

## A Perspective on Catalysis in the Immiscible Liquid-Liquid System

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### Abstract

This manuscript provides a perspective on research work related to the catalysis in the immiscible liquid-liquid system. Three catalytic concepts, *i.e.*, phase-transfer catalysis (PTC), triphase catalysis (TPC), and phase-boundary catalysis (PBC), are presented as well as their use for the design of a better catalytic system. This perspective emphasizes based on the SWO (Strengths, Weaknesses, and Opportunities) analysis of PTC, TPC, and PBC and advances concept uses for future directions of research in this area.

### Author Biography



**Hadi Nur** obtained his S.Si. and M.T. degrees in 1992 and 1995, respectively, from Institut Teknologi Bandung (ITB). He received his Ph.D. degree from Universiti Teknologi Malaysia (UTM) in 1998. From 1999 to 2002, he was a postdoctoral researcher at Catalysis Research Center, Hokkaido University, Sapporo, Japan. He was a visiting scientist at the Institute for Heterogeneous Materials Systems, Helmholtz-Zentrum Berlin for Materials and Energy, Germany in 2015. Currently, he is a Full Professor and Director of Ibnu Sina Institute for Scientific and Industrial Research, at UTM, and Adjunct Professor of Universitas Negeri Malang.

**Keywords:** Immiscible liquid-liquid system, Phase-transfer catalysis, Triphase catalysis, Phase-boundary catalysis

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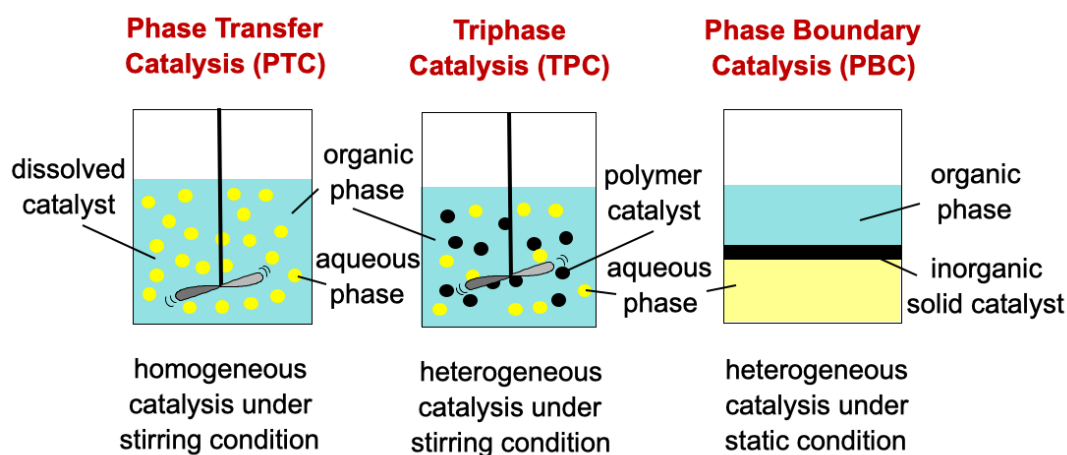
### Overview

*“Creativity is just connecting things.” (Steve Jobs)*

Steve Jobs quote is also relevant to the creative design of catalysis. Modern concepts in catalysis that emerge currently use of the existing basic principles of physics and chemistry of catalytic processes. One of the important catalytic systems is catalysis in the immiscible liquid-liquid system. It has attracted broad interest due to its potential applications as the catalyst system in various chemical reactions for the synthesis of useful chemical products. It realized that

the utilization of immiscible liquid-liquid systems is technologically and theoretically relevant. Several catalyst systems, *i.e.*, phase-transfer catalysis (PTC), triphase catalysis (TPC), and phase-boundary catalysis (PBC) have been reported in the scientific literature. The concept of PTC was first published in the years 1971 by C. M. Starks [1], while TPC and PBC were first reported in 1975 by S. L. Regen [2], and in 2000 by H. Nur *et al.* [3], respectively.

