions, mass transfer and phase equilibria of several anionic species involved in the catalytic cycle may have to be considered. A detailed analysis of these cases is beyond the scope of this paper, but the classification can be useful for the analysis of the rate processes and reactor models.

8. Conclusions

Catalysis by soluble metal complexes in gas–liquid–liquid reactions have potential applications for a variety of industrially important reactions. The most attractive feature is easy and energy efficient separation of the catalyst and products. The recent developments also indicate wide scope for designing catalysts with higher activity and selectivity. However, complexities due to multi-phase nature of the systems, interfacial phenomena, role of phase equilibria and reaction engineering aspects need to be understood further.

Acknowledgements

The authors wish to acknowledge Indo French Center for Promotion of Advanced Research (Centre Franco-Indien Pour La Promotion de la Recherche Avancee), New Delhi for the financial support to this work. NCL Communication No.: 6113.

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