PTC has been widely used in the chemical industry mainly to produce monomers and



**Figure 1.** The differences between phase-transfer catalysis (PTC), triphase catalysis (TPC), and phase-boundary catalysis (PBC).

polymers, pharmaceuticals, and agrochemicals products. Besides, PTC is also used in making flavors, fragrances, and dyes. The catalytic reactions, among others, include polymerization, oxidation, reduction, esterification, alkylation, and condensation [4]. For TPC, although this catalyst system has the advantage in terms of separation, reusability, and use in continuous reactor systems, it has not been used in the chemical industries. The low catalytic activity due to the diffusional limitations of TPC is the main reason why this system has not received the attention of the industry [5]. It also applies to PBC since this catalyst system is so far only at the proof of concept level. Many articles describing the utilization of homogeneous and heterogeneous catalysts in the immiscible liquid-liquid system have been published. Nevertheless, here in this paper, the author proposed a better catalysis system utilizing PTC, TPC, and PBC concepts by the SWO (Strengths, Weaknesses, and Opportunities) analysis.

The main difference between PTC, TPC, and PBC lies in their respective catalytic system. While PTC belongs to a homogeneous catalytic system, TPC and PBC are heterogeneous and use solid catalysts. Another significant difference is the condition of the reactions. Mechanical agitation, i.e., stirring, is necessary for the PTC and TPC, while for PBC, the reaction is carried out under static conditions without any mechanical agitation. This is an excellent feature of PBC. From the viewpoint of conceptual design, the PTC and PBC systems are the same. The only difference between TPC and PBC is the type of catalyst used. TPC uses organic polymer, whereas PBC uses inorganic porous material. PBC catalyst is

designed so that the location of the catalytic active site is located precisely on liquid-liquid interphase. To further clarify this, Fig. 1 shows the differences between PTC, TPC, and PBC.

Because of slight differences in the catalytic action of PTC, TPC, and PBC, it has been suggested that TPC (and maybe PBC) could be categorized as a subcategory of PTC since it would not be in the interests of utilizable documentation and literature search systems by creating a new definition [6]. However, in this paper, the author does not want to be involved with the debate of the definition of PTC, TPC, and PBC but focuses on how the design of catalysts for immiscible liquid-liquid systems provides conceptual advances into a better catalytic system.

To understand the catalysis phenomena, the basic idea that underlies the immiscible liquid-liquid system and the catalyst used will be described in brief. Finally, the future direction of this topic will be explained at the end of this paper

### The basic idea of catalysis in the immiscible liquid-liquid system

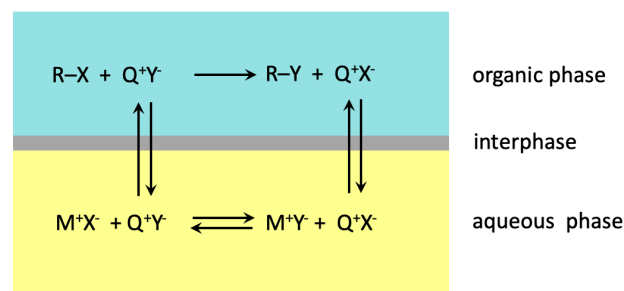
The phase-transfer catalysis (PTC) can be considered a mature concept because the mechanism of this catalytic system has been widely investigated and understood [7]. However, the requirements of PTC continue to grow in line with the needs of PTC in the synthesis of fine chemicals, including in the field of asymmetric phase-transfer catalysis [8]. Triphase catalysis (TPC) is a considerably solid phase-transfer catalysis, an extended type of PTC,

where the catalytic active site used is the same, for example, ammonium and phosphonium salts, but differ in phase. The phase-transfer catalyst is a homogeneous catalyst, while the triphase catalyst is a heterogeneous catalyst by immobilizing catalytic active site on polystyrene. In a series of papers published between 2000 and 2004, H. Nur *et al.* studied the PBC by using amphiphilic NaY zeolite particles [3,9-12]. However, the mechanistic understanding of phase-boundary catalysis (PBC) is very limited. Only one kinetic investigation of PBC [13] has been reported in the literature.

In 1971, Starks published a paper proposing a new approach to utilize a miscible liquid-liquid by quaternary ammonium halide catalyst, currently known as phase-transfer catalysis [1]. It was explained that a water-soluble quaternary ammonium halide undergoes anion exchange with anion from reactant molecules dissolved in the aqueous phase to produce ion-pairs ( $Q^+X^-$ ). Because of its lipophilic nature, these ion-pairs can transfer from the aqueous phase to the organic phase. Then, the ion-pair undergoes the nucleophilic substitution reaction with an organic reactant to produce R-Y product. Subsequently, the catalyst, a quaternary ammonium halide, will then return to the aqueous phase. This process continues in a cycle manner. Phase-transfer catalysts for anionic reactants are often quaternary ammonium salts. Fig. 2 is a schematic diagram of a phase-transfer catalysis using a quaternary ammonium halide catalyst. PTC of uncharged species [14] and electron transfer catalysis for redox systems [15] are other mechanisms of PTC. Currently, hundreds of catalysts have been used as phase-transfer catalysts [16].

As explained above, one of the uniqueness of phase boundary catalysis (PBC) is that the chemical reaction can take place under static conditions. The location of the solid catalyst at the phase boundary is one of the main factors that make this system work without any mechanical agitation. In this condition, the interfacial interaction between the solid catalyst and the immiscible liquid-liquid system is maximum. In the conventional system, the hydrophilic solid catalyst disperses in the aqueous phase. In order to achieve maximum interfacial interaction between the three phases, i.e. solid and two immiscible liquids, therefore, a vigorously stirring is needed. In this situation, an emulsion will form. The emulsion will disappear if stirring stops. If the solid catalyst is hydrophilic, the emulsion will consist of the bubble

of aqueous phase containing particles dispersed in the organic phase.

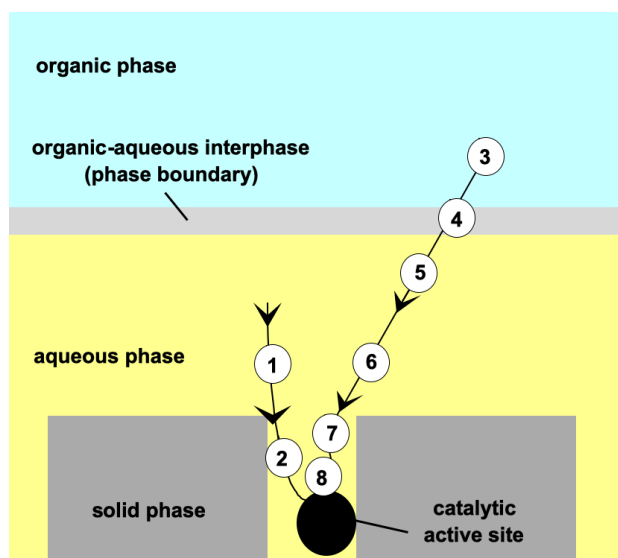


**Figure 2.** Nucleophilic substitution reaction mechanism in the immiscible liquid-liquid system:  $R-X + M^+Y^- \rightarrow R-Y + M^+X^-$ .  $M^+$  = metal cation,  $Q^+$  = quaternary ammonium ion.  $Q^+X^-$  is the phase-transfer catalyst.

In a conventional catalysis system that consists of solid and two immiscible phases, the mass transfer involves the migration of substrate molecules from one phase to another phase. Fig. 3 shows the migration process of substrate molecule dissolved in organic and aqueous phases involving several steps as follows: (1) transfer of substrate from the aqueous phase to the outer surface of the porous catalyst, (2) diffusion of substrate from the aqueous phase into the pore of the porous catalyst, (3) transfer of substrate from the organic phase to the aqueous phase over the phase boundary, (4) transfer of substrate from the phase boundary to the aqueous phase, (5) mixing and diffusion of substrate in the aqueous phase, (6) transfer of the substrate to the outer surface of the catalyst, (7) diffusion of the substrate into the catalyst pore and lastly (8) a process involving the adsorption of substrates, chemical reactions and desorption of the reaction product. Based on the chemical transport knowledge, the steps numbers (2), (7) and (8) was not affected by the stirring. The stirring process can influence all the other steps shown in Fig. 3. Since the catalytic active site is located in a phase-boundary, the stirring process is unnecessary in the PBC system. The mass transfer is not the rate-determining step in this catalytic system.

The purpose of mechanical agitation or stirring is to get good contact between the phases and also increase the interfacial surface area so that the efficiency of the mass transfer increases. It is clear that the catalytic performance of PTC is very dependent on stirring, and hence mass transfer. The understanding of the mechanism of these catalysis systems is very dependent on the understanding of the transport process. This process includes both

reactions of enhanced transport and mass-transfer limited reaction. Recently, an experiment to visually study the interphase mass transfer in an immiscible liquid-liquid system has been reported using the planar laser-induced fluorescence method combined with the refractive index matching technique [17]. The experimental results show that the mass transfer equilibrium time decreases with the increase of agitation speed.



**Figure 3.** Schematic representation of the mass transfer in the conventional catalytic system where the porous inorganic catalyst dispersed in the aqueous phase.

### SWO analysis and the future direction of the immiscible liquid-liquid catalysis research

It is rather challenging to compare the catalytic activities and selectivities of PTC, TPC, and PBC because the active sites, reaction types, reactors, and parameters used are different. Unfortunately, there is no research conducted to compare the catalytic performance of PTC, TPC, and PBC. However, it can still be concluded that PTC is a better system in terms of catalytic activity compared to TPC due to the diffusion constraints of TPC [18,19]. Several excellent reviews on PTC [4,7,8,14,16] and TPC [5] have been published, and their catalytic activities and selectivities can be referred to them and the references therein. The data of catalytic activities and selectivities of PBC can be referred to as manuscripts previously published [9-13,20].

Based on the catalytic performance and reaction condition, the strengths and weaknesses of each of the catalytic systems can be identified. PTC has several advantages, such as high conversion, high reaction rates, and high selectivity. The

disadvantages of PTC are the difficulty of separating the product, and the reaction needs mechanical agitation. Since TPC is heterogeneous catalysis, separation from the product is more straightforward than PTC. Mass transfer limitation is still a weakness of PTC and TPC, so stirring is yet required to increase interactions between phases. Although there is no requirement of stirring in PBC, the main weakness of PBC is low conversion, reaction rate, and selectivity.

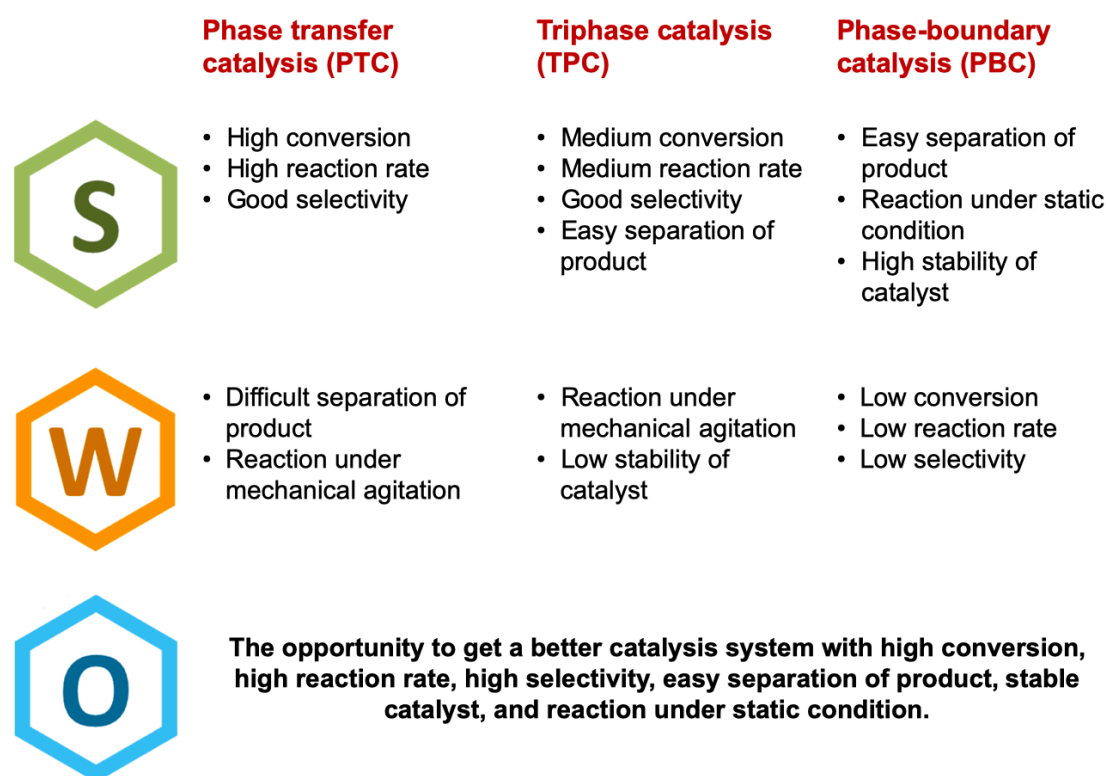
Since the TPC uses a polymer as catalyst support, the low stability of the catalyst has become the central issue of this catalytic system [5]. The PBC uses an inorganic porous material catalyst that is chemically more stable than PTC polymer catalyst.

If the strengths and weaknesses of PTC, TPC, and PBC are combined; it is possible to connect and translate them into the opportunity to get a better catalysis system with high conversion, high reaction rate, high selectivity, easy separation of product, stable catalyst, and reaction under static conditions. The SWO (Strengths, Weaknesses, and Opportunities) analysis of catalysis in immiscible liquid-liquid systems is depicted in Fig. 4.

Since the mass transfer is not the rate-determining step of PBC, it is clear that low catalytic activity of PBC is not related with the mass transfer but due to the low activity of the catalytic active site. As shown in Fig. 4, the strength of PBC only lies in the reaction that can be carried out under static conditions. One considers that the amphiphilic character of the catalyst support contributes to the efficient supply of hydrophilic and hydrophobic substrates to react at the catalytic active site so that the reaction can take place without stirring. Based on these considerations, the design of the catalyst for the immiscible liquid-liquid system is directed to synthesize the solid catalyst which has the following properties, possess amphiphilic character and the location of the catalytic active site in such a way that can be easily reached by hydrophilic and hydrophobic substrates without limitation of mass transfer. Catalytic active sites could mimic the active site used by PTC.

### Conclusions and Perspectives

All the heterogeneous catalysis research has similar issues to be solved, which are how to improve the efficiency of adsorption, chemical reaction, and desorption in catalytic cycle processes and how to design an active catalytic site. While the homogeneous catalysis has dominated the



**Figure 4.** The SWO (Strengths, Weaknesses, and Opportunities) analysis of catalysis in immiscible liquid-liquid systems, (a) phase-transfer catalysis (PTC), (b) triphase catalysis (TPC), and (c) phase-boundary catalysis (PBC).

development in this research area, the author suggests that future research will be in the direction of the synthesis of solid catalysts that possess amphiphilic characters so that they can be positioned at liquid-liquid interphase. Besides, the design of the catalyst needs to pay attention to the location of the active site so that hydrophilic and hydrophobic substrate should easily reach the catalytic active site without limitation of mass transfer. Since many phase-transfer catalyzes (PTC) showed excellent catalytic performance, the catalytic active sites of the phase-transfer catalyst can be mimicked and attached to the amphiphilic solid catalyst. Thus, the design of the catalytic active site of solid catalysts and mass transport phenomena of the immiscible liquid-liquid catalysis are the potential topics to be explored in the future.

